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Blending Study of MgO-Based Separator Materials for Thermal Batteries

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Abstract

The development and testing of a new technique for blending of electrolyte-binder (separator) mixes for use in thermal batteries is described. The original method of blending such materials at Sandia involved liquid Freon TF® as a medium. The ban on the use of halogenated solvents throughout much of the Department of Energy complex required the development of an alternative liquid medium as a replacement. The use of liquid nitrogen (LN) was explored and developed into a viable quality process. For comparison, a limited number of dry-blending tests were also conducted using a Turbula mixer. The characterization of pellets made from LN-blended separators involved deformation properties at 530°C and electrolyte-leakage behavior at 400° or 500°C, as well as performance in single-cells and five-cell batteries under several loads. Stack-relaxation tests were also conducted using 10-cell batteries. One objective of this work was to observe if correlations could be obtained between the mechanical properties of the separators and the performance in single cells and batteries.

Separators made using three different electrolytes were examined in this study. These included the LiCl-KCl eutectic, the all-Li LiCl-LiBr-LiF electrolyte, and the low-melting LiBr-KBr-LiF eutectic. The electrochemical performance of separator pellets made with LN-blended materials was compared to that for those made with Freon TF® and, in some cases, those that were dry blended. A satisfactory replacement MgO (Marinco 'OL', now manufactured by Morton) was qualified as a replacement for the standard Maglite 'S' MgO that has been used for years but is no longer commercially available. The separator compositions with the new MgO were optimized and included in the blending and electrochemical characterization tests.

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Blending Study of MgO-Based Separator Materials for Thermal Batteries

INTRODUCTION

To ensure good homogeneity when blending electrolyte and MgO binder in the preparation of separator (electrolyte-binder or EB) mixes, Sandia developed a process that used liquid Freon TF® as the medium together with an industrial Waring-type blender.[1] The use of a liquid medium is preferable to simply dry blending because of the poor flow characteristics of the MgO powder. In dry blending, complete mixing is not always ensured because of the tendency of the MgO to hang up on the walls of the container; *i.e.,* the MgO has a high angle of repose. This was found to occur even with multi-axis blenders such as the Turbula blender.

In the early 1990s, the environmental awareness of the dangers of halogenated solvents and cleaners to the protective ozone layer surrounding the earth resulted in restrictions on the production and use of these materials. In response to these concerns, the Department of Energy (DOE) began restricting and eliminating several of these common halogenated organics, included Freons. Since less-than-satisfactory results were sometimes obtained when using dry blending of electrolyte and MgO powders, alternative liquid media were considered as possible replacements for Freon TF® for the blending of separator materials.

A number of criteria were considered in evaluating candidate media. These included flammability, vapor pressure, toxicity, cost, ease of removal, and disposal. Common solvents such as hexane, benzene, and similar organics would be too volatile and flammable and would pose risks to employees exposed to them during processing of separator mixes. Short-chain alcohols such as ethanol and isopropanol were felt to be much safer and were subjected to screening tests. Ultimately, the best candidate for meeting all of the screening criteria was liquid nitrogen (LN). This material is nontoxic, relatively inexpensive, readily removed, and easily disposed of without special treatment. The results of these screening tests are described in this report, along with comparable data for materials processed by Freon TF® and, in more limited cases, by dry blending using a three-axis Turbula blender. Pellets pressed from the various separator mixes were characterized for their mechanical properties and electrolyte leakage at elevated temperature (530°C) and their electrochemical performance was evaluated in single cells and five-cell batteries under several loads. In addition, the stack relaxation was monitored in ten-cell batteries.

A separate part of the study involved development of a suitable replacement MgO for the current Maglite 'S' material that had been used in the past. The lack of commercial availability of the Maglite 'S' required finding a suitable replacement that would result in equivalent mechanical and electrochemical properties of separator pellets as those made with Maglite 'S'. In earlier work, 13 different MgOs were evaluated and most did not have the required pore-size distribution to immobilize the salt phase when liquid at thermal-

battery operating temperatures.[2] One material that showed promise, however, was Marinco 'OL' MgO, manufactured by Marine Products, Inc. (Subsequently, Morton has assumed the manufacture of this material.) As part of the separator study, equivalent compositions of separators made with the above three electrolytes were developed using Marinco 'OL' MgO.

EXPERIMENTAL

Separator Preparation

The separator mixes were prepared in batch sizes of between 250 g and 1,000 g, with most batches being 500-g in size. The two MgO sources were Maglite 'S' MgO (Merck) and Marinco 'OL' MgO (Marine Products Inc., now made by Morton). The oxides were first calcined at 650°C for four hours in a dry room (maintained at <3% relative humidity) to decompose hydroxide, carbonate, and bicarbonate impurities. The calcined MgOs were then blended with the various electrolytes using Freon TF®, liquid nitrogen, or were dry blended in a Turbula blender (Model T10B, Willy A. Bachoten AG Maschinenfabrik, Basel, Switzerland). The standard eutectic electrolyte was 45% LiCl/55%[a] KCl and melts at 352°C. The all-Li, minimum-melting electrolyte was 68.4% LiBr/22% LiCl/9.6% LiF and melts at 436°C. The low-melting eutectic electrolyte was 57.33% LiBr/42% KBr/0.67% LiF and melts at 324.5°C.

The Freon was removed in a convection oven at 35°C while the nitrogen was simply allowed to evaporate naturally. During dry blending, at least 25% free headspace was maintained in the sealed glass container used for blending. Care must be exercised during LN blending to prevent sudden boiling of the liquid nitrogen, which will eject material from the blender. The blender must be first cooled with the liquid nitrogen prior to addition of the pre-cooled electrolyte and MgO powders. The liquid nitrogen was then carefully added after turning on the blender. The blended powders were then fused in the dry room in quartz trays at 400°C for the separators based on standard electrolyte and low-melting electrolyte and at 500°C for the separators based on the all-Li electrolyte. The separator mixes were fused for 16 hours and were then granulated through a 60-mesh sieve, except for the all-Li separator mix where a 100-mesh screen was used to enhance pelletization. The mixes were pressed to 75.6% of theoretical density (TD) to prepare pellets for characterization tests.

In a limited number of tests, anhydrous isopropanol was used as the liquid medium for blending. In one instance, the alcohol was removed by trapping in a liquid-nitrogen trap while the sample was placed under dynamic vacuum. In a second case, the excess alcohol was allowed to evaporate in the dry room at <3% relative humidity. In the third case, the alcohol was ignited and allowed to burn off while the quartz tray was in a cold furnace. When alcohol removal was complete, the mixes were then fused per normal procedures.

Deformation Tests

[a] Unless otherwise specified, all compositions are in weight percent.

The deformation of separator pellets was measured using an experimental setup that has been previously described.[2] It consisted of heated platens with a moveable upper fixture instrumented with a linear variable displacement transducer (LVDT) to measure the change in thickness when a separator pellet was placed between the heated platens at 530°C and 14.3 psig. The pellets used for these tests were 1.25" in diameter and 0.0602" thick. Typically, an instantaneous reduction in thickness (deformation) occurred within 30 s, after which an invariant steady-state thickness value was attained. The deformation at 3 min was taken as the metric for these tests.

Electrolyte-Leakage Tests

The electrolyte leakage of separator pellets was measured by immersing a weighed pellet in a bed of high-surface-area alumina and heating the sample at 400°C for 30 min, except for the all-Li electrolyte, in which a temperature of 500°C was used.[2] After cooling, the excess alumina was brushed from the pellet and the pellet was reweighed. The mass loss of the pellet was taken as a measure of the amount of electrolyte that leaked from the pellet. The electrolyte leakage was reported on an area basis (*i.e.*, mg/cm^2). The tests were run in triplicate and the results averaged.

Single-Cell Tests

The various separators were evaluated in 1.25"-dia. single cells with unflooded 44% Li/56% Si anodes and unfused, lithiated FeS_2 cathodes (73.5% FeS_2/25% separator/1.5% Li_2O). (The same separator was used in both the catholyte and separator mixes.) The typical anode weight was 0.7 g, the cathode weight was 1.05 g, and the separator weight was 1.0 g. All pellets were pressed to 72.5% TD for the anodes and 75.6% TD for the separators and cathodes. The cells were tested with a background load of 1.0 A with a 2.0-A pulse load applied for 5 s every 60 s. (This corresponds to current densities of 125 mA/cm^2 and 250 mA/cm^2, respectively.) A limited number of tests were also conducted using a 7.0-A pulse, which corresponds to a current density of 925 mA/cm^2. The cells were discharged under computer control to a cutoff voltage of 1.25 V. Three cells were typically discharged under each test condition and the results averaged for comparison among the various separator-processing techniques or compositions.

Five-Cell Battery Tests

Battery tests were carried out using five-cell stacks at activation temperatures of –54° and +74°C. Fe/$KClO_4$ heat powder of 88/12 composition was used for these tests. The heat balance for batteries built with the LiCl-KCl eutectic and all-Li LiCl-LiBr-LiF electrolyte was 98.6 cal/g. The heat balance for the batteries built with the low-melting LiBr-KBr-LiF eutectic was only 95.4 cal/g because of its lower heat of fusion. The batteries were built using a reusable test vehicle with provisions for measuring the stack temperature of the first cell at the bottom end of the stack (opposite the header). Four wraps of 0.080"-thick Fiberfrax® ceramic blanket were used to insulate the battery stack. The batteries were closed at a stack pressure of 253 psig and were discharged to a cutoff voltage of 6.25 V (1.25 V/cell). The batteries were discharged under computer control using a steady-state load of 50 ohms, with a pulse load of 1.05 ohms applied for 5 s every 60 s to obtain polarization data. This is equivalent to a steady-state current density of 25 mA/cm^2 and a pulse current density of 1,200 mA/cm^2 based on a nominal battery voltage of 10 V.

Ten-Cell Battery Tests

Similar battery tests were carried out using ten-cell stacks activated at room temperature. For these tests, the batteries were instrumented with a 0-2500 lb Strainsert load cell (Model FL2-5C-2S6K) and a thermocouple. A Doric Model 420 readout was used for recording the stack pressure. The purpose of the tests was to measure the stack relaxation for the various separator materials. The batteries were built using a reusable test vehicle with provisions for measuring the stack temperature of the bottom cell of the stack. The stack pressure relaxed immediately upon melting of the separator and stabilized within 30 s. The stack pressure after one minute was taken as a metric of the relaxation process. No electrochemical performance data were recorded for these tests.

RESULTS AND DISCUSSION

Deformation Tests

LiCl-KCl Eutectic – The deformation behavior of a number of separator mixes made with Maglite 'S' and Marinco 'OL' MgO are shown in Figure 1 for the LiCl-KCl eutectic electrolyte. The average deformation values along with the standard deviations are summarized in Table 1. The optimum value of 35% Maglite 'S' MgO was based on earlier deformation studies.[3] The purpose of the reformulation work was to develop a composition based on Marinco 'OL' MgO that would approximate that previously observed for the separators based on Maglite 'S' MgO.

From empirical observations, it is desirable to maintain the deformation (reduction in thickness) between 15% and 30% if possible.[4] At higher deformation values, the extent of electrolyte leakage and separator extrusion can become unacceptable. At deformation under 15%, interfacial wetting of the separator with the anode and cathode can be less than optimum, which can result in a higher interfacial impedance.

LN blending of the separator mix with 35% Maglite 'S' MgO resulted in a deformation of 13.9% relative to 22.2% for Freon blending, but with a smaller standard deviation. The direct substitution of Marinco 'OL' MgO for Maglite 'S' MgO resulted in a considerable increase in deformation to 27.3% for LN-blended mixes at a level of 35% MgO. However, by increasing the Marinco 'OL' MgO content to 37.5%, the deformation for LN-blended material was reduced to only 20.5%, which was comparable to that of the original standard EB made by Freon blending with 35% Maglite 'S' MgO. Thus, the difference in pore-size distributions between the two MgOs requires that a greater amount of the Marinco 'OL' MgO must be used for the same equivalent immobilization obtained for Maglite 'S' MgO by liquid-medium processing. The dry Turbula-blended separator with 35% Marinco 'OL' MgO showed a much greater deformation relative to its LN-blended counterpart. When the MgO level was increased to 40%, however, the deformation of the Turbula-blended separator became comparable to that of the LN-blended separator with 35% Maglite 'S' MgO. Similar results were obtained for the LN-blended and Turbula-blended separators with 40% Maglite 'S' MgO.

These data indicate that the manner of blending can have a dramatic impact on the properties of the separator material. The relative particle-particle interactions will be

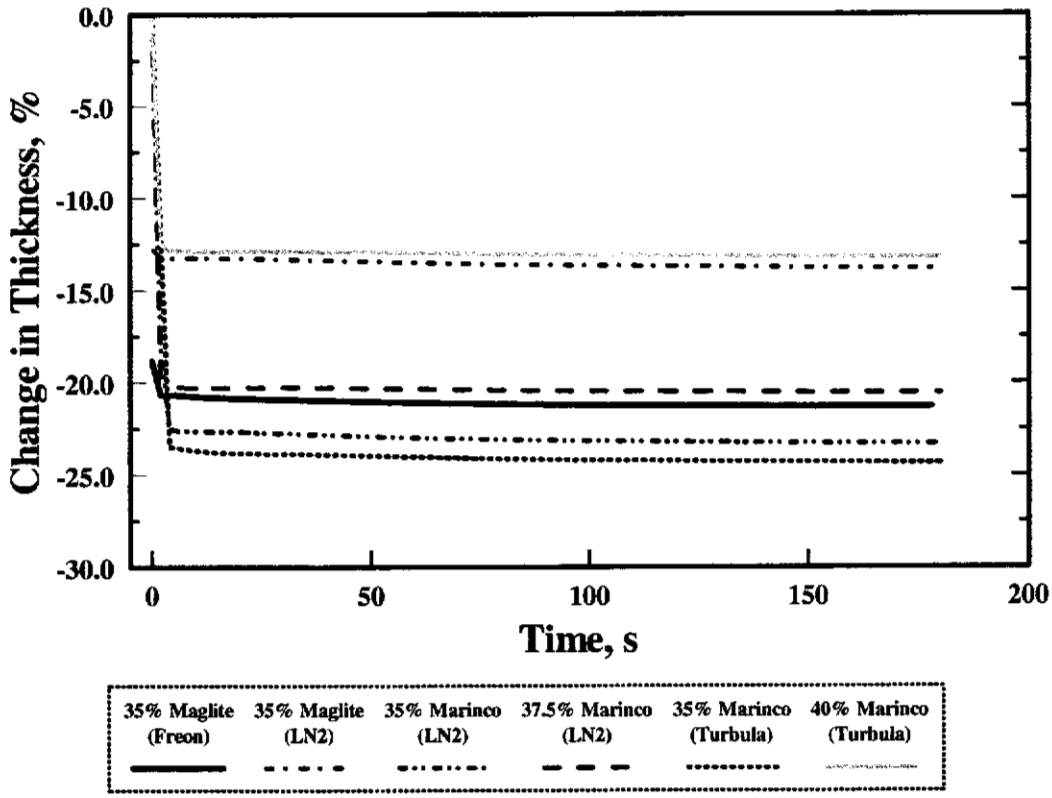

Figure 1. Typical Deformation Curves at 530°C and 14.3 Psig for Separators Based on LiCl-KCl Eutectic.

Table 1. Summary of Average Deformation Behavior after 3 Min. at 530°C and 14.3 Psig of Various Separators Based on LiCl-KCl Eutectic.

MgO Source	MgO Content, %	Blend Method	Deformation at 3 Min, %*	Standard Deviation
Maglite 'S'	35.0	Liquid Freon	22.2	1.97
Maglite 'S'	35.0	LN	13.9	0.70
Maglite 'S'	35.0	Turbula	25.2	0.90
Maglite 'S'	35.0	Ball-mill	15.8	1.20
Marinco 'OL'	35.0	LN	27.3	2.15
Marinco 'OL'	35.0	Turbula	32.7	0.10
Marinco 'OL'	37.5	LN	20.5	0.22
Marinco 'OL'	40.0	LN	13.7	0.70
Marinco 'OL'	40.0	Turbula	13.2	0.90

* Deformation is defined here as the reduction in thickness; *i.e.*, 10% reduction in thickness means 10% deformation.

different in a liquid medium relative to that involving dry blending. Dry ball milling adds an additional factor to the equation, in that grinding can potentially take place during mixing. Deformation for separator pellets made by ball milling a mixture of 35% Maglite 'S' MgO and the LiCl-KCl eutectic was 15.8%, which is much lower than the value of 25.2% observed for the Turbula-blended counterpart.

LiCl-LiBr-LiF Electrolyte – The same type of compositional adjustments was carried out using the all-Li LiCl-LiBr-LiF electrolyte. This electrolyte normally requires a minimum of 35% Maglite 'S' MgO for adequate immobilization. The deformation behavior of the separator pellets for a number of materials prepared with liquid Freon and liquid nitrogen is summarized in Figure 2. Note that the relaxation processes occur somewhat more gradually than noted for the LiCl-KCl eutectic (Figure 1). This indicates some difference in rheology between the two materials that may be related to the much higher melting point of the all-Li electrolyte or to differences in viscosity or surface tension of the electrolytes. The deformation data for the various mixes are summarized in Table 2.

