

## HIGH-TEMPERATURE BATTERIES FOR GEOTHERMAL AND OIL/GAS BOREHOLE APPLICATIONS

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**Abstract**

A literature survey and technical evaluation was carried out of past and present battery technologies with the goal of identifying appropriate candidates for use in geothermal borehole and, to a lesser extent, oil/gas boreholes. The various constraints that are posed by such an environment are discussed. The promise as well as the limitations of various candidate technologies are presented. Data for limited testing of a number of candidate systems are presented and the areas for additional future work are detailed. The use of low-temperature molten salts shows the most promise for such applications and includes those that are liquid at room temperature. The greatest challenges are to develop an appropriate electrochemical couple that is kinetically stable with the most promising electrolytes—both organic as well as inorganic—over the wide operating window that spans both borehole environments.

**Introduction**

Currently, modified Li-Mg/SOCl<sub>2</sub> cells are used for powering instrumentation used in deep boreholes involved in oil and gas exploration. These cells are rated for operation at 180°C and are manufactured by Battery Engineering, Inc. (Canton, MA). Similar power requirements exist for measurement while drilling for geothermal boreholes. In the latter case, the temperature limitations of the cells require that they be insulated from the immediate thermal environment—which can be over 300°C—by the use of a very expensive metallic vacuum dewar.

Sandia National Laboratories has been involved in the design and development of high-temperature batteries (so-called "thermal-batteries") since the late 1940s for nuclear-weapon applications. This technology is based on the use of highly conductive molten salts as the ionic media to provide power at temperatures between 400°C and 600°C during operation of the batteries.

Thermal batteries have a long history of reliability and being robust. The molten-salt medium provides an intrinsic high-power capability that is absent with ambient-temperature technologies. For example, the ionic conductivity of many molten salts is two orders of magnitude greater than that of electrolytes used in Li ambient-temperature cells. The challenge in meeting the needs of the wide range of borehole conditions lies in modification of the current thermal-battery technology or developing alternate suitable technology to allow the batteries to operate without the use of a dewar at the much lower temperatures encountered in oil/gas and geothermal boreholes. The temperature range is above that for the Li-ambient batteries and below that of conventional thermal batteries. Therein lies the challenge.

Over the last several years, Sandia has been evaluating potential technologies that would be suitable for temperatures of 200°C - 400°C encountered in various geothermal well-drilling operations.<sup>1,3</sup> This paper presents possible approaches to meeting the borehole requirements with current thermal-battery technology as well as potentially suitable new electrochemical technology. The primary emphasis of this work will be the geothermal borehole, where the temperatures are much higher than oil/gas boreholes. The possible approaches suitable for oil/gas boreholes will also be discussed but in less detail.

The technical challenges that must be overcome will be addressed and will include materials issues (kinetic and thermodynamic stabilities) as well as engineering issues. Various scenarios for providing downhole power for data logging will be presented and the promise and limitations of each will be described. Preliminary results with some of the electrochemical couples currently under investigation with several low-melting electrolytes will be presented.

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## Experimental

A limited number of single-cell tests were carried with components made from cold-pressed powders. The Li(Si)/FeS<sub>2</sub> couple was tested in several of the low-melting halide electrolyte systems. Preliminary tests with the Li(Si)/LiMn<sub>2</sub>O<sub>4</sub> couple in low-melting nitrates were also conducted. The cells were 1.25" in diameter and were tested using flooded anodes that contained 20% - 25% of the electrolyte used in the separator. The catholytes typically contained 73.5% to 75% active cathode material, with the balance being separator. The cells were tested over a temperature range of 200°C to 400°C. The separators contained electrolyte and 25% - 35% MgO powder as a binding agent. All cell testing was performed galvanostatically under computer control in a glovebox under high-purity argon (<1 ppm each of oxygen and water vapor).