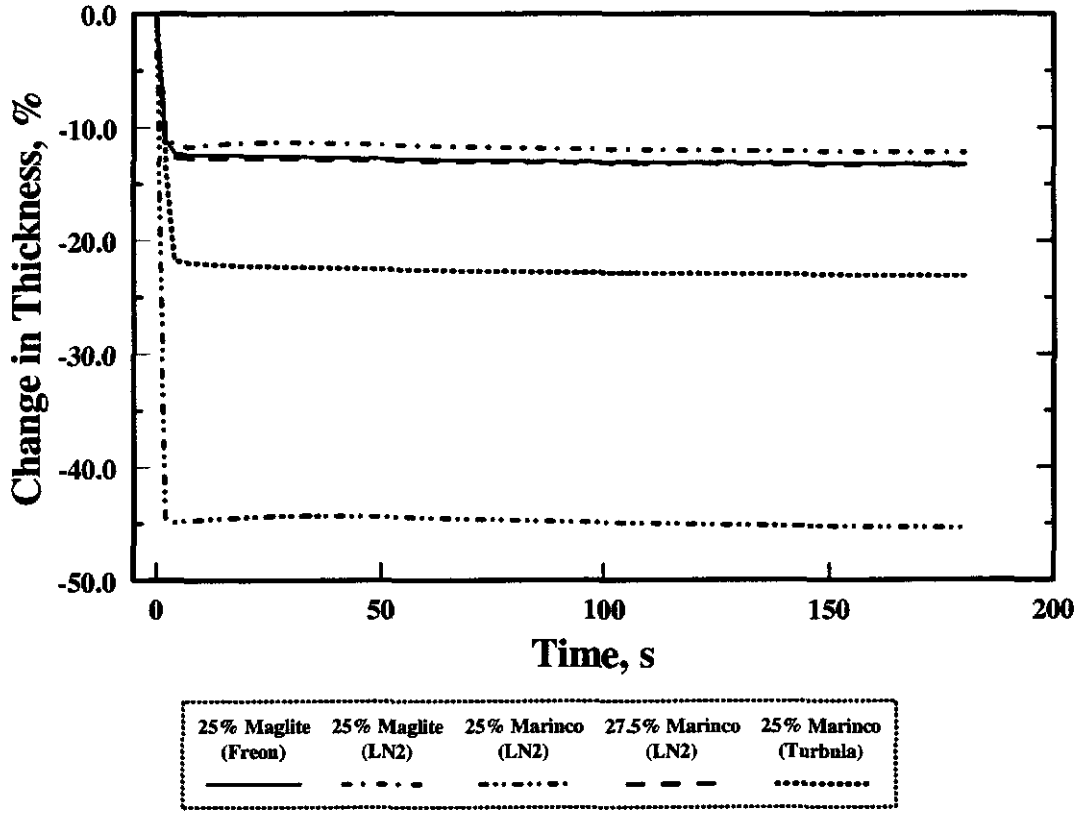

Figure 2. Typical Deformation Curves at 530°C and 14.3 Psig for Separators Based on LiCl-LiBr-LiF Electrolyte.

The LN-blended separator with 35% Maglite 'S' had similar deformation as the standard Freon-blended material. Dry blending with the Turbula resulted in a 21% increase in the deformation of the separator compared to the control. Dry ball milling resulted in separators pellets with almost half of the deformation (10.6%) of pellets from Turbula-blended separators (19.8%), but reproducibility of the deformation behavior was better.

Table 2. Summary of Average Deformation Behavior after 3 Min. at 530°C and 14.3 Psig of Various Separators Based on LiCl-LiBr-LiF Electrolyte.

MgO Source	MgO Content, %	Blend Method	Deformation at 3 Min, %	Standard Deviation
Maglite 'S'	35.0	Liquid Freon	15.6	0.87
Maglite 'S'	35.0	LN	13.0	0.53
Maglite 'S'	35.0	Turbula	19.8	6.60
Maglite 'S'	35.0	Ball mill	10.6	0.30
Marinco 'OL'	35.0	LN	28.3	0.65
Marinco 'OL'	35.0	Turbula	16.8	1.2
Marinco 'OL'	37.5	LN	9.9	0.86

When the Maglite 'S' MgO was replaced by Marinco 'OL' MgO at a level of 35%, the deformation for LN-blended material increased by a factor of 1.8, to a value that was considered marginally acceptable. However, by increasing the Marinco 'OL' MgO content to 37.5%, the resulting deformation was reduced to less than 10%, which is less than the desired minimum value of ~15%. The relaxation process for this material was almost instantaneous—much like that for the separators based on LiCl-KCl eutectic (Figure 1)—and did not show the gradual increase up to 3 min observed with the other compositions (Figure 2).

These data suggest that an intermediate level of the Marinco 'OL' MgO (*e.g.*, 36.5%) would be close to optimum when using LN processing. They also show that the composition of the electrolyte can significantly influence the wetting behavior, likely due to differences in surface tension and, to a lesser extent, viscosity. The high sensitivity to small changes in the content of Marinco 'OL' MgO content in the separator during LN processing is undesirable from a production standpoint, in that tighter control on processing will be needed to avoid potential problems when subsequently used in thermal batteries.

In contrast, dry Turbula blending of the separator mix made with 35% Marinco 'OL' MgO resulted in deformation that was only slightly more than the standard Freon-blended material made with Maglite 'S'. This again demonstrates that the manner of mixing of separator materials can make a dramatic difference in the physical properties of the resulting separator pellets. These data indicate that Turbula blending of 35% Marinco OL' MgO with the all-Li electrolyte will provide material with deformation characteristics comparable to those of the standard separator made with the same amount of Maglite 'S' MgO.

LiBr-KBr-LiF Eutectic – Compositional adjustments were carried out with the low-melting LiBr-KBr-LiF eutectic electrolyte. This electrolyte has a much lower melting point than the LiCl-KCl eutectic or the all-Li electrolyte. It requires a much lower binder content of only 25% Maglite 'S' MgO for adequate electrolyte immobilization. This reflects

differences in surface tension and viscosity at thermal-battery operating temperature, relative to the other two electrolytes. The deformation behavior of separator pellets made with liquid Freon and liquid nitrogen is summarized in Figure 3. The deformation data for the various mixes are summarized in Table 3.

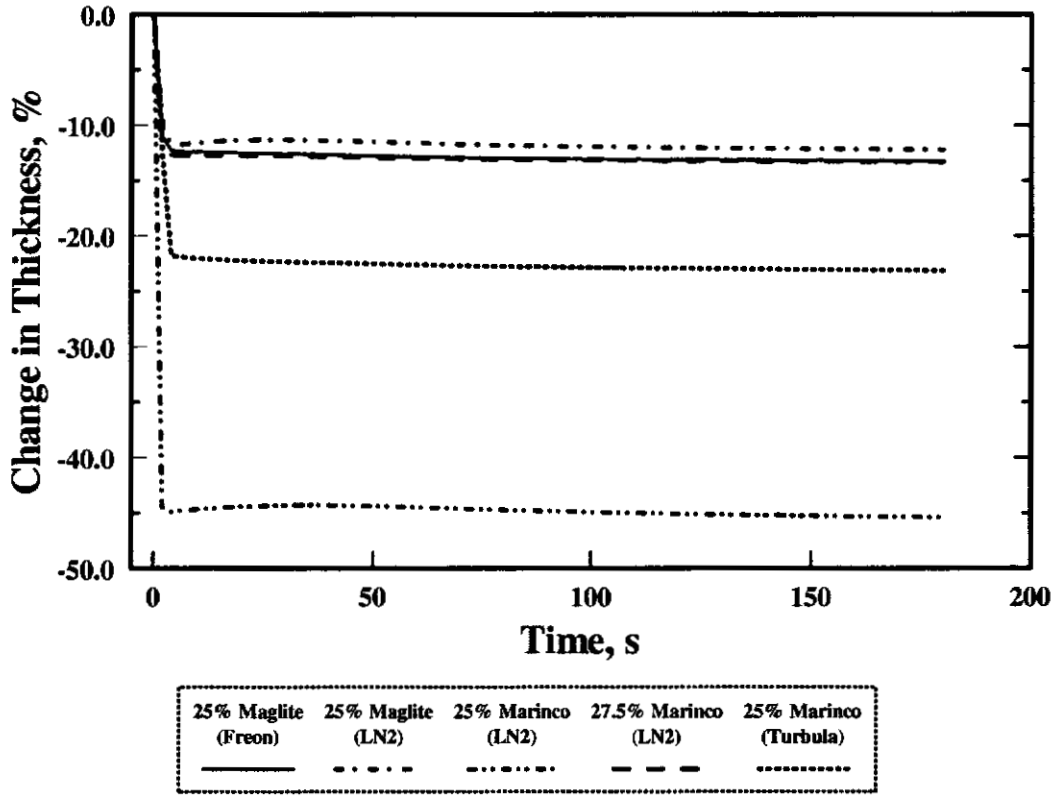

Figure 3. Typical Deformation Curves at 530°C and 14.3 Psig for Separators Based on LiBr-KBr-LiF Eutectic.

An increase in the Maglite 'S' MgO content from 25% to 30% did not make a significant change in the deformation behavior for the Freon-blended separator materials. The LN-blended mix with 25% Maglite 'S' MgO showed comparable deformation behavior as the Freon-blended counterpart. However, when Marinco 'OL' MgO was substituted at the same level, the deformation for the LN-blended mix increased by a factor of 4! This was entirely unexpected. When the MgO level was increased from 25% to 27.5% for the LN-blended separator, deformation closer to that of the Freon-blended control with 25% Maglite 'S' MgO was attained. The deformation behavior of the LN-blended separator made with the low-melting electrolyte shows a much greater sensitivity to small changes in the content of Marinco 'OL' MgO than even the all-Li electrolyte. When the MgO level was increased further to 30%, the deformation was reduced to <10%, which is less than optimum. These data indicate that a level of 27.5% Marinco 'OL' MgO is optimum for the low-melting electrolyte for LN blending.

The dry-blended mixes made with the Turbula blender and Marinco 'OL' MgO showed much less deformation relative to their LN-blended counterparts. The data for compositions with 25% and 30% MgO suggest a MgO level near 27.5% would be closer to

the optimum value for deformation with this blending method. The deformation for ball-milled material showed over twice the deformation than the Turbula-blended counterpart, which is opposite to what was observed for the LiCl-KCl eutectic and the all-Li electrolyte (Tables 1 and 2, respectively).

Table 3. Summary of Average Deformation Behavior after 3 Min. at 530°C and 14.3 Psig of Various Separators Based on LiBr-KBr-LiF Eutectic.

MgO Source	MgO Content, %	Blend Method	Deformation at 3 Min, %	Standard Deviation
Maglite 'S'	25.0	Liquid Freon	11.4	0.40
Maglite 'S'	25.0	LN	12.2	1.06
Maglite 'S'	25.0	Turbula	12.6	1.00
Maglite 'S'	25.0	Ball mill	25.7	1.6
Maglite 'S'	30.0	Liquid Freon	10.6	1.1
Maglite 'S'	30.0	Turbula	7.9	0.70
Marinco 'OL'	25.0	LN	45.3	1.07
Marinco 'OL'	25.0	Turbula	23.1	1.3
Marinco 'OL'	27.5	LN	13.2	0.50
Marinco 'OL'	30.0	LN	9.0	0.94
Marinco 'OL'	30.0	Turbula	7.9	0.7

Electrolyte-Leakage Tests

LiCl-KCl Eutectic – The results of electrolyte-leakage tests with separators based on the LiCl-KCl eutectic are compared to the corresponding deformation data in Figure 4. No distinction was made as to which method was used for blending or which MgO was involved. The data are separated by composition, however, for ease of analysis. There was a strong correlation between the deformation and leakage behavior for pellets made with 35% MgO; pellets with high deformation also showed high electrolyte leakage. This is consistent with what has been observed in previous work.[2] Given the wide range of processing and types of MgO involved, this agreement is considered very good. In contrast, the data for mixes with 40% MgO were clustered.

LiCl-LiBr-LiF Electrolyte – The corresponding deformation and electrolyte-leakage data for separators made with the all-Li electrolyte are plotted in Figure 5. A similar correlation as that for the LiCl-KCl eutectic electrolyte was observed, but with twice the slope.

LiBr-KBr-LiF Eutectic – The deformation and corresponding electrolyte leakage for separators made with the LiBr-KBr-LiF eutectic electrolyte are summarized in Figure 6. Again, a reasonably good correlation was obtained between the two sets of data, with a slope about half of that for separators based on the LiCl-KCl eutectic (Figure 4). This means that either of these methods of pellet characterization would be useful for batteries. The electrolyte-leakage test takes longer to do, but does not require special

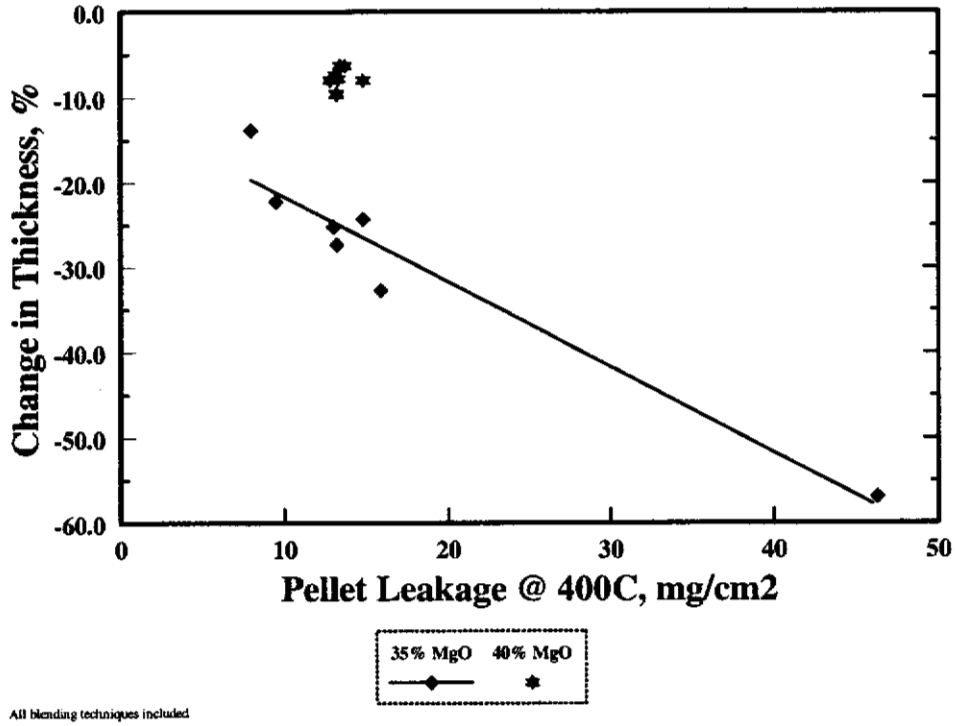

Figure 4. Comparison of Deformation and Electrolyte Leakage for Separator Pellets based on LiCl-KCl Eutectic Electrolyte.

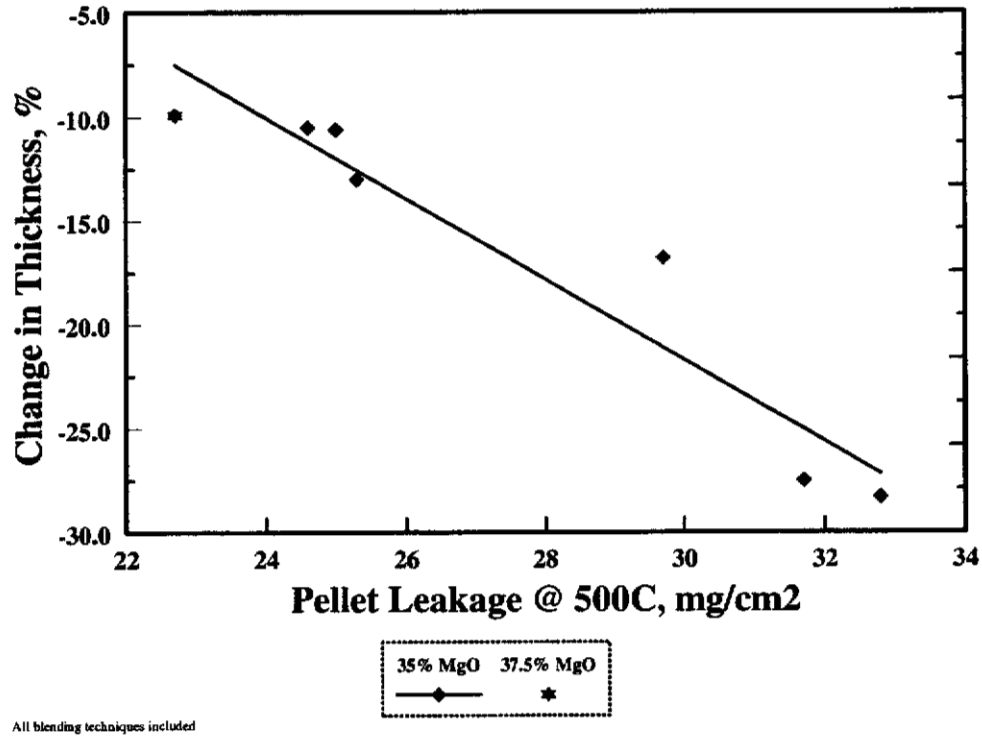

Figure 5. Comparison of Deformation and Electrolyte Leakage for Separator Pellets based on LiCl-LiBr-LiF Electrolyte.