## Results and Discussion

### Background

A cross-sectional representation of a thermal cell is shown in Figure 1. Each cell consists of an anode and cathode separated by an ionically conducting separator layer. Every cell requires the use of these three components, regardless of the chemistry involved, be it a thermal battery or a lead-acid battery

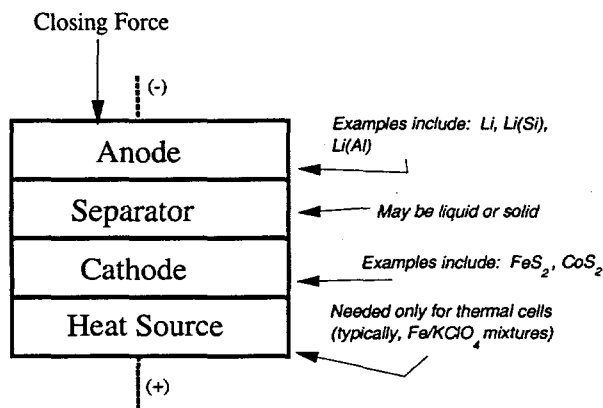


Figure 1. Cross-section of a Typical Thermal Cell.

Thermal-battery technology is based on pelletized, circular discs of the various components of the cell. In the case of the Li(Si)/FeS<sub>2</sub> couple, the cell

potential is a nominal 2 V at 500°C. The desired voltage for a 10-V battery, for example, is obtained by simply stacking five cells in series.

It may be possible to adapt thermal-battery technology to function in a geothermal borehole environment where temperatures of 250°C to over 400°C are encountered. The heat pellet (thermal source) may be optional, if adequate heat is available from the ambient borehole environment. This will necessitate the use of salt mixtures that have much lower melting points than the LiCl-KCl eutectic salt that melts at 352°C. The electrolyte will have to be molten or liquid at the operating temperatures of the boreholes, which can be less than 200°C for oil and gas boreholes.

### Electrochemistry

Regardless of the final chemistry of the couple used in the borehole environment, certain issues must be addressed. The electrochemistry must be stable for the proposed environment over the temperature range of operation. This includes thermal stability as well as mechanical stability. The anolyte consists of active anode material (typically a Li alloy) with the ionic electrolyte or separator material. Similarly, the catholyte is a mixture of active cathode with electrolyte or separator.

Equally as important is the chemical stability of the various mixtures of materials over the envisioned operating range. Some materials may not be thermodynamically stable but could be kinetically stable enough to permit their use for reasonable periods at operating temperature.

The capabilities of any given electrochemical system for a borehole application will be strongly dependent upon the rate capabilities of the couple and the type of separator used. Each of the half cells (anode and cathode) will have some kinetic limitations that will manifest themselves as an upper practical current density (e.g., A/cm<sup>2</sup>). Since these processes are strongly temperature dependent, the rate capability of the couple will likewise be strongly temperature dependent. One half cell will likely be rate limiting. This will have to be taken into account when designing a battery. These rate capabilities will ultimately determine the size of the final engineered battery. In some cases, it may be necessary to parallel several battery stacks to realize the desired output voltage and current.

Similarly, the separator properties have a major impact upon the performance of any electrochemical couple. The separator serves as a physical barrier between the anode and cathode of a cell to prevent direct contact and chemical reaction. At the same time, it must provide a low-resistance path for ionic transfer. Thus, the ideal separator has a high transference number (fraction of the current that is ionic) and high ionic conductivity. This minimizes ohmic (IR) losses during discharge.

Separators can be inorganic as well as organic in nature and can be either liquid or solid at the operating temperature of the battery. Ambient-temperature lithium cells, for example, use lithium salts dissolved in a variety of organic solvents or dispersed in organic polymers as separators. Thermal cells use molten salts—typically alkali-metal halides—in their separators.

The ionic conductivity of the various types of separator varies widely, as shown in the data of Table 1. The highest conductivities are shown by the molten salts, which is the primary reason for the high-power capabilities of thermal batteries.