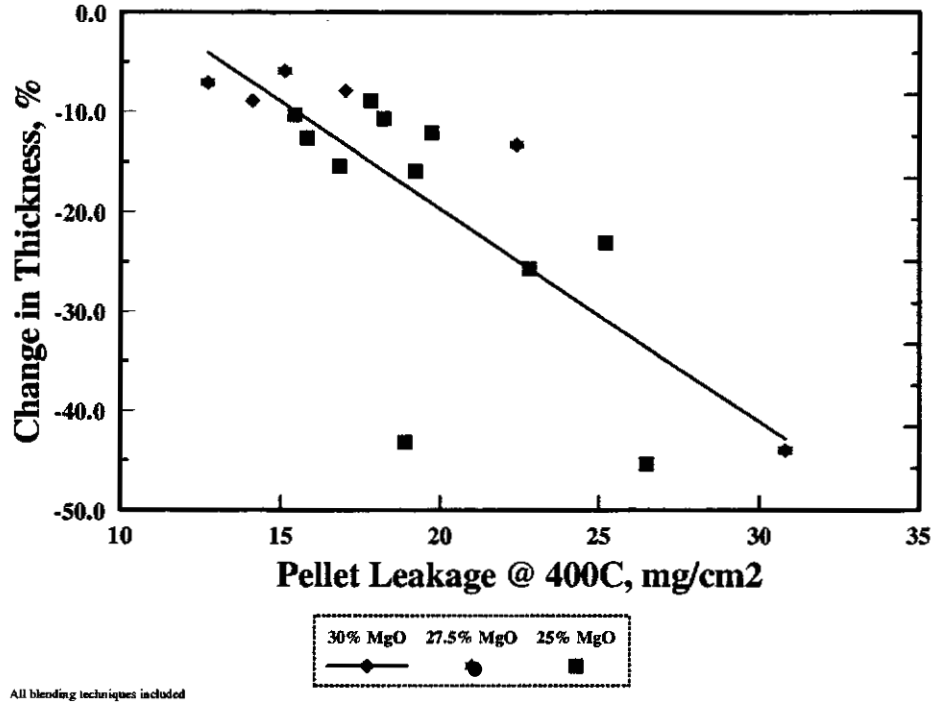

Figure 6. Comparison of Deformation and Electrolyte Leakage for Separator Pellets based on LiBr-KBr-LiF Eutectic Electrolyte.

equipment or calibration as does the deformation test.

Single-Cell Tests

LiCl-KCl Eutectic – The reproducibility of the voltage and polarization profiles of Li(Si)/FeS_2 single-cell tests at 500°C with Freon-blended separators based on LiCl-KCl eutectic and 35% Maglite 'S' MgO are shown in Figures 7 and 8, respectively, for a steady-state load of 125 mA/cm^2 with pulses of 250 mA/cm^2. The voltage response showed good repeatability (Figure 7) and correlates well with the total polarization (resistance) (Figure 8). The first hump in the polarization curves is observed at the same time that a voltage transition occurs (Figure 7) and reflects the increase in resistance of the first discharge phase, $Li_3Fe_2S_4$, relative to that of FeS_2. The second, smaller hump in the polarization curves also occurs near a voltage transition, where formation of the next discharge phase, Li_2FeS_2, begins. Comparable behavior was also observed for similar cells with pulses of 975 mA/cm^2 (Figures 9 and 10). The sharp drops in voltage during discharge occurred during application of the heavy pulse. The cells recovered quickly at the lighter (250 mA/cm^2) pulse load so that the voltage traces under those conditions did not show these voltage drops (Figure 8).

The performance of Li(Si)/FeS_2 single cells at 500°C built with the various separators based on LiCl-KCl eutectic and processed by various methods are summarized in Figures 11 and 12 for a steady-state load of 125 mA/cm^2 and a pulse load of 250 mA/cm^2. The corresponding data for the pulse load of 975 mA/cm^2 are shown in Figures 13 and 14. Each set of data represents the average of three single-cell tests. The cells with the LN-blended separators with 35% Maglite 'S' MgO showed a somewhat lower voltage and

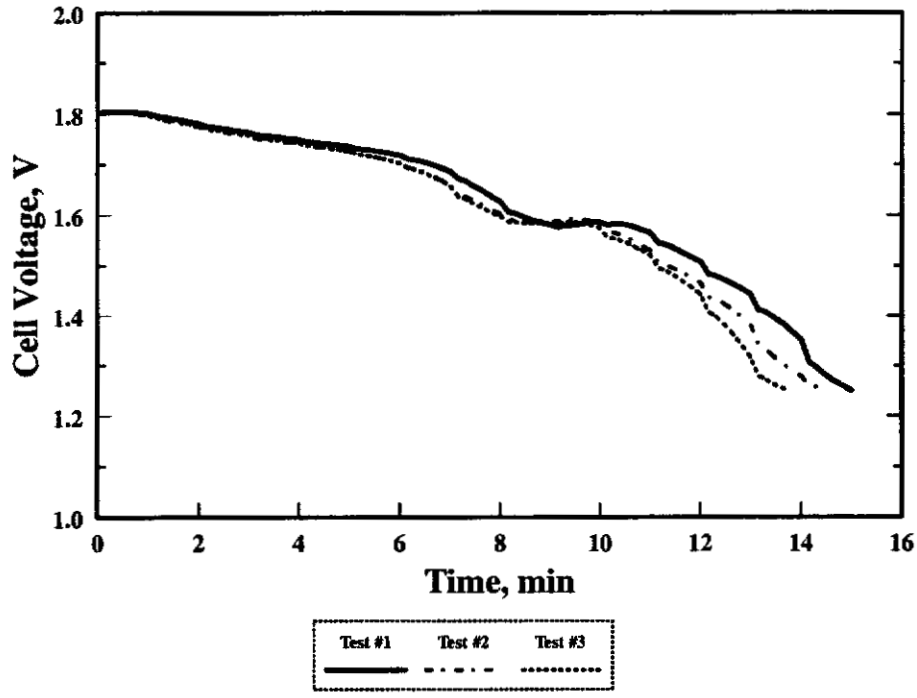

Figure 7. Voltage Response of Li(Si)/FeS_2 Cells Built with Freon-Blended Separator Made with 35% Maglite 'S' MgO and LiCl-KCl Eutectic and Discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

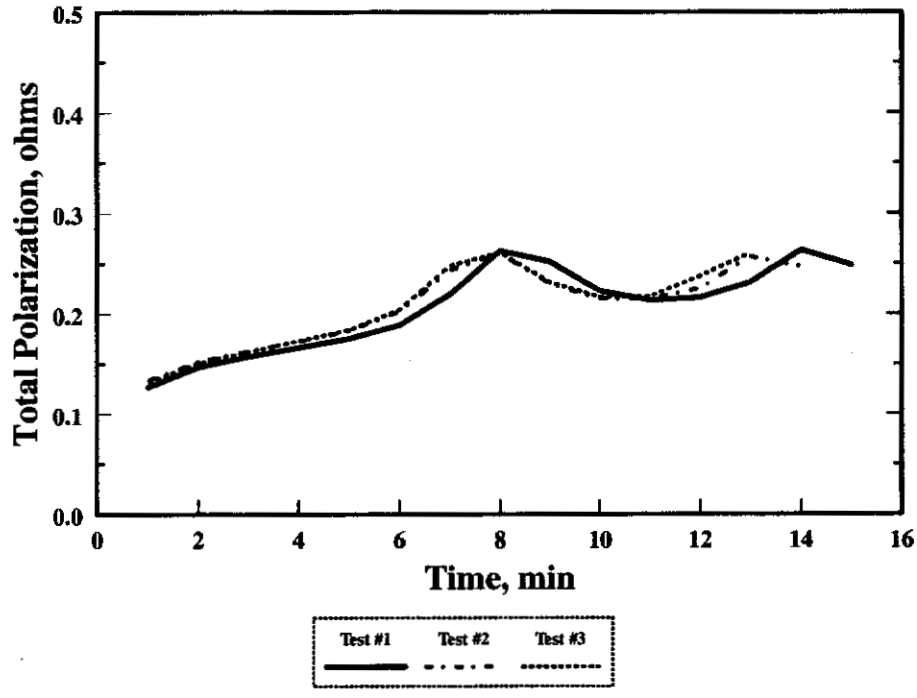

Figure 8. Total Polarization of Li(Si)/FeS_2 Cells Built with Freon-Blended Separator Made with 35% Maglite 'S' MgO and LiCl-KCl Eutectic and Discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

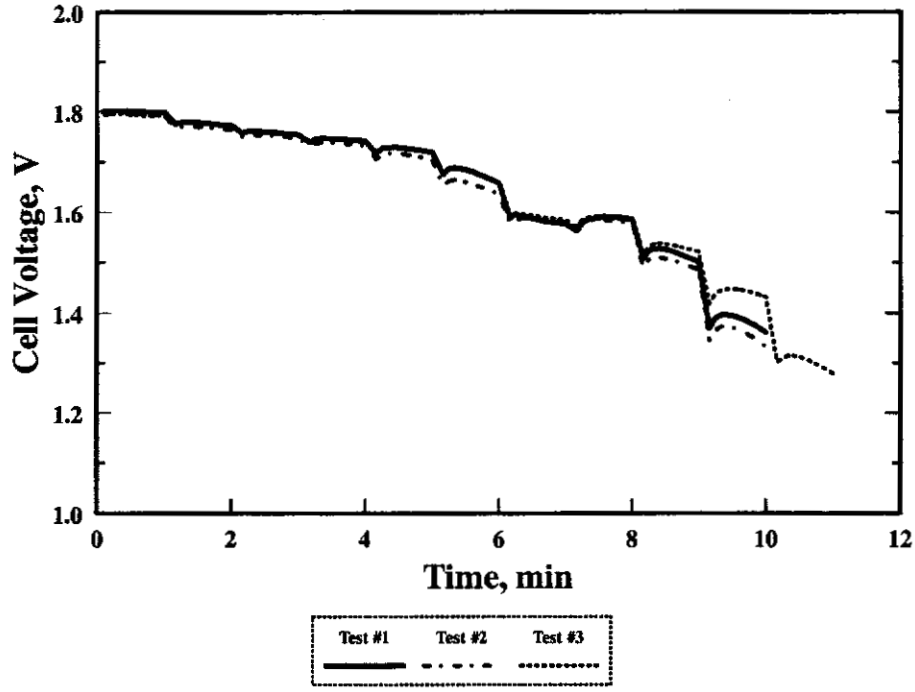

Figure 9. Voltage Response of Li(Si)/FeS_2 Cells Built with Freon-Blended Separator Made with 35% Maglite 'S' MgO and LiCl-KCl Eutectic and Discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

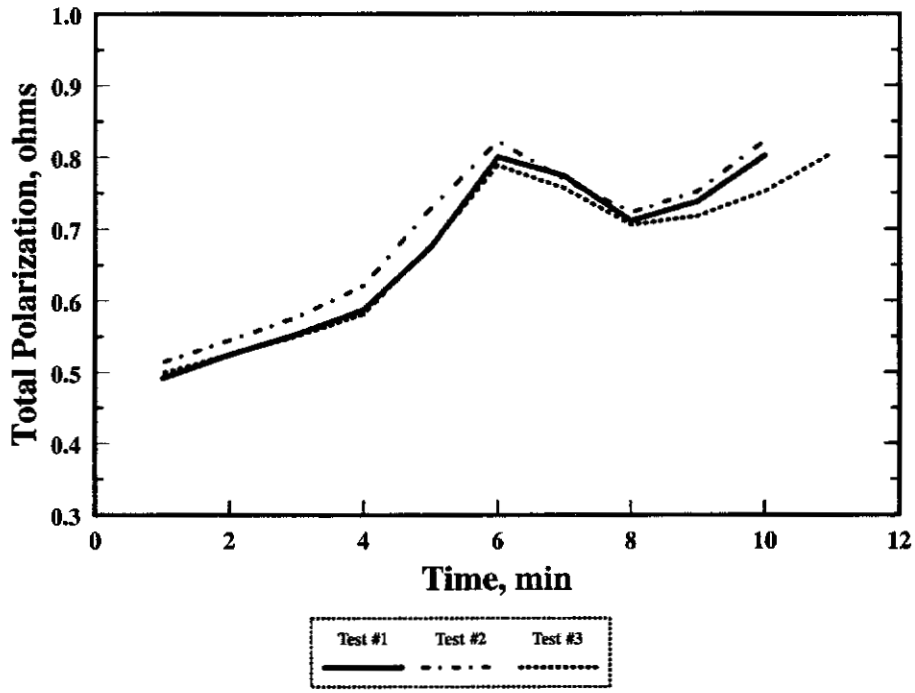

Figure 10. Total Polarization of Li(Si)/FeS_2 Cells Built with Freon-Blended Separator Made with 35% Maglite 'S' MgO and LiCl-KCl Eutectic and Discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

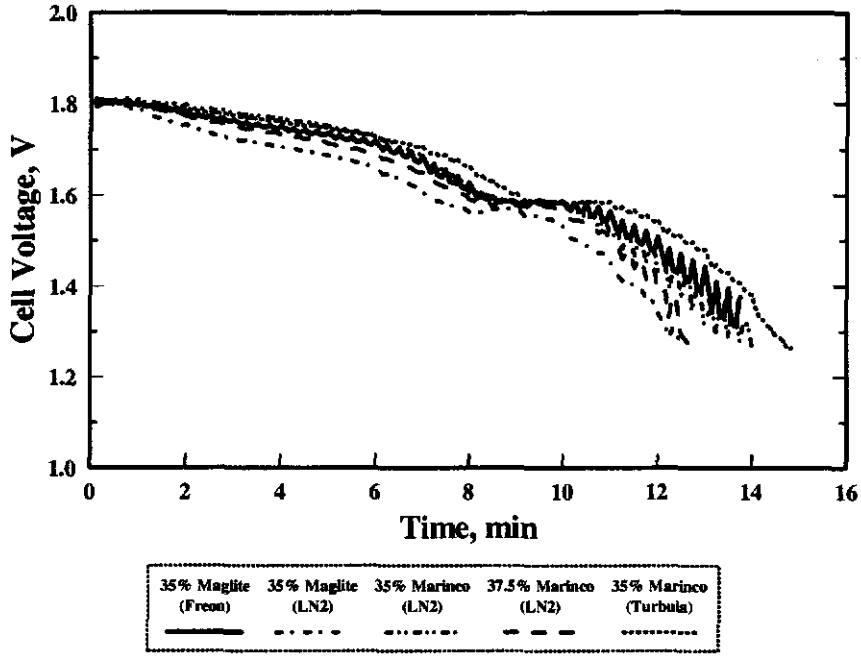

Figure 11. Voltage Response of Li(Si)/LiCl-KCl (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

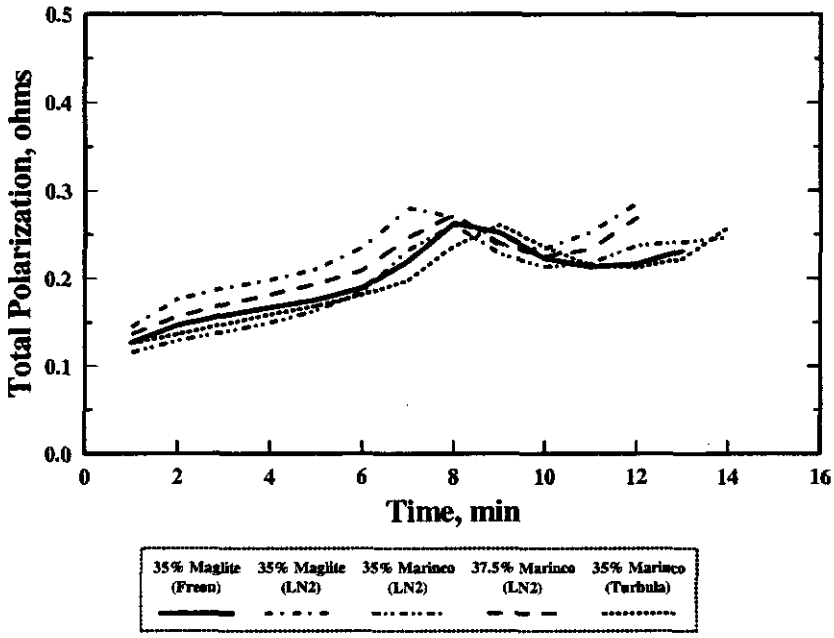

Figure 12. Total Polarization of Li(Si)/LiCl-KCl (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

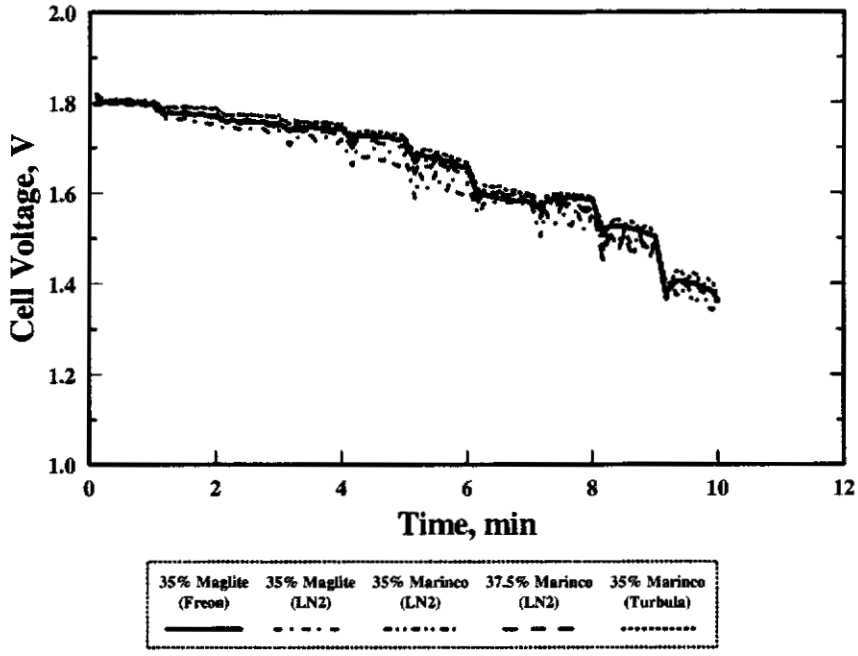

Figure 13. Voltage Response of Li(Si)/LiCl-KCl (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

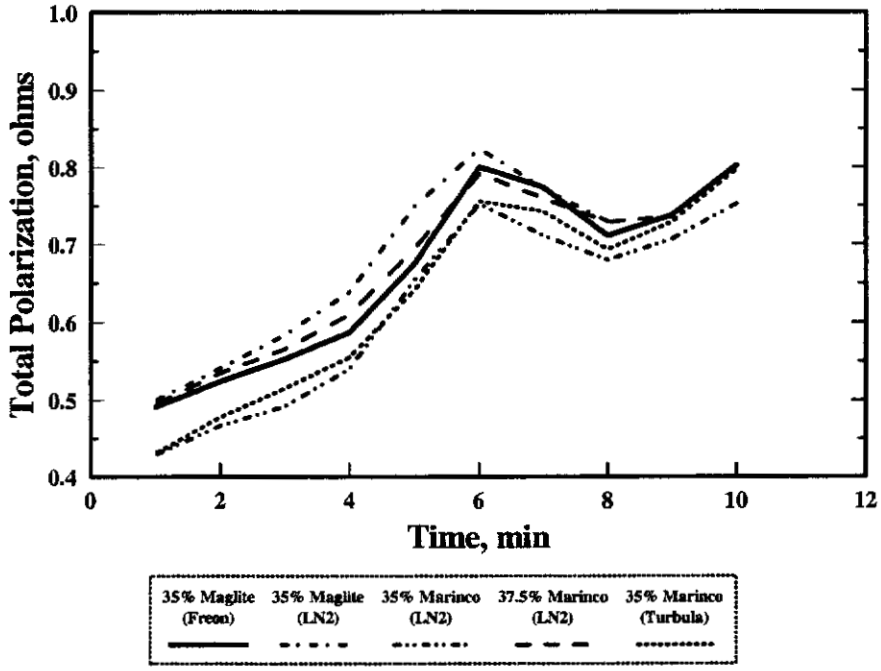

Figure 14. Total Polarization of Li(Si)/LiCl-KCl (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

higher polarization than the Freon-blended counterpart. The cells with the LN-blended separators with 35% Marinco 'OL' MgO showed slightly higher voltages and lower polarization than the Maglite 'S' counterpart. The cells with the sister separator mix with 37.5% Marinco 'OL' MgO were comparable in performance to those that used the standard Freon-blended separator with 35% Maglite 'S' MgO. The cells with the Turbula-blended separator with 35% Marinco 'OL' MgO showed the highest voltage (Figure 11) and the lowest total polarization (Figure 12). Similar results were observed at the higher pulse current density (Figures 13 and 14).

The results of the discharge tests are summarized in Table 4, in terms of activated life to a cutoff voltage of 1.25 V. Slightly longer activated lives were obtained at the lower pulse load for the LN-blended and Turbula-blended separator with 35% Marinco 'OL' MgO. The cells with LN-blended version containing 37.5% Marinco 'OL' MgO had activated lives slightly less than those of the standard cells made with Freon-blended separator with 35% Maglite 'S' MgO. The cells with the LN-blended separators with 35% Maglite 'S' MgO run slightly shorter than the standard cells with Freon-blended material. Similar behavior was noted at the heavier pulse load. The cells with the LN-blended separator with 37.5% Marinco 'OL' MgO also had slightly shorter lives relative to the standard cells at the heavier pulse load. The best overall performance was obtained using the dry-blended Turbula separators with 35% Marinco 'OL' MgO.

Table 4. Summary of Activated Lives of Li(Si)/FeS_2 Single Cells tested at 500°C and 125 mA/cm^2 Steady-State Current with Various Separators and MgOs for LiCl-KCl Eutectic.

MgO	% MgO	Blending Process	Pulse Current Density, mA/cm^2	Avg.* Activated Life, min	Standard. Dev., min
Maglite 'S'	35.0	Freon	250	14.4	0.67
	35.0	LN		13.1	0.64
Marinco 'OL'	35.0	Turbula		14.9	0.13
	35.0	LN		14.8	0.67
	37.5	LN		13.8	1.06
Maglite 'S'	35.0	Freon	975	10.4	0.58
	35.0	LN		9.10	1.00
Marinco 'OL'	35.0	Turbula		10.4	0.58
	35.0	LN		10.1	0.00
	37.5	LN		9.70	0.58

* Average of 3 tests.

There was evidence for some differences among the mixes under the light-load discharge condition when the statistical F test was applied. The cells with the LN-blended separators

with 35% Maglite 'S' showed more difference than those with the other separators. However, there was no statistical difference among the various cells under the high-load discharge condition. *The performance of cells with the LN-blended separator with 35% Marinco 'OL' MgO was comparable to that with the Freon-blended separator with 35% Maglite 'S' MgO for the LiCl-KCl eutectic under these test conditions.*

The use of unflooded anodes results in some movement of electrolyte from the separator into the anode. There is a lesser likelihood of electrolyte movement into the catholyte, since it already contains electrolyte in the form of separator material. This movement mitigates electrolyte leakage into the ceramic-fiber wrap used to insulate the battery stack. The electrolyte-leakage tests are done using discrete separator pellets, so that the type of interaction in single cells cannot occur under those test conditions. Therefore, one must be careful in comparing deformation and electrolyte-leakage data for discrete separator pellets to performance in single-cell tests, where electrolyte in the separator can communicate with the anode and, to a lesser degree, the cathode. A high deformation observed for a discrete separator pellet will be mitigated in a single cell by electrolyte movement into the adjacent anode and cathode.

LiCl-LiBr-LiF Electrolyte – The performance of Li(Si)/FeS_2 single cells at 500°C built with the various separators based on LiCl-LiBr-LiF electrolyte and processed by various methods are summarized in Figures 15 and 16 for a steady-state load of 125 mA/cm^2 and a pulse load of 250 mA/cm^2. The corresponding data for the pulse load of 975 mA/cm^2 are shown in Figures 17 and 18. The variability in voltage (Figure 15) and total polarization (Figure 16) among the various cells was much less than for the corresponding voltage response for cells based on the LiCl-KCl eutectic (Figures 11 and 12, respectively). The voltage traces were smoother with reduced maxima in the total polarization. The polarization data (Figure 16) suggest that the higher level of Marinco 'OL' of 37.5% is somewhat higher than optimum, although the performance was comparable to that for the cell with the Freon-blended separator with 35% MgO Maglite 'S'. The polarization was less for the cell with LN-blended separator with 35% Marinco 'OL' than for 37.5%. This was especially true for the higher-current pulses (Figure 18). The best overall performance was shown by the cells with the Turbula-blended separator with 35% Marinco 'OL' MgO.

The results of the discharge tests are summarized in Table 5, in terms of activated life to a cutoff voltage of 1.25 V. As expected, the activated lives for cells with the all-Li electrolyte were slightly greater than those with the LiCl-KCl eutectic (Table 4) —especially at the higher pulse load. The activated lives at the lower pulse load obtained for cells with the LN-blended and Turbula-blended separators with 35% Marinco 'OL' MgO were slightly greater than those for the standard cells with 35% Freon-blended Maglite 'S' MgO. The cells with LN-blended version containing 37.5% Marinco 'OL' MgO had comparable lives as the standard cells. At the heavier pulse load, the differences among the various cells was not as great as those observed for the LiCl-KCl eutectic (Table 4).

The optimum MgO level for the LN-blended separator is ~35% when using Marinco 'OL' with the all-Li electrolyte. Comparable results are obtained for the Turbula-bended

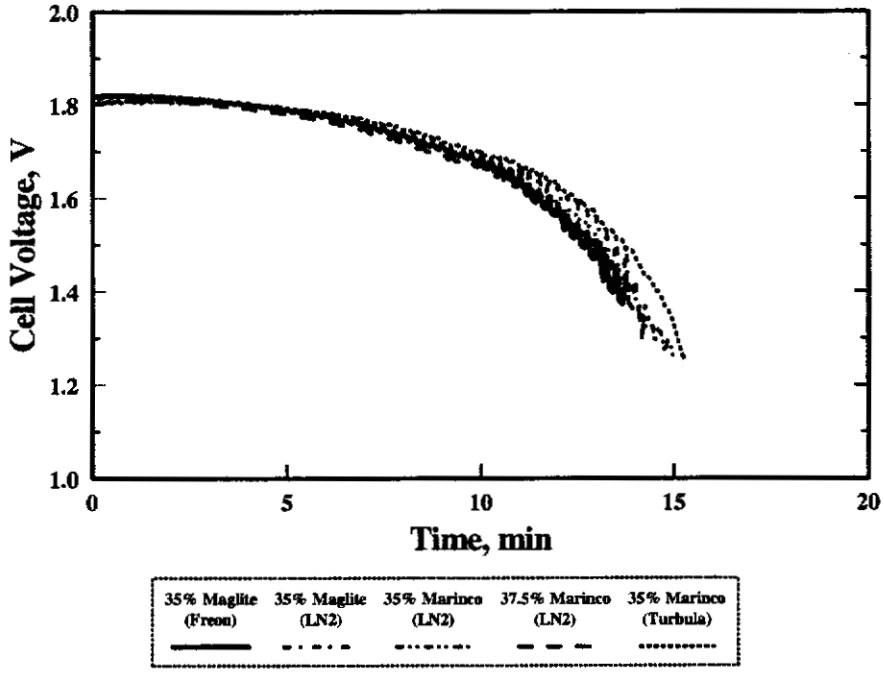

Figure 15. Voltage Response of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

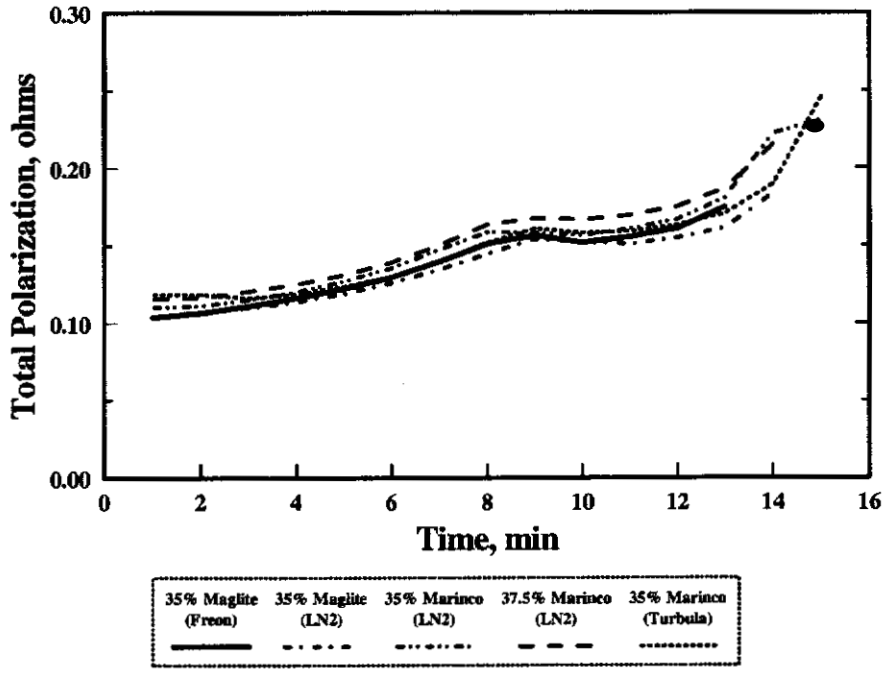

Figure 16. Total Polarization of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

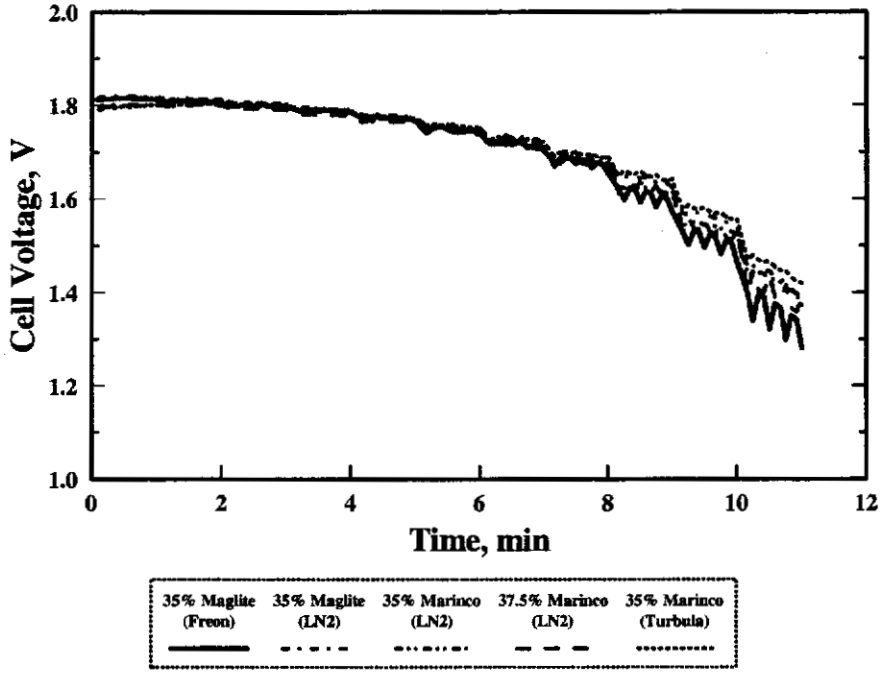

Figure 17. Voltage Response of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

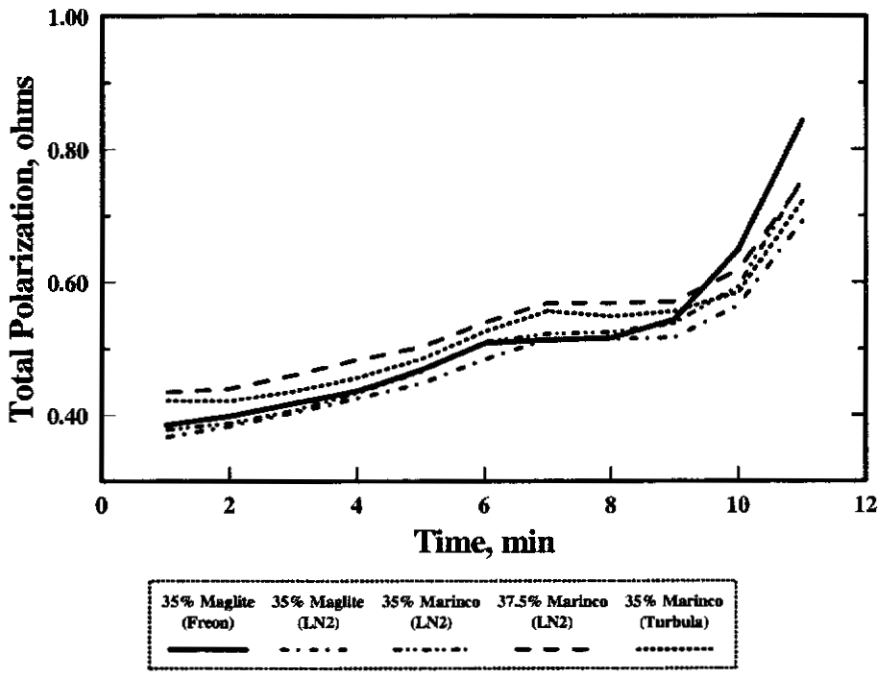

Figure 18. Total Polarization of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

separator with 35% Marinco 'OL' MgO. Statistically, there were no differences among the cells for the various separator mixes under both the light load and heavy load when applying the F test.

Table 5. Summary of Activated Lives of Li(Si)/FeS_2 Single Cells tested at 500°C and 125 mA/cm^2 Steady-State Current with Various Separators and MgOs for LiCl-LiBr-LiF Electrolyte.

MgO	% MgO	Blending Process	Pulse Current Density, mA/cm^2	Avg.* Activated Life, min	Standard. Dev., min
Maglite 'S'	35.0	Freon	250	14.5	0.63
	35.0	LN		14.8	0.68
Marinco 'OL'	35.0	Turbula		15.4	0.05
	35.0	LN		15.2	0.29
	37.5	LN		14.6	0.44
Maglite 'S'	35.0	Freon	975	11.3	0.39
	35.0	LN		11.5	0.42
Marinco 'OL'	35.0	Turbula		11.4	0.29
	35.0	LN		11.4	0.53
	37.5	LN		11.1	0.00

* Average of 3 tests.

LiBr-KBr-LiF Eutectic – The performance of Li(Si)/FeS_2 single cells at 500°C built with the various separators based on LiBr-KBr-LiF eutectic and processed by various methods are summarized in Figures 19 and 20 for a steady-state load of 125 mA/cm^2 and a pulse load of 250 mA/cm^2. The corresponding data for the pulse load of 975 mA/cm^2 are shown in Figures 21 and 22. The performance of cells with Freon-blended and LN blended separators made with 35% Maglite 'S' MgO were comparable. When substituting Marinco 'OL' MgO, an improvement in performance was realized at a level of 27.5% MgO for LN-blended material. Except for the superior-performing cells with the Turbula-blended separator, the cell voltages were similar for the various separators. The hump in polarization observed in earlier tests (*e.g*, Figures 8, 10, 12, 14, and 18) was essentially gone for this electrolyte (Figure 20).