Temperature Effects

When a battery must operate over a wide temperature range, the rate-limiting steps in the electrochemical process can change as a function of temperature. In the Li(Si)/FeS<sub>2</sub> thermal battery, for example, the operating temperature range is typically 400°C - 550°C. At the upper temperature limit, the cathode performance accounts for the bulk of the polarization; at the lower temperature limit, the anode becomes rate limiting. The relative importance of temperature will vary with the particular cell electrochemistry.

Strategies

Several strategies can be considered for batteries for geothermal applications. One involves the use of separators—either liquid or solid—that are good ionic conductors over the entire temperature range of operation (e.g. from room temperature to 300°C). The electrochemical couple would also have to have reasonable rate capabilities under the same conditions. The battery based on this technology would be turned on at the surface prior to lowering the instrumentation package into the borehole. The battery would then have to continue to function at the upper operating temperature of

300°C when in place in the borehole.

The second approach involves the use of high-temperature technology in which the separator functions adequately only at elevated temperatures (e.g., above 300°C). In this scenario, the battery would require internal heat (such as a pyrotechnic) to function properly at the start of a test. (The pyrotechnic heat source is an integral part of every thermal battery.) The battery would be activated on the surface using an electrical igniter (squib) or match that would, in turn, ignite the heat source; this process takes 100 ms or less for small batteries (e.g., "D"-sized). The battery would require sufficient insulation to keep the active stack hot while being lowered to the hot part of the borehole. Here, the surrounding temperature would be sufficient to keep the battery functioning throughout its mission. A cross-sectional representation of a typical thermal-battery stack is shown in Figure 2.

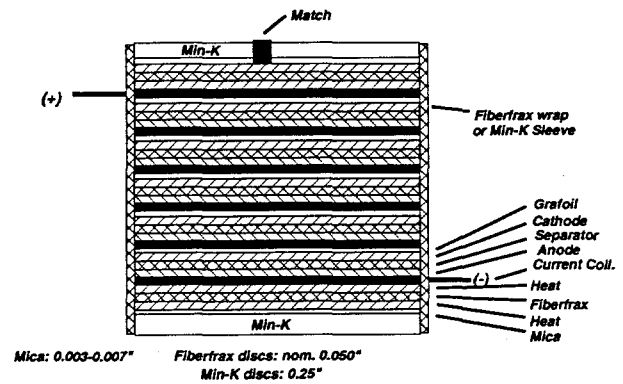


Figure 2. Cross-sectional Representation of a 5-Cell Thermal-Battery Stack.

Ideally, it would be preferable to not use an internal heat source because it would result in a battery with a smaller mass and height and would simplify battery design. It would also allow the battery to be used from ambient to the maximum temperature in the borehole without any auxiliary heat. Battery recharging would be greatly facilitated, as well. (Rechargeability is a very desirable feature for a borehole power supply.) The battery, however, would have to provide the necessary power over the entire temperature range—from ambient to 300°C. This requirement may be difficult—if not impossible—to meet.

The use of an internally heated battery (similar to a conventional thermal battery) would overcome the performance obstacles posed for a battery

Table 1. Ionic Conductivity of Typical Materials Used as Separators in Cells

<u>Material</u>	<u>Ionic Conductivity, mS/cm</u>	<u>Temperature, °C</u>
High-temperature molten salts	1,100-3,700	50-300
Low-temperature molten salts	20-770	25
Organic solutions of Li salts	3-12	25
Solid polymer electrolytes	4-32	25
Li <sup>+</sup> -conducting glasses	10 <sup>-7</sup> -1	25-600
Li <sup>+</sup> -conducting ceramics	0.1-160	25-300
Li <sup>+</sup> -conducting salts	10 <sup>-2</sup> -300	25-400
Na <sup>+</sup> -conducting ceramics	0.1-150	25-300

\* mS/cm = milliSiemens/cm.

operating over a wide temperature window. However, thermal management becomes critical for this approach; it will be necessary to maintain the battery stack within the proper operating-temperature window for the electrolyte used. The rate of descent of the battery into the borehole will be critical for this approach to be feasible. If the descent rate is too slow, the electrolyte could freeze before reaching the required thermal zone for sustaining battery operation. The possibility of recharging the battery is more unlikely with this scenario; i.e., the battery would become a "one-shot" device.

An alternate approach for internally heating the battery involves the use of a resistance source (electric heater) incorporated into the assembly. This would be activated on the surface using available on-site power to bring the battery stack to operating temperature. The heater would then be turned off prior to lowering of the data logger (battery) into the borehole. Alternatively, auxiliary battery power could be provided by the primary battery stack, or a second stack could be incorporated for just the heater. The descent rate with this approach is also important. Too slow a descent will consume excessive amounts of energy to power the heater.

This method could allow for recharging of the battery for an appropriate couple. There would be a space and weight penalty associated with this approach, however. Tradeoffs would have to be made for the final battery design.

#### Candidate Separators

There are a number of categories of materials that can be considered for potential use as separators for geothermal power-source applications.

Aqueous Systems – The low boiling point of water (100°C) precludes serious consideration of aqueous-based system at operating temperatures of up to 300°C.

Organic Systems – Organic liquids and solids are used in a number of Li-ambient cells. The majority of the organic liquids that are used have relatively low boiling points or high vapor pressures at the elevated temperatures that would be encountered in a geothermal borehole. Propylene carbonate has been used in Li-ambient cells and has a boiling point of 240°C at 1 atm. While this is quite high, it would still boil in a battery at a borehole temperature of 300°C and would generate large internal pressures under these conditions.

In addition to the issue of high vapor pressure, there are compatibility issues with the anode. At room temperatures, many of the organic solvents used in Li-ambient cells are kinetically stable in contact with elemental Li. At elevated temperatures, however, the possibility for pronounced reaction with Li becomes quite significant. This can lead to solvent polymerization or the generation of large volumes of gas, both of which are detrimental to cell performance.

The use of solid polymer materials for the separator poses similar types of problems. A material can be selected to be solid with reasonable ionic conductivity at ambient

temperature but must still function at elevated temperatures. Most polymeric materials will melt or begin to decompose at 300°C, which limits their usefulness as separators. The potential chemical reaction with Li at high temperatures will still be an issue under these conditions.

There are several categories of organic compounds that could potentially be used as separators for batteries. Sulfones have been examined for use in Li cells at moderate temperatures (60°-150°C) but would not be very good conductors at room temperature.<sup>4,11</sup> Imides have also been examined.<sup>12</sup> The Li-reactivity problem would still remain at the higher temperatures and longer times necessary for practical operation.

Similarly, a number of salt mixtures based on amides or acetamides,<sup>13-15</sup> acetates, thiocyanates,<sup>16,17</sup> and mixtures thereof have reasonable melting points (<300°C) but relatively low ionic conductivities. Recent work with urea-based electrolytes has been reported.<sup>18</sup> Again, the lack of long-term stability in contact with high-activity anodes (e.g., Li, Ca, or alloys of high Li or Ca activities, respectively) would preclude their use as separators for geothermal-battery applications.

As discussed above, most organic materials will have intrinsic difficulties when attempts are made to use them in a geothermal borehole environment. For these reasons, while they should not be discarded outright, they are not likely to be viable candidates for this application.

High-temperature Molten Salts — For the purposes of this paper, high-temperature molten salts are defined as those melting above 300°C. This category of materials includes the salts used in conventional thermal batteries, such as those listed in Table 2.

It should be noted here that the conductivities of the pure molten salts listed should only be used as a general guideline for comparison purposes. In an actual battery, the salt phase will be immobilized—much as water in a sponge—by a porous inert material (binder) to form the actual separator. The amount of this material that is necessary for effective immobilization will depend on the surface tension of the particular electrolyte and the pore-size distribution of the binder. These properties are important because the electrolyte is

held in place by capillary action. The final conductivity of the separator will be strongly dependent upon the binder content. Table 3 lists the ionic conductivities for separators with optimized binder content for the electrolytes listed in Table 2.