The results of the discharge tests are summarized in Table 6, in terms of activated life to a cutoff voltage of 1.25 V. The activated lives of cells with the low-melting electrolyte were slightly shorter than those for cells with the LiCl-KCl eutectic. There was generally a greater range in the activated lives, however, for the cells with the low-melting electrolyte. As was noted for the other electrolytes, the cells that used the Turbula-blended separator (with 25% Marinco 'OL' MgO) showed the longest activated lives for both pulse loads. Slightly improved performance was attained with cells that used the LN-blended separator

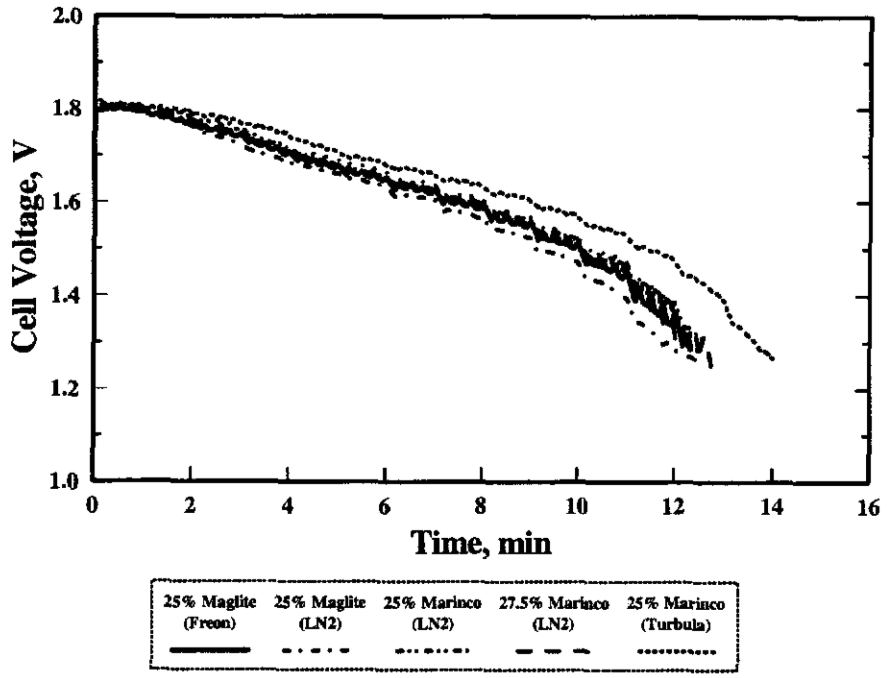

Figure 19. Voltage Response of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

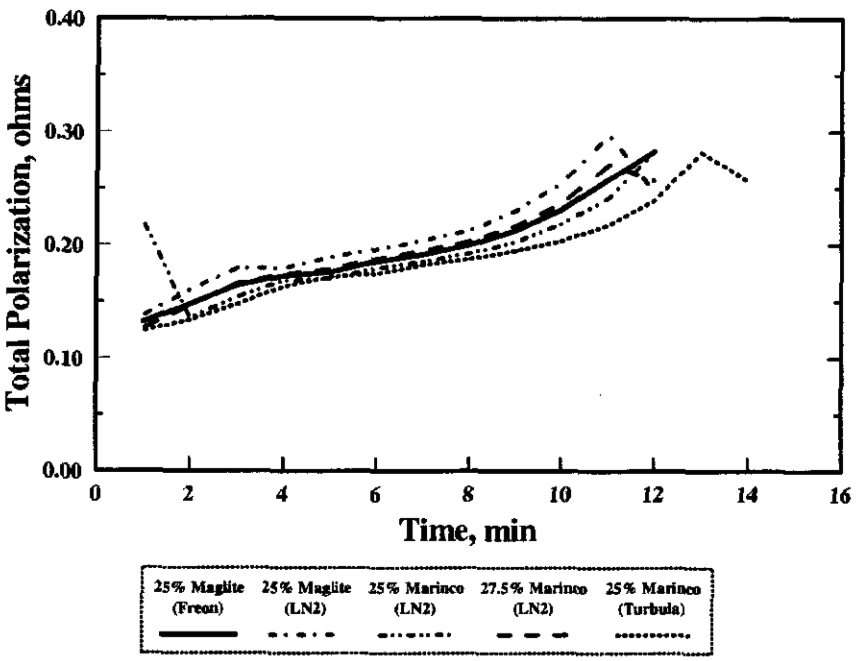

Figure 20. Total Polarization of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 250-mA/cm^2 Pulses Applied every Minute.

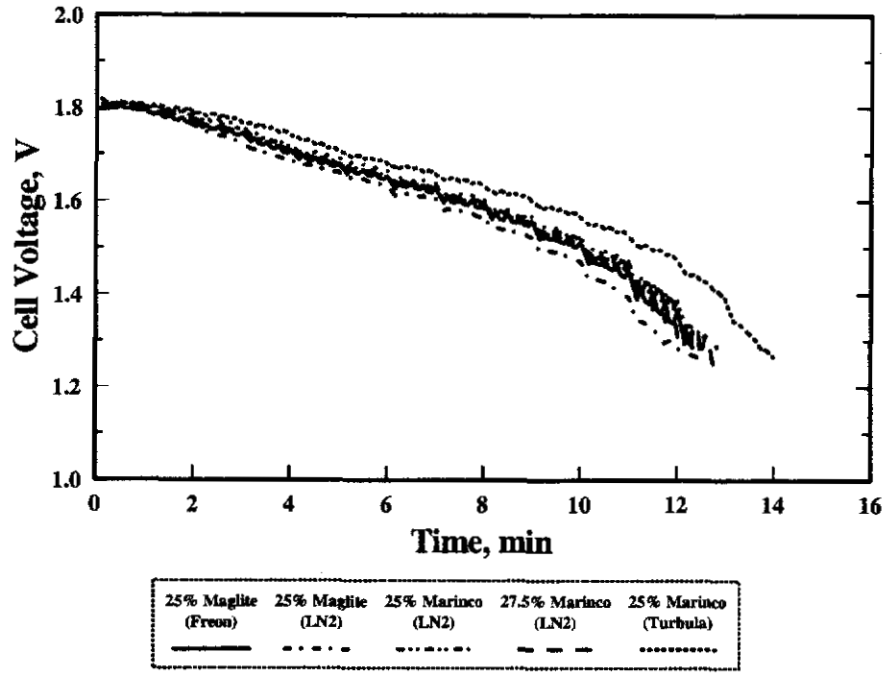

Figure 21. Voltage Response of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

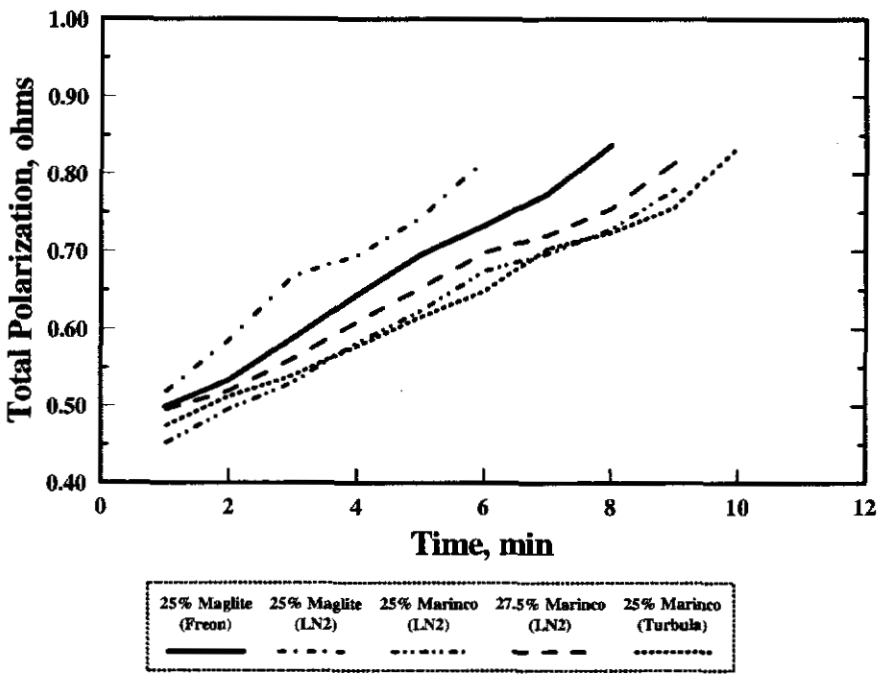

Figure 22. Total Polarization of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 Cells Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged at 500°C at 125 mA/cm^2 with 5-s, 975-mA/cm^2 Pulses Applied every Minute.

with 27.5% Marinco 'OL' compared to the standard cells with the Freon-blended separator with 25% Maglite 'S' MgO.

Table 6. Summary of Activated Lives of Li(Si)/FeS_2 Single Cells tested at 500°C and 125 mA/cm^2 Steady-State Current with Various Separators and MgOs for LiBr-KBr-LiF Eutectic.

MgO	% MgO	Blending Process	Pulse Current Density, mA/cm^2	Avg.* Activated Life, min	Standard. Dev., min
Maglite 'S'	35.0	Freon	250	13.0	0.63
	35.0	LN		12.8	0.30
Marinco 'OL'	35.0	Turbula		14.3	0.43
	35.0	LN		13.7	0.91
	37.5	LN		13.5	0.57
Maglite 'S'	35.0	Freon	975	8.70	1.15
	35.0	LN		6.70	1.15
Marinco 'OL'	35.0	Turbula		10.1	0.00
	35.0	LN		9.40	0.58
	37.5	LN		9.10	0.00

* Average of 3 tests.

The best overall performance was provided with the Turbula-blended separator with 25% Marinco 'OL' MgO. Applying the F test to the data, the cells with LN-blended, 35% Marinco 'OL' were statistically different than those with the other separators when tested under both the light and heavy loads.

Five-Cell Battery Tests

LiCl-KCl Eutectic – The voltage responses of Li(Si)/FeS_2 5-cell batteries activated at -54°C for the various separator mixes are shown in Figure 23 for the LiCl-KCl eutectic. The corresponding total-polarization data are shown in Figure 24. (In most cases, the data are averages of at least three tests per condition. The data for the standard Freon-blended mixes are averages of 10 tests.) The battery voltages were comparable for the initial portion of the discharge up to ~8 min, at which point electrolyte freezing started. The battery voltage afterwards was the highest for the batteries that used the standard Freon-blended separators with 35% Maglite 'S' MgO. The next highest voltage was shown by batteries using Turbula-blended separator with 40% Marinco 'OL' MgO. (This composition was not included in mixes tested in single cells.) The batteries that used the LN-blended counterpart were slightly lower under the same conditions. The batteries that used the LN-blended separator with 37.5% Marinco 'OL' MgO showed the lowest voltages (Figure 23) and highest polarization (Figure 24) after 8 min. To a large extent, these differences reflect the slight differences in thermal history of the batteries (Figure 25),

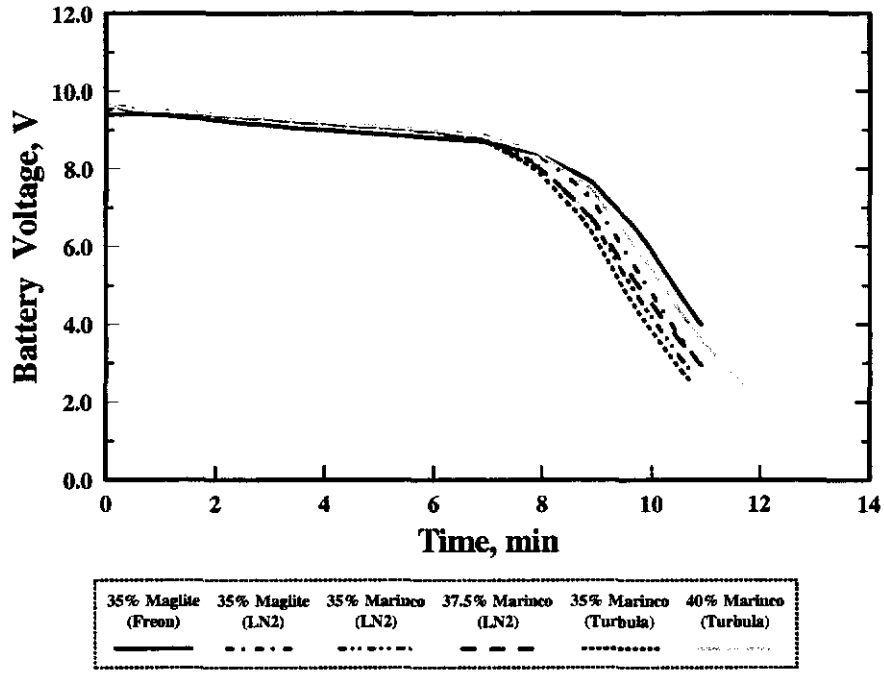

Figure 23. Voltage Response of Li(Si)/LiCl-KCl (MgO)/FeS_2 5-Cell Batteries Activated at –54°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

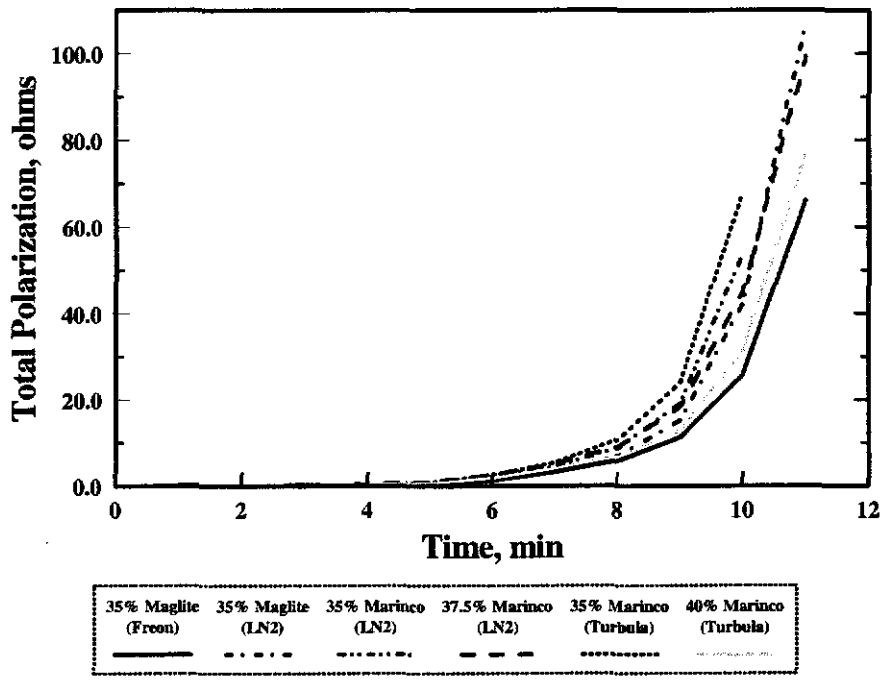

Figure 24. Total Polarization of Li(Si)/LiCl-KCl (MgO)/FeS_2 5-Cell Batteries Activated at –54°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

which can significantly influence performance. The trends in performance for batteries with the various separators did not track those observed in the isothermal single-cell tests at 500°C in terms of activated lives at loads of 125 mA/cm^2 with 250 mA/cm^2 pulses (Table 4). This indicates that single-temperature isothermal tests are not adequate for predicting trends in battery performance. What performed best in single-cells tests performed the worst in 5-cell battery tests. It is not possible to simulate the dynamic temperature environment of a battery in single-cell tests. The thermal impulse caused when the heat pellet ignites is not generated during isothermal testing of single cells.

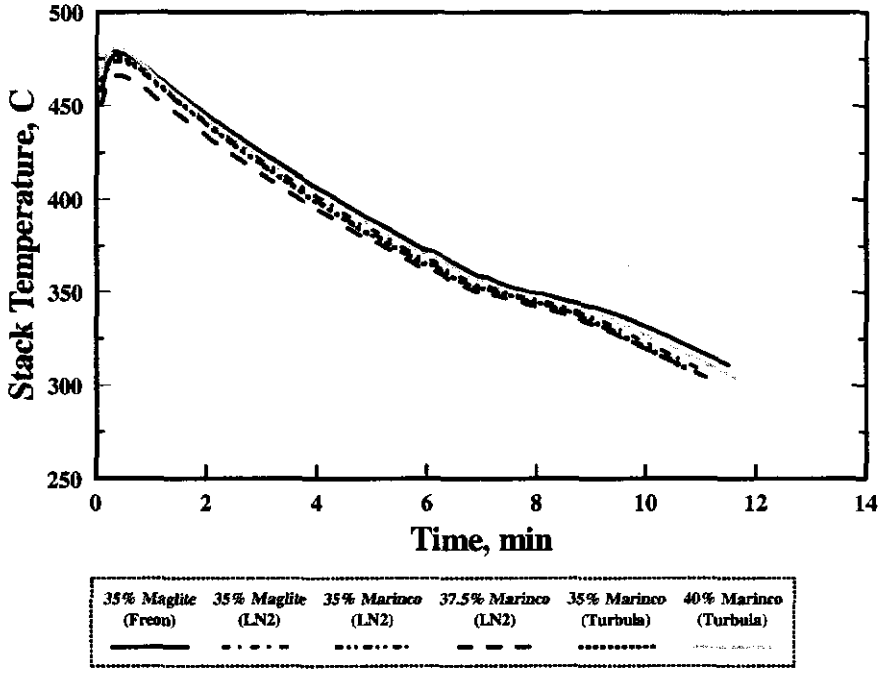

Figure 25. Battery Stack-Temperature Profile for the Batteries of Figures 23 and 24.

The corresponding voltage, polarization, and temperature data for batteries activated at +74°C are shown in Figures 26, 27, and 28, respectively. The performance among the various types of batteries was consistent out to a time of ~12 min when electrolyte freezing began (Figure 26). The total polarization showed similar trends with time (Figure 27). Later in discharge, differences in performance started to become noticeable. The best overall results were obtained with the batteries that used the Turbula-blended separator with 40% Marinco 'OL'. The next best performance was for those that used LN-blended separators containing 37.5% Marinco 'OL' MgO. There were minimal differences in the thermal responses of the various batteries (Figure 28). Except for the worst performing batteries, the relative ranking was not the same for the hot and cold batteries, which shows that relative temperature effects are important.