Table 2. Ionic Conductivity of Several High-Temperature Molten Salts at 500°C.<sup>19,20</sup>

Molten Salt	Melting Point, °C	Ionic Cond. @ 500°C, mS/cm	Application
KCl-LiCl eut.	352.0	1,898	General
LiBr-KBr-LiF eut.	324.5	1,845	Long-life
LiCl-LiBr-LiF	426.0	3,367	Power

Table 3. Ionic Conductivities of Some Optimized Separator Materials at 500°C.<sup>21</sup>

Molten Salt	% MgO	Ionic Cond. @ 500°C, mS/cm
KCl-LiCl eut.	35	1,000
KCl-LiCl eut.	25	1,250
LiCl-LiBr-LiF	35	1,890

Any binder that is used in the separator of a molten-salt battery must be thermodynamically compatible with the high-activity of the anode and chemically inert toward the active cathode material. In addition, the material must have the proper pore-size distribution to allow effective immobilization with the minimum amount of binder. The binder that is most commonly used in thermal batteries is MgO powder. Other materials that are suitable are: ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, BeO, BN, and AlN. These binders have been used as powders and sintered discs, as well as woven felts and papers. MgO is preferred because of its low cost and ready availability.

The current standard Sandia thermal-battery technology is based on an anode of 44% Li/56% Si and a cathode of FeS<sub>2</sub> (pyrite). The Li(Si)/FeS<sub>2</sub> couple has an open-circuit voltage of ~2 V at a temperature of 500°C. This technology is quite reliable (>99.5%) and mature (20 years old) and has been used extensively in thermal batteries for DOE weapons applications. All of the electrolytes of Table 2 have been used successfully in various thermal batteries placed into production for DOE; similar batteries have been produced in large numbers for use by the Dept. of Defense (DOD), as well. The Li(Al) system with 20% Li was the primary anode for DOD applications in the past.

The Li-alloy/FeS<sub>2</sub> technology has an excellent rate and power-delivering capability because of the high conductivity of the molten salts. With the all-Li electrolyte, current densities well over 1 A/cm<sup>2</sup> are easily attainable at 500°C, with short (e.g., 1 s) pulses ten times that. While these high rates are not needed for the envisioned geothermal application, they serve to reduce the necessary cross-sectional area of a battery stack for a given current; i.e., the battery size and mass can be proportionally reduced. Power densities >1,000 mW/cm<sup>2</sup> are possible with Li(Si)/FeS<sub>2</sub> cells using the all-Li electrolyte at a temperature of 500°C. The maximum current and power densities are very dependent upon temperature and, to a much lesser degree, the depth of discharge.

The present technology—based on even the lowest-melting electrolyte of Table 2 could not be used to design a battery that would be suitable for geothermal use, as now envisioned. The melting point of the low-melting electrolyte is still higher than the desired operating temperature of 300°C. Such a system *could* function, however, if the borehole temperatures were 350°C or higher.

The low-melting electrolyte of Table 2 has a lower melting point and heat of fusion compared to the other electrolytes; this minimizes the heat requirements for bringing the battery to operating temperature. The melting point needs to be much lower, however, for the geothermal application as originally envisioned. There are halide mixtures that melt at temperatures below 300°C; these will be described in the next section.

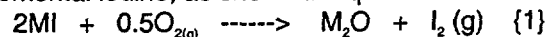
Low-Temperature Molten Salts – For the purposes of this paper, low-temperature molten salts are defined as those melting below 300°C. Most of the

salt mixtures that melt at <300°C contain halides of Rb, Cs, or Al as a foundation. Several of the more common electrolytes of this type are listed in Table 4 along with their electrical conductivities, where available.

The conductivities of separators based on Cs and Rb halides will be significantly lower than those based on the high-temperature molten salts of Table 2. For examples, a separator containing 70% CsBr-LiBr-KBr eutectic and 30% MgO has a conductivity of 300 mS/cm at 500°C; this drops to 43 mS/cm at 290°C.<sup>21</sup> (The electrolyte melts at 228.5°C.) The conductivity at 500°C is less than one-third of that for the LiCl-KCl/MgO separator under the same conditions (Table 3). The power density of a Li(Si)/FeS<sub>2</sub> cell using the low-melting, CsBr-based separator is only ~500 mW/cm<sup>2</sup> at 500°C, this is only half of that for the corresponding cell using the LiCl-KCl separator. The capability would be much less at lower temperatures. However, this may still be adequate for the proposed geothermal battery application (100 mW steady state; 300 mW pulse), since the cell area and number of cells in the battery can be adjusted to meet the desired power requirements.

Batteries that are designed with such a low-melting material will have to address the polarization losses that will result at the *lower* temperature of operation; the rate capabilities can be severely limited by the separator resistance under these conditions.

The alkali halides of Cs and Rb are very expensive, in comparison to the other alkali halides, and the same holds true for iodide salts. However, the final electrolyte costs may not be a limiting factor in the overall battery cost. The iodides have several other properties that may limit their use. They have a lower thermodynamic voltage-stability window than the bromides and chlorides. In addition, the iodide salts cannot be fused in air because of oxidation of iodide to elemental iodine, as shown in equation 1.



Thus, they would have to be processed in a glovebox environment that would add to processing costs.

The fluorides have the highest thermodynamic decomposition voltages, while the iodides have the lowest. The stabilities of a number of common alkali-bromide salts are shown as a function of



Table 4. Common Molten-Salt Mixtures with Melting Points Below 300°C.

Salt Mixture	Melting Point, °C	Electrical Conductivity, mS/cm	Temperature, °C
<u>Alkali-Halide Based</u>			
LiCl-CsCl-KCl	258	N/A	N/A
LiBr-CsBr	278	N/A	N/A
LiBr-CsCl	260	N/A	N/A
LiBr-KBr-CsBr	238	N/A	N/A
LiBr-LiI-KI-CsI	189	N/A	N/A
LiCl-LiBr-LiI-KI-CsI	184	N/A	N/A
LiBr-RbBr	271	602	300
LiCl-KCl-RbCl	265	N/A	N/A
LiCl-KCl-RbCl-CsCl	258	280	280
LiI-KI	260	1,280	300
LiCl-LiI-KI	265	N/A	N/A
<u>AlCl<sub>3</sub>-Based</u>			
50 m/o LiCl-AlCl <sub>3</sub>	143.5	392	200
		616	300
40 m/o LiCl-AlCl <sub>3</sub>	103	238	200
		389	300
50 m/o NaCl-AlCl <sub>3</sub>	154	511	200
		768	300
40 m/o NaCl-AlCl <sub>3</sub>	108	314	200
		487	300
50 m/o KCl-AlCl <sub>3</sub>	256	250	200
		457	300
31 m/o KCl-AlCl <sub>3</sub>	128	167	200
		291	300
KAICl <sub>4</sub> -LiAlBr <sub>4</sub> -NaAlCl <sub>4</sub>	<200	368	200
		573	300
LiAlBr <sub>4</sub> -NaAlCl <sub>4</sub> -KAICl <sub>4</sub>	86	142	100
33 m/o methylimidazolium chloride-AlCl <sub>3</sub>	-90	12.1	25
33 m/o n-butylpyridinium chloride-AlCl <sub>3</sub>	-52	4.13	25
<u>Nitrate-Based</u>			
LiNO <sub>3</sub>	252.6	N/A	N/A
LiNO <sub>3</sub> -KNO <sub>3</sub> -CsNO <sub>3</sub>	96	N/A	N/A
LiNO <sub>3</sub> -LiCl	244	N/A	N/A
LiNO <sub>2</sub>	222	N/A	N/A
LiNO <sub>2</sub> -LiNO <sub>3</sub>	193	N/A	N/A
<u>Others</u>			
1-ethyl-3-methylimidazolium triflate	liq. @ RT	9.3	25
1-ethyl-3-methylimidazolium mesylate	liq. @ RT	2.7	25

temperature in Figure 3. The most stable bromide is CsBr, while LiBr is the least stable. The LiBr would be thermodynamically unstable at 300°C with a cathode with a potential of more than ~3.3 V vs. Li.