The activated lives for the various batteries are summarized in Table 7. Applying the F tests to these data showed that for the cold batteries, only the batteries with the Turbula-blended separator with 40% Marinco 'OL' MgO were comparable to the standard Freon-blended separator with 35% Maglite 'S'. All of the others were statistically different (p=0.05). This was not true for the hot batteries, where the batteries with 35% LN-blended

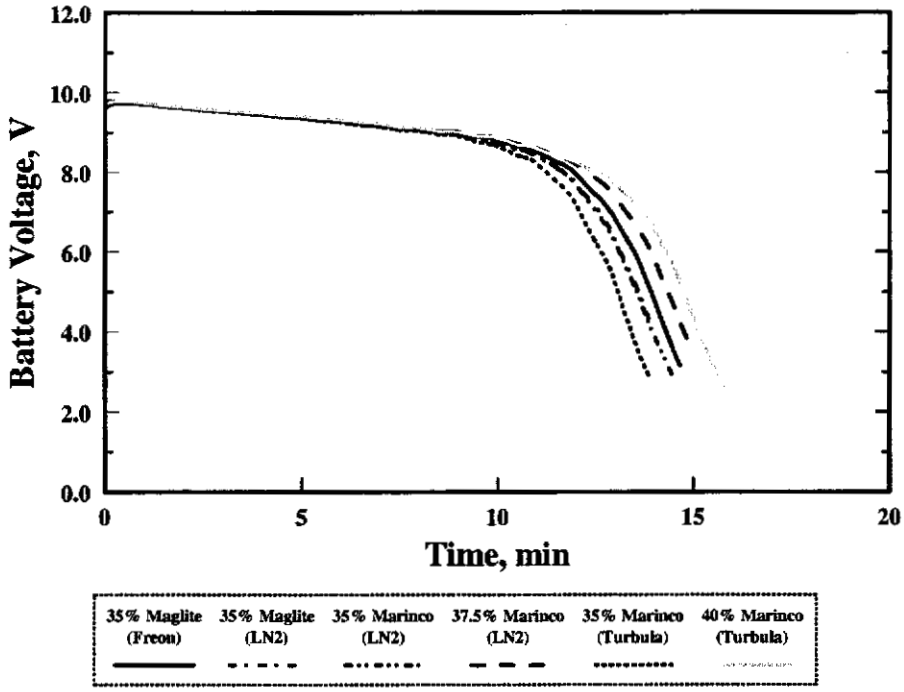

Figure 26. Voltage Response of Li(Si)/LiCl-KCl (MgO)/FeS_2 5-Cell Batteries Activated at +74°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

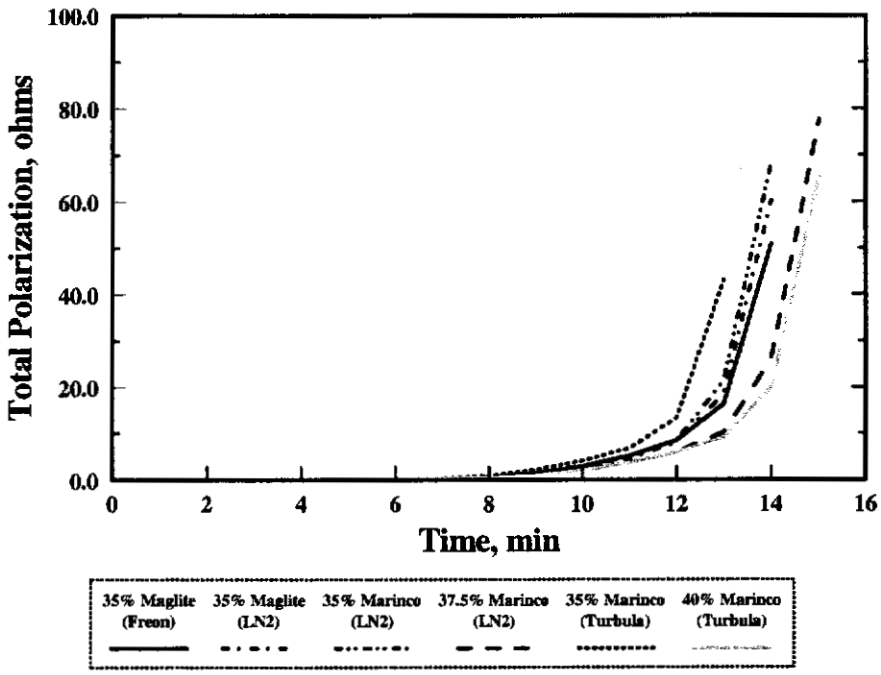

Figure 27. Total Polarization of Li(Si)/LiCl-KCl (MgO)/FeS_2 5-Cell Batteries Activated at +74°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

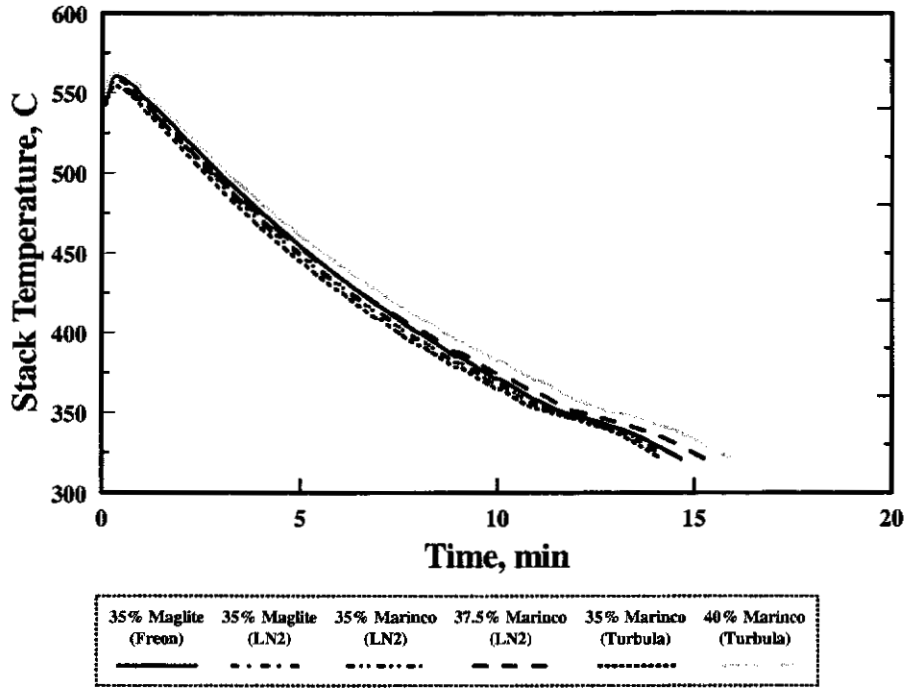

Figure 28. Battery Stack-Temperature Profile for the Batteries of Figures 26 and 27.

Table 7. Summary of Activated Lives of Li(Si)/FeS_2 5-Cell Batteries tested with 50-Ohm Steady-State Load with Various Separators and MgOs for LiCl-KCl Eutectic.

MgO	% MgO	Blending Process	Activ. Temp., °C	Avg.* Activated Life, min	Standard. Dev., min**
Maglite 'S'	35.0	Freon	-54	9.82	0.24 (10)
	35.0	LN		9.33	0.22 (3)
Marinco 'OL'	35.0	Turbula		9.00	--- (1)
	35.0	LN		9.03	0.05 (3)
	37.5	LN		9.21	0.21 (3)
	40.0	Turbula		9.58	--- (1)
Maglite 'S'	35.0	Freon	+74	13.3	0.32 (10)
	35.0	LN		12.9	0.24 (3)
Marinco 'OL'	35.0	Turbula		12.6	--- (1)
	35.0	LN		13.0	0.13 (3)
	37.5	LN		13.9	0.17 (3)
	40.0	Turbula		14.1	--- (1)

* Average of 3 tests. ** Number of tests is indicated in parentheses.

Marinco 'OL' was statistically equal to those with the standard separator.

LiCl-LiBr-LiF Electrolyte – The voltage responses of Li(Si)/FeS_2 5-cell battery tests at -54°C for the various separator mixes are shown in Figure 29 for the all-Li electrolyte. The corresponding total-polarization data are shown in Figure 30 and the stack-temperature profiles are shown in Figure 31. The voltage response for the batteries that used the LN-blended separator mix with 37.5% Marinco 'OL' MgO was identical to those that used the standard Freon-blended separator mix with 35% Maglite 'S' MgO (Figure 29). The polarization behaviors were also the same (Figure 30). There was very little difference in the stack-temperature profiles for the various batteries (Figure 31).

The trend in performance is similar to what was observed in single-cell tests at 500°C, where identical activated lives were observed for cells with these two separators at a load of 125 mA/cm^2 with 250 mA/cm^2 pulses (Table 5).

The corresponding voltage, polarization, and temperature data for batteries activated at +74°C are shown in Figures 32, 33, and 34, respectively. The performance among the various types of batteries was comparable out to a time of ~8 min when electrolyte freezing began (Figure 32). The total polarization showed similar trends as the voltage (Figure 33). Differences in performance became evident later in discharge. The best overall results were obtained with the batteries that used the LN-blended separators containing 37.5% Marinco 'OL' MgO. There were slight differences in the thermal responses of the battery stacks, with the batteries with the standard Freon-blended separator being slightly cooler (Figure 34).

The activated lives for the various batteries are summarized in Table 8. Applying the F test to these data, only the cold batteries with the LN-blended separator with 37.5% Marinco 'OL' MgO were statistically similar to those with the standard Freon-blended separator with 35% Maglite 'S' MgO. Completely different results were obtained for the hot batteries, where those with LN-blended separator with 35% Maglite 'S' MgO and Turbula-blended and LN-blended separators with 35% Marinco 'OL' were comparable to batteries with the standard Freon-blended separator.

Note that even though the all-Li electrolyte melts at a much higher temperature (436°C) than does the LiCl-KCl eutectic (352°C), cells built with it ran longer—especially at the higher activation temperature. This is a direct consequence of the much higher ionic conductivity of the all-Li electrolyte. (The conductivity of a separator pellet made with 35% Maglite 'S' MgO and the all-Li electrolyte is 1.84 S/cm at 500°C; this compares to only 0.97 S/cm for the same composition with LiCl-KCl eutectic.)[5]

The high ionic conductivity of the all-Li electrolyte is reflected in the voltage response of the battery as the electrolyte freezes. Even in the presence of significant amounts of solids, the ionic conductivity is still surprisingly good. Consequently, the voltage roll-off during freezing is much more gradual than that observed for batteries with the LiCl-KCl eutectic (Figure 28).

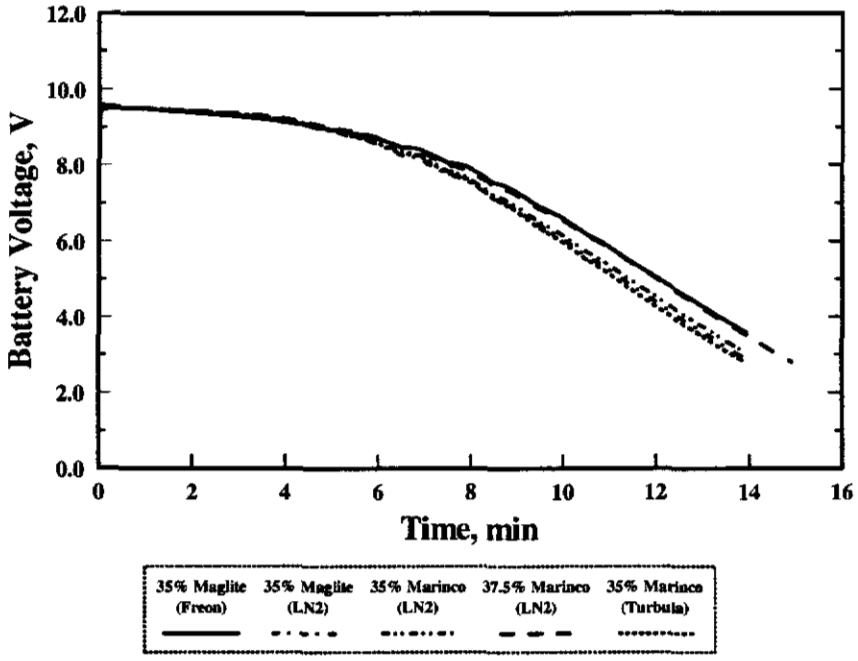

Figure 29. Voltage Response of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at –54°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

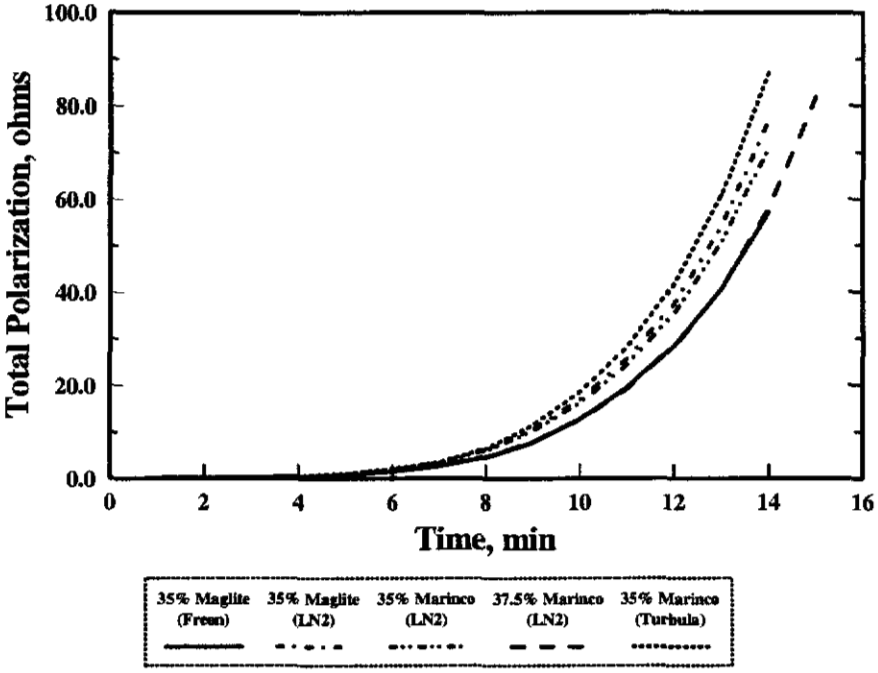

Figure 30. Total Polarization of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at –54°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

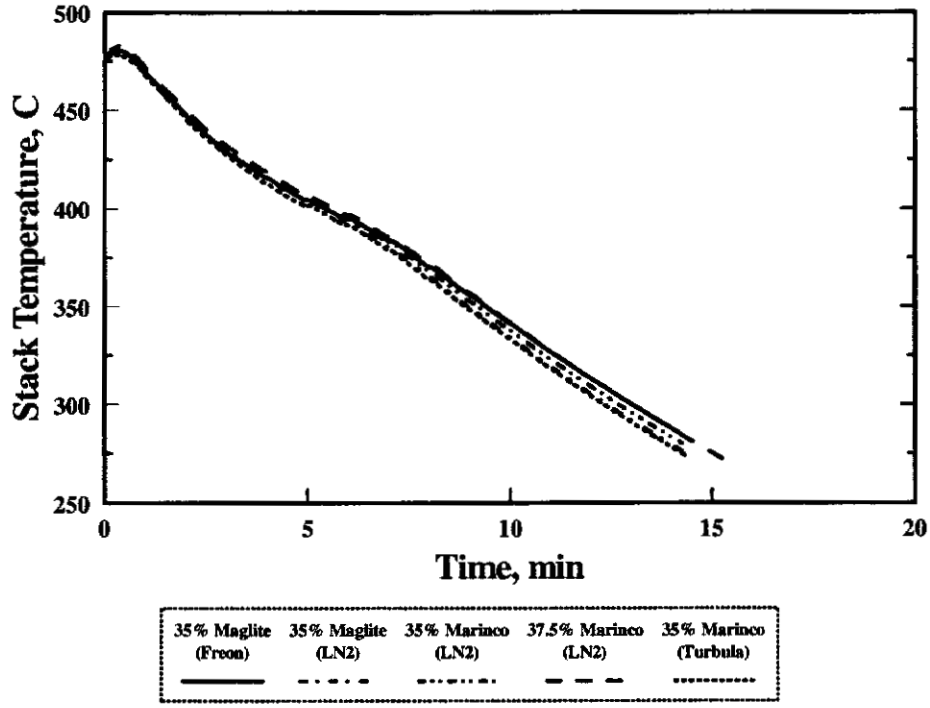

Figure 31. Battery Stack-Temperature Profile for the Batteries of Figures 29 and 30.

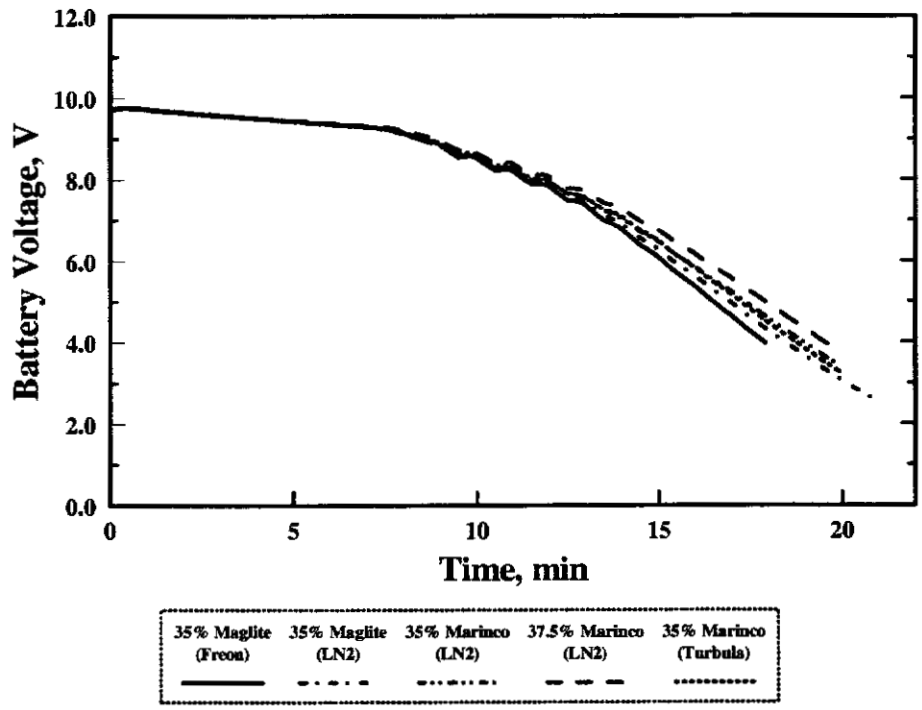

Figure 32. Voltage Response of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at +74°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

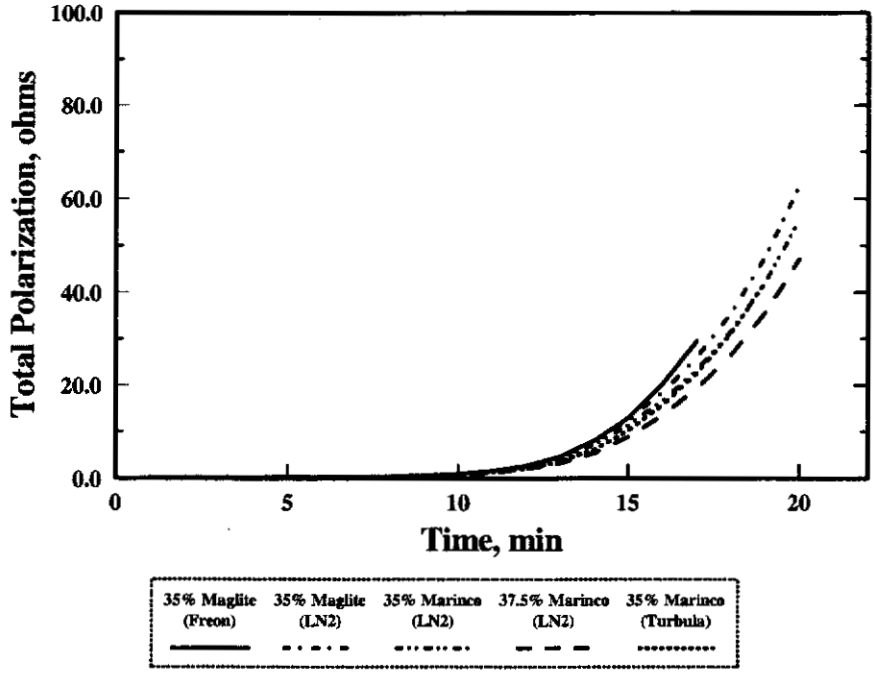

Figure 33. Total Polarization of Li(Si)/LiCl-LiBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at +74°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

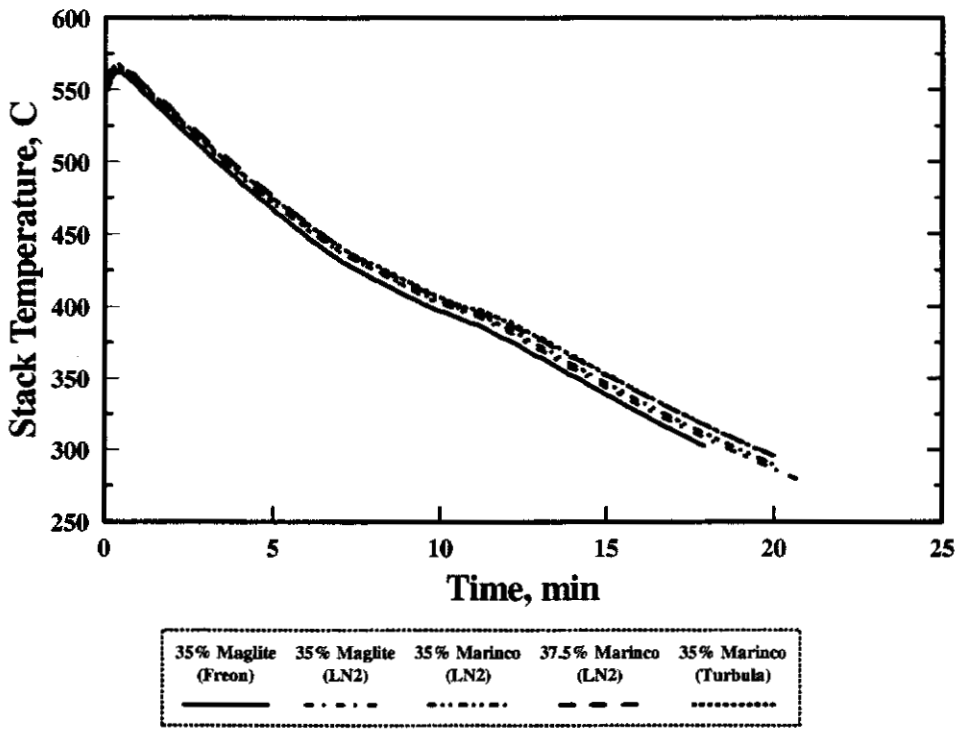

Figure 34. Battery Stack-Temperature Profile for the Batteries of Figures 32 and 33.

Table 8. Summary of Activated Lives of Li(Si)/FeS_2 5-Cell Batteries tested with 50-Ohm Steady-State Load with Various Separators and MgOs for LiCl-LiBr-LiF Electrolyte.

MgO	% MgO	Blending Process	Activ. Temp., °C	Avg.* Activated Life, min	Standard. Dev., min**
Maglite 'S'	35.0	Freon	-54	10.4	0.45 (10)
	35.0	LN		9.78	0.10 (3)
Marinco 'OL'	35.0	Turbula		9.08	---- (1)
	35.0	LN		9.86	0.21 (3)
	37.5	LN		10.1	0 (3)
Maglite 'S'	35.0	Freon	+74	14.6	0.67 (10)
	35.0	LN		15.0	0.14 (3)
Marinco 'OL'	35.0	Turbula		15.1	---- (1)
	35.0	LN		15.1	0 (3)
	37.5	LN		15.9	0.13 (3)

* Average of 3 tests. ** Number of tests is indicated in parentheses.

LiBr-KBr-LiF Eutectic – The voltage responses of Li(Si)/FeS_2 5-cell battery tests at -54°C for the various separator mixes are shown in Figure 35 for the low-melting eutectic. The corresponding total-polarization data are shown in Figure 36 and the stack-temperature profiles are shown in Figure 37. There was a noticeable spread in the voltage traces for the batteries that used the low-melting electrolyte, compared to batteries based on the LiCl-KCl eutectic. In the latter case, the initial voltage responses for the various separators were essentially identical for the early part of the discharge. That was not observed for the batteries with the low-melting electrolyte.

The initial voltage plateau was slightly lower for the batteries with the standard Freon-blended separator with 25% Maglite 'S'. These batteries, however, had the longest activated lives and slightly higher stack temperatures (Figure 37). The batteries that used the LN-blended separator with 27.5% Marinco 'OL' MgO and the Turbula-blended separator with 25% Marinco 'OL' MgO showed the closest performance to the standard batteries with the standard Freon-blended separator (Figure 35). The relative polarization behaviors were also comparable (Figure 36). In the single-cell tests at 500°C at 125 mA/cm^2 with 250 mA/cm^2 pulses, the cells with the Turbula-blended separator with 25% Marinco 'OL' MgO actually ran the longest. The temperatures for the batteries with the Turbula-blended separators were identical to those with the standard Freon-blended separators.

The corresponding voltage, polarization, and temperature data for batteries activated at +74°C are shown in Figures 38, 39, and 40, respectively. The performance among the various types of batteries showed a spread in voltages as was observed for the cold batteries

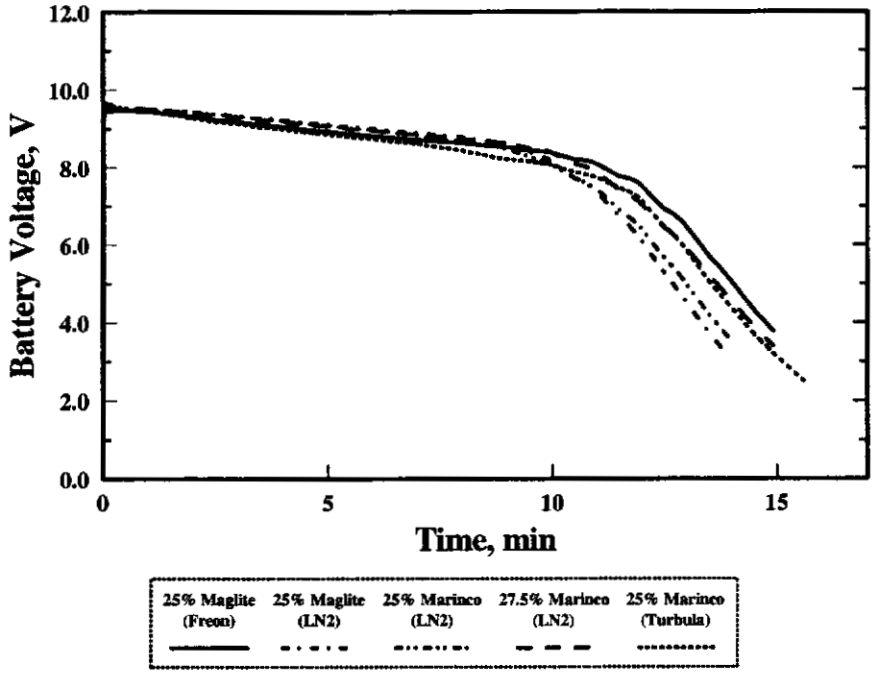

Figure 35. Voltage Response of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at –54°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

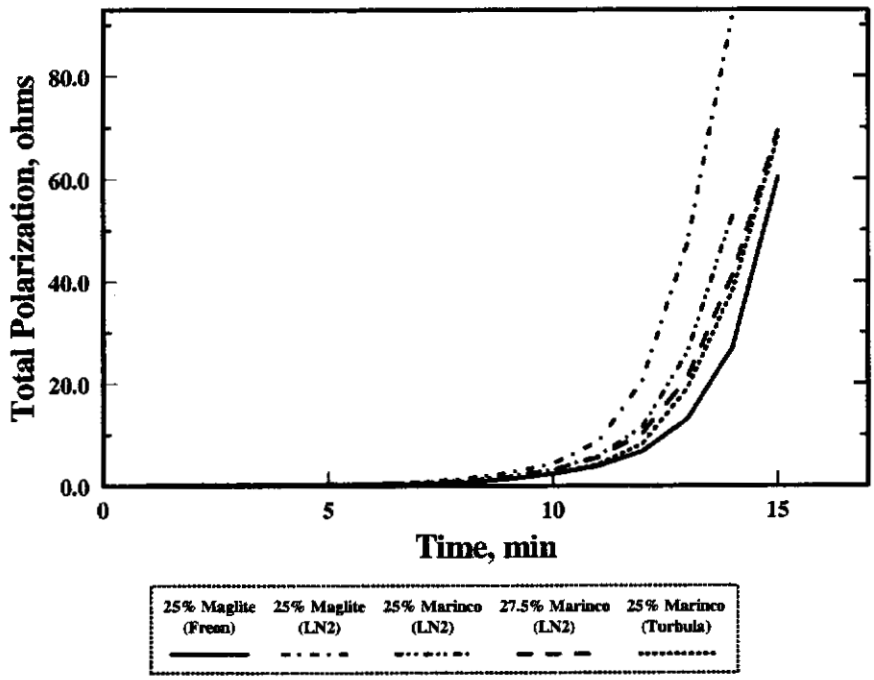

Figure 36. Total Polarization of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at –54°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

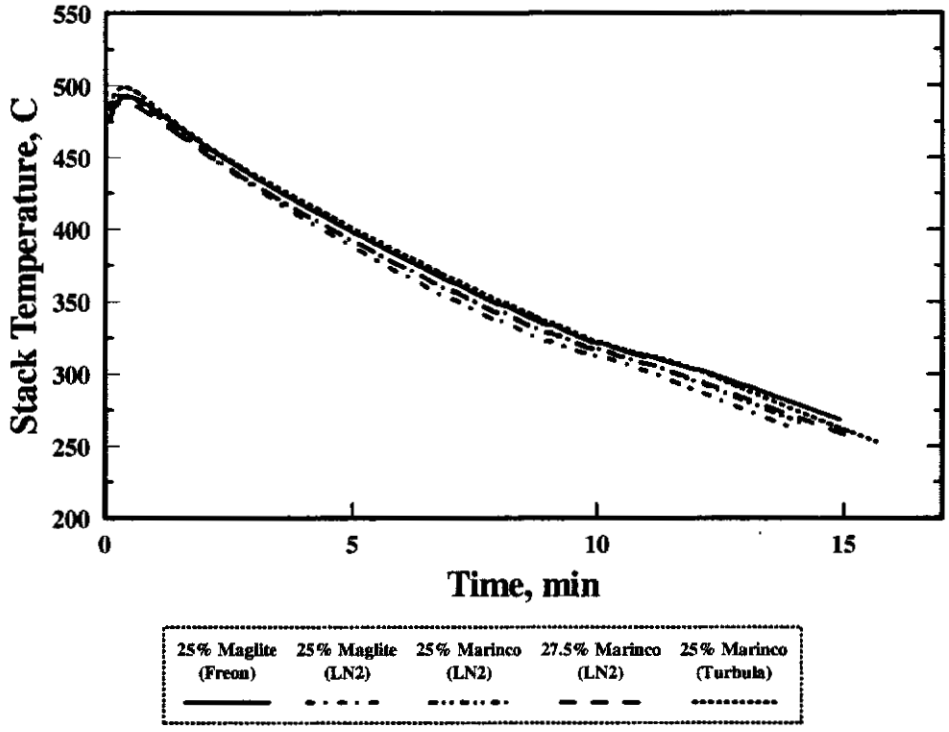

Figure 37. Battery Stack-Temperature Profile for the Batteries of Figures 35 and 36.

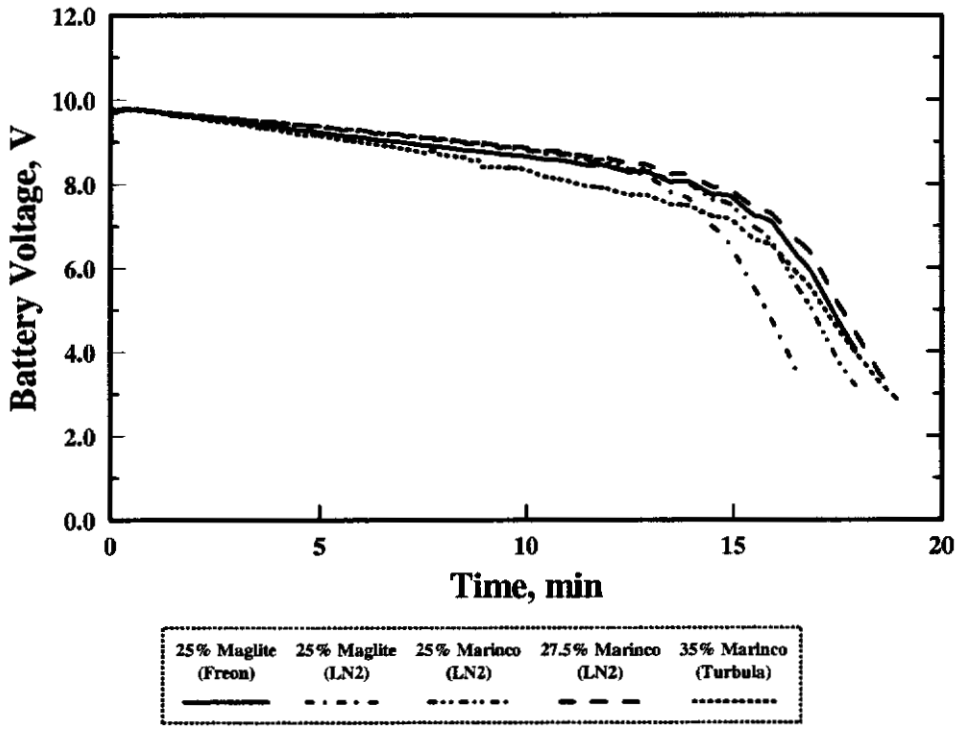

Figure 38. Voltage Response of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at +74°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

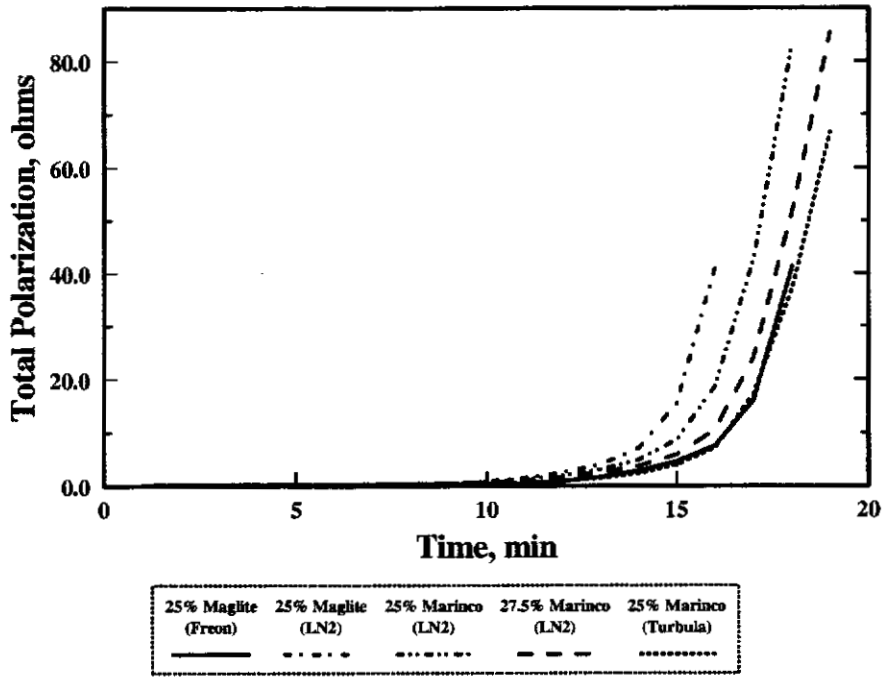

Figure 39. Total Polarization of Li(Si)/LiBr-KBr-LiF (MgO)/FeS_2 5-Cell Batteries Activated at +74°C and Built with Separators Processed by Various Methods and Made with Maglite 'S' and Marinco 'OL' MgO. Cells were discharged with a 50-Ohm Steady-State Load with 5-s, 1.05-Ohm Pulses Applied every Minute.