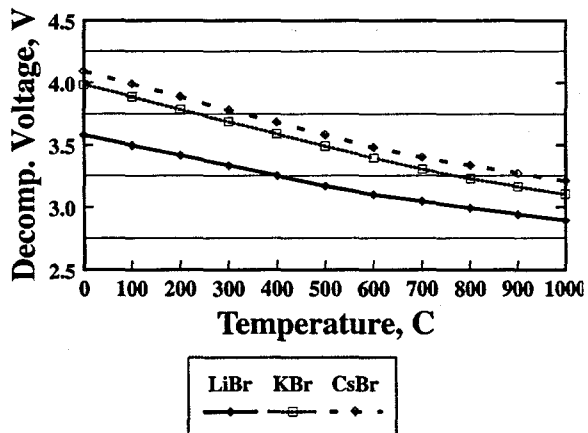


Figure 3. Thermodynamic Decomposition Voltages of Various Halides as a Function of Temperature.

The low melting points of salt mixtures based on  $\text{AlCl}_3$  make them attractive for geothermal applications. The wide range of compositions available with the various alkali-metal halides offers a broad range of possibilities. Their electrical conductivities at 200°C - 300°C are comparable to those of the low-melting eutectic electrolytes based on Rb and Cs halides at near 300°C. They have the capability of operating at much lower temperatures, however.

There are organic tetrachloroaluminate compounds that are actually a liquid at room temperature. Some of these materials are thermally stable at 300°C, but their long-term compatibility with high-activity anodes (e.g., Li alloys) at this temperature is not known. Their conductivities at room temperature are similar to those of organic solutions of Li salts, which are relatively low. Use of these materials at ambient conditions would severely limit the rate capabilities of any battery because of the resulting high IR polarization associated with the separator.

The relative molar ratio of  $\text{AlCl}_3$  and halide salt (e.g., MX) affects the conductivity and melting point of the system as well as the vapor pressure of  $\text{AlCl}_3$  over the salt. (For example, the vapor pressure of  $\text{AlCl}_3$  at 200°C is 634 mm of Hg for an  $\text{AlCl}_3$  mole fraction of 0.65 and <9 mm for a mole fraction of 0.52 for the  $\text{LiCl}-\text{AlCl}_3$  system.) These

factors have to be considered when designing a battery for long-term use in a geothermal environment.

The low reduction potential of the  $\text{AlCl}_3$  in the tetrachloroaluminate melts would preclude their use in a separator in batteries that used high-activity anodes; the  $\text{Al}^{3+}$  would not be stable in this environment and would be reduced to elemental Al. This problem could be eliminated by the use of a solid, ionically conductive separator, such as the  $\text{Na}^+$  conductor,  $\beta''\text{-Al}_2\text{O}_3$ . This has been used as a separator with liquid-Na/polysulfide cells in a cylindrical configuration. Unfortunately, such cells would not work well much below 300°C. These cells would not survive the rough borehole environment and making them in thin (0.010"-thick) discs would be difficult and impractical.

An alternative would be to use Al metal as the anode. This would not develop as high a potential as would alloys of Li but would avoid the compatibility problems associated with their use. For example, the  $\text{Li}/\text{NiCl}_2$  couple would produce 2.59 V at 500°C; this compares to only 1.77 V for the  $\text{Al}/\text{NiCl}_2$  couple. The lower voltage could be compensated for by using more cells in the battery. Preliminary tests cells at 200°C to 250°C with  $\text{Al}/\text{NaAlCl}_4/\text{FeS}_2$  at Sandia showed that this combination has severe performance problems.

**Nitrates/Nitrites** – A fair amount of work has been done evaluating low-melting combinations of alkali-metal nitrates and nitrate/nitrite mixtures for use as liquid cathodes with Li alloys.<sup>22,23</sup> The low melting points make these materials