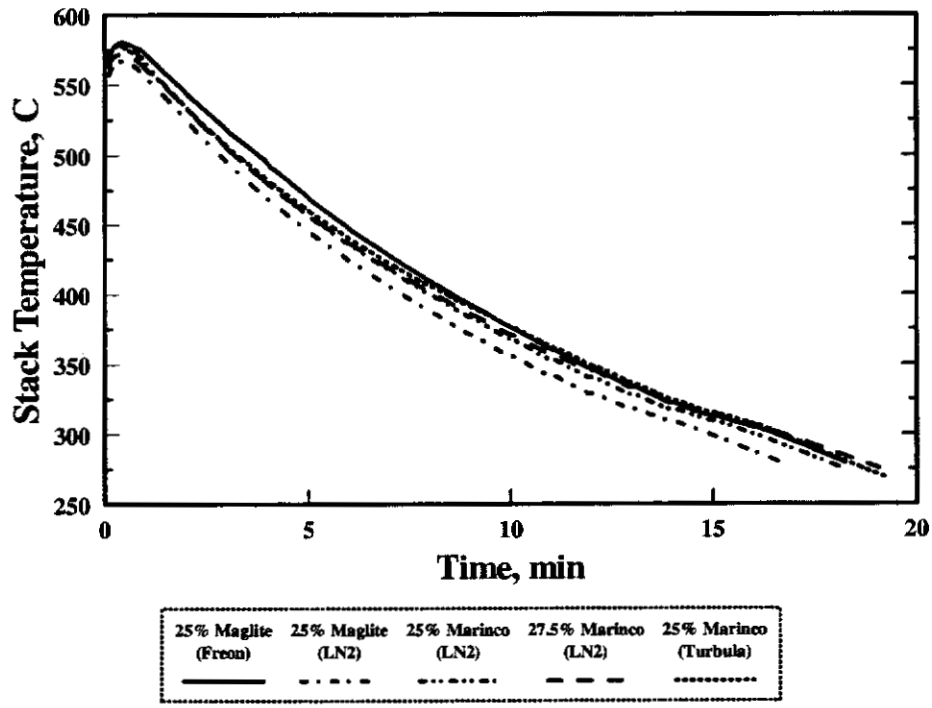

Figure 40. Battery Stack-Temperature Profile for the Batteries of Figures 38 and 39.

(Figure 35) even before electrolyte freezing began. There was a fair amount of scatter in the thermal responses for the various batteries for these tests—more than for the cold batteries (Figure 37). This scatter was, in part, responsible for the observed differences. The voltages for the batteries with the LN-blended separator with 27.5% Marinco 'OL' were very similar to those with the standard Freon-blended separator (Figure 38). The relative performance of the batteries with Turbula-blended separators was somewhat inferior under the hot conditions, even though the temperature profiles were comparable to those of the batteries with the standard Freon-blended separator. The total polarization (Figure 39) showed similar trends as the voltage.

The activated lives for the various batteries are summarized in Table 9. The activated lives for batteries with the low-melting electrolyte were comparable to those with the LiCl-KCl eutectic for an activation temperature of –54°C (Table 8), even though this material has a somewhat higher ionic conductivity and a larger liquidus range. However, at the higher activation temperature, the performance was superior for the batteries with the low-melting electrolyte.

Using the F test, the batteries that gave results that were statistically similar to those built with the standard Freon-blended Maglite 'S' MgO contained the Turbula-blended separator with 25% and the LN-blended separator with 27.5% Marinco 'OL' MgO. This was true for both the hot and cold batteries. In addition, hot batteries with the LN-blended separator made with 25% Marinco 'OL' MgO also fell into this category.

Table 9. Summary of Activated Lives of Li(Si)/FeS_2 5-Cell Batteries tested with 50-Ohm Steady-State Load with Various Separators and MgOs for LiBr-KBr-LiF Eutectic.

MgO	% MgO	Blending Process	Activ. Temp., °C	Avg.* Activated Life, min	Standard. Dev., min
Maglite 'S'	25.0	Freon	-54	13.0	0.57 (10)
	25.0	LN		11.9	0.17 (3)
Marinco 'OL'	25.0	Turbula		12.8	----(1)
	25.0	LN		12.0	0.17 (3)
	27.5	LN		12.4	0.58 (3)
Maglite 'S'	25.0	Freon	+74	16.5	0.52 (10)
	25.0	LN		15.0	0.88 (3)
Marinco 'OL'	25.0	Turbula		16.5	----(1)
	25.0	LN		16.0	0.96 (3)
	27.5	LN		16.4	0.58 (3)

* Average of 3 tests. ** Number of tests is indicated in parentheses.

Ten-Cell Battery Tests

LiCl-KCl Eutectic – The stack pressure relaxation at 0.5 min and 1.0 min are shown in Table 10 for 10-cell Li(Si)/FeS_2 batteries built with various separator mixes based on LiCl-KCl eutectic. The peak stack temperatures are also shown for comparison. The nominal separator thickness was 0.68 – 0.69 mm (0.0268 – 0.0272") for these tests. All batteries were activated at room temperature and used a heat input of 98.6 cal/g of total cell mass.

Table 10. Summary of Results of Stack-Relaxation Tests with 10-Cell Li(Si)/FeS_2 Batteries Built with Separators Based on LiCl-KCl Eutectic and Processed by Various Methods.* (Heat Balance of 98.6 Cal/g.)

MgO	% MgO	Blending Process	Avg. Start Stack Press., psig	Avg. Stack Pressure @ 0.5 min, psig	Avg. Stack Pressure @ 1.0 min, psig	Avg. Peak Stack Temp., °C
Maglite 'S'	35.0	Freon	247 (8.7)	23.3 (4.5)	18.0 (3.6)	529 (5.9)
Maglite 'S'	35.0	LN	252 (1.5)	25.3 (2.5)	20.3 (4.2)	524 (2.5)
Marinco 'OL'	35.0	LN	254 (2.5)	14.7 (1.5)	12.3 (0.6)	509 (21.2)
Marinco 'OL'	37.5	LN	252 (3.5)	24.8 (9.9)	21.8(9.9)	530 (5.4)

* Numbers in parentheses are the standard deviations associated with the means.

The average stack pressures at 0.5 min and 1.0 min for the battery stacks that used the Freon-blended and LN-blended separators with Maglite 'S' were very similar and of the same statistical population. The pressures at 1.0 min were ~22% lower than at 0.5 min. The final stack pressures were <8% of the original closing pressure. In contrast, when the Marinco 'OL'-based separator was used at a level of 35.0%, the stack pressures were much lower, only 15 psig vs. 23 – 25 psig, respectively, at 0.5 min. The scatter in the data was also much greater and the peak stack temperature was significantly less. At 1.0 min, the stack pressure was only ~63% of that for the batteries that used Maglite 'S' MgO. However, when the content of the Marinco 'OL' was increased to 37.5%, the final relaxed stack pressures were comparable to those for batteries that used Maglite 'S' MgO. The relative effect of the increased content of Marinco 'OL' on increasing the final stack pressures in activated batteries is consistent with the observed deformation behavior at 530°C and 14.3 psig (Table 1), which is comparable to the final stack pressures observed for these batteries (Table 10). The higher MgO content in those cases resulted in less deformation. The stack relaxation that occurs on activation of the battery is a direct reflection of the deformation that takes place in the separator upon electrolyte melting. The rather rigid nature of the anode and cathode under these same conditions is due to the high loading of relatively coarse Li(Si) and FeS_2, respectively. (Deformation tests on individual anodes and cathodes have shown that deformation is typically <1%.) It should be noted that the thickness of the separator pellets used for deformation tests was much greater than that used in the 10-cell batteries (0.059" vs. 0.027", respectively).

(In earlier work, it was determined that the factors that influence the stack relaxation process in thermal batteries are the *number of cells* in the stack, *initial closing pressure*, and *separator thickness*. There is an apparent interaction between the closing pressure and number of cells. These three factors account for as much as 94% of the variance in the experimental data.[6])

The batteries with the lowest final stack pressure also had the lowest average peak stack temperature. The lower stack pressure resulted in higher interfacial resistance in 5-cell battery tests with these same material combinations and is reflected in their poorer performance (Table 7).

LiCl-LiBr-LiF Electrolyte – The stack pressure relaxation at 0.5 min and 1.0 min are shown in Table 11 for 10-cell Li(Si)/FeS_2 batteries built with various separator mixes based on the all-Li electrolyte. The peak stack temperatures are also shown for comparison. The nominal separator thickness was 0.52 mm – 0.53 mm (0.0205" – 0.0209") for these tests. All batteries were activated at room temperature and used a heat input of 98.6 cal/g of total cell mass.

Table 11. Summary of Results of Stack-Relaxation Tests with 10-Cell Li(Si)/FeS_2 Batteries Built with Separators Based on LiCl-LiBr-LiF Electrolyte and Processed by Various Methods.* (Heat Balance of 98.6 Cal/g.)

MgO	% MgO	Blending Process	Avg. Start Stack Press., psig	Avg. Stack Pressure @ 0.5 min, psig	Avg. Stack Pressure @ 1.0 min, psig	Avg. Peak Stack Temp., °C
Maglite 'S'	35.0	Freon	254 (1.5)	32.0 (4.6)	26.0 (5.3)	527 (2.5)
Maglite 'S'	35.0	LN	254 (2.5)	28.3 (10.0)	23.2 (9.2)	532 (7.0)
Marinco 'OL'	35.0	LN	254 (0.6)	33.7 (3.8)	28.7 (3.1)	534 (6.6)
Marinco 'OL'	37.5	LN	258 (5.7)	33.0 (14.5)	28.0(13.2)	533 (8.3)

* Numbers in parentheses are the standard deviations associated with the means.

The average stack pressures at 0.5 min and 1.0 min for the battery stacks that used the Freon-blended separators with Maglite 'S' were slightly lower than those for the LN-blended counterparts, which also had slightly higher peak stack temperatures. The pressures at 1.0 min were 18% - 19% lower than at 0.5 min. The final stack pressures were ~10% of the original closing pressure. The final stack pressures for batteries that used the Marinco 'OL'-based separator were similar to each other at the two levels of MgO and slightly higher than those of the batteries that used the Maglite 'S' MgO. The relative stack pressures for the batteries with two levels of Marinco 'OL' in the separators did not correlate with the deformation behavior of these two separators at 530°C and 14.3 psig (Table 2). In the latter case, there was a dramatic reduction in deformation at 37.5% MgO relative to 35.0% MgO. This was not reflected in the stack-relaxation behavior in ten-cell

battery tests (Table 8). The batteries that used the separator with 37.5% MgO showed a much higher standard deviation than the other batteries.

The activated lives of 5-cell batteries that used these same materials showed trends similar to those noted for those based on the LiCl-KCl eutectic. The batteries that performed the best had lower internal impedance, which reflects better interfacial contact in the cells resulting from the higher average stack pressures noted for the 10-cell battery counterparts (Table 11).

LiBr-KBr-LiF Eutectic – The stack pressure relaxation at 0.5 min and 1.0 min are shown in Table 12 for 10-cell Li(Si)/FeS_2 batteries built with various separator mixes based on the low-melting eutectic. The peak stack temperatures are also shown for comparison. The nominal separator thickness was 0.48 mm – 0.49 mm (0.0189" – 0.0193") for these tests. All batteries were activated at room temperature and used a heat input of 95.4 cal/g of total cell mass.

Table 12. Summary of Results of Stack-Relaxation Tests with 10-Cell Li(Si)/FeS_2 Batteries Built with Separators Based on LiBr-KBr-LiF Eutectic and Processed by Various Methods.* (Heat Balance of 95.4 Cal/g.)

MgO	% MgO	Blending Process	Avg. Start Stack Press., psig	Avg. Stack Pressure @ 0.5 min, psig	Avg. Stack Pressure @ 1.0 min, psig	Avg. Peak Stack Temp., °C
Maglite 'S'	35.0	Freon	260 (13.0)	38.0 (7.4)	31.5 (6.0)	542 (1.7)
Maglite 'S'	35.0	LN	254 (2.5)	24.0 (1.0)	19.0 (0)	543 (4.2)
Marinco 'OL'	35.0	LN	265 (24.0)	33.0 (10.5)	31.0 (10.5)	543 (11.0)
Marinco 'OL'	37.5	LN	259 (7.2)	43.3 (15.5)	36.3(16.6)	543 (3.8)

* Numbers in parentheses are the standard deviations associated with the means.

The pressures at 1.0 min were ~19% lower than at 0.5 min, which is similar to what was observed for the all-Li system. The final stack pressures were 8% - 14% of the original closing pressures. The differences in relative stack relaxation did not appear to be temperature related, as the average peak stack temperatures were very close for all batteries. The average stack pressures at 0.5 min and 1.0 min for the battery stacks that used the Freon-blended separators with Maglite 'S' were substantially lower than those for the LN-blended counterpart. This does not reflect the relative deformation behavior at 530°C and 14.3 psig (Table 3). This same behavior was also noted for batteries built with the all-Li separator. However, the relative average stack-relaxation pressures for the batteries that used separators with 25% and 27.5% Marinco 'OL' MgO were consistent with the observed deformation behavior of these separators at 530°C and 14.3 psig (Table 3). The separator with the higher MgO content deformed less and had a higher final average stack pressure. This is the same behavior exhibited by the separators with LiCl-

KCl eutectic but was not observed for the all-Li system. Thus, there is no consistent correlation between the deformation behavior noted under isothermal conditions for discrete separator pellets and the final stack pressures in 10-cell batteries that use these pellets.

Correlations

One of the primary goals of this study was to determine if meaningful correlations could be made between select physical properties of separator pellets (*e.g.*, pellet deformation and electrolyte leakage) and the performance and behavior observed in 5-cell and 10-cell batteries (*e.g.*, activated lives and final stack pressures). Separator-pellet deformation, in general, did correlate reasonable well with the observed electrolyte leakage, even though different temperatures were used for the two tests.

In the case of the LiCl-KCl eutectic, good correlation between separator-pellet deformation and electrolyte leakage from such pellets was obtained for the various materials containing 35% MgO (including both Marinco 'OL' and Maglite 'S' sources) and processed by various means. (A correlation coefficient of 0.93388 was obtained for a least-squares fit of the data of Figure 4). However, a separate grouping was observed at a level of 40% MgO. In the case of the all-Li electrolyte, the correlation was almost as good ($r^2 = 0.9108$) over the full composition range regardless of type of MgO used or processing conditions (Figure 5). The worst correlation was shown by the separators based on the low-melting electrolyte ($r^2 = 0.4230$) (Figure 6).

It was also hoped that the deformation behavior could be correlated to the observed stack-relaxation process observed in 10-cell batteries. In some cases, a reasonable correlation was observed, while in others, the agreement was only fair. There was a general trend with all of the electrolytes explored that the lowest stack pressure in 10-cell batteries was observed with separators that had high deformation. Deformation and electrolyte-leakage tests are better suited for troubleshooting materials for a given battery application, where a baseline has already been established for materials that have the desired mechanical and electrochemical characteristics. It is also a good technique for establishing quality control.

The mechanical behavior of the various separator materials as discrete pellets could not generally be correlated to their electrochemical performance in single-cell and 5-cell battery tests. In addition, the single-cell data could not generally be correlated to the 5-cell battery data. Isothermal tests do not adequately simulate the dynamic thermal environment of a battery, especially the thermal impulse generated upon ignition of the pyrotechnic pellets.

CONCLUSIONS

The deformation behavior of separator pellets is only one metric that is important for proper functioning of a thermal battery. Excessive deformation can lead to breaching of the anode and cathode in a cell, in the worst case, to parasitic leaking currents across cells, in less severe cases. Some deformation is necessary to allow good interfacial contact between cell components (*e.g.*, anode-separator and cathode-separator). The results of the

characterization tests conducted in this study have defined the best processing conditions and compositions that are necessary to attain ideal mechanical behavior.

In most cases, reasonably good correlation is found between the deformation behavior of separator pellets at 530°C and 14.3 psig and the observed electrolyte leakage at 400°C (500°C for the all-Li electrolyte) after one-half hour immersion in a bed of activated alumina. These techniques are best suited for quality control or for troubleshooting battery issues related to separator performance. They do not correlate to the electrochemical performance observed in either single-cell tests at 500°C at 125 mA/cm^2 or in 5-cell battery tests under similar discharge loads. There is no good correlation between the single-cell data and the 5-cell battery data for the same types of cells, since the isothermal tests do not adequately simulate the dynamic thermal environment of a thermal battery. In addition, the batteries were tested under constant-resistance loads while the single cells were tested under constant current.

In terms of qualifying the new source of MgO, Marinco 'OL' MgO, the best compositions and processing for the various electrolytes are summarized in Table 13. The best overall results observed in 5-cell battery tests are summarized in Table 14. As can be seen, there is not always a one-to-one match between the data of these two tables. Ultimately, the results of the battery tests take precedence and should serve as guidelines for the thermal-battery engineer.

This study shows that liquid-nitrogen blending is a viable alternative to the former Freon-blending method for the preparation of separator mixes for use in thermal batteries. Comparable results can be obtained when using Marinco 'OL' MgO as a replacement for Maglite 'S' MgO by appropriate blending techniques and compositional adjustments.

Table 13. Compositions and Processing of Separator Mixes based on Marinco 'OL' MgO for Optimized Pellet Deformation Properties.

Electrolyte	MgO Content, %	Processing
LiCl-KCl eutectic	37.5	Liquid-nitrogen blending
LiCl-LiBr-LiF min. melting	35.0	Turbula blend
LiBr-KBr-LiF eutectic	27.5	Liquid-nitrogen blending

Table 14. Compositions and Processing of Separator Mixes based on Marinco 'OL' MgO for Optimized Electrochemical Performance in 5-Cell Li(Si)/FeS_2 Battery Tests.

Electrolyte	MgO Content, %	Processing
LiCl-KCl eutectic	40.0	Turbula blend
LiCl-LiBr-LiF min. melting	37.5	Liquid-nitrogen blending
LiBr-KBr-LiF eutectic	27.5	Liquid-nitrogen blending

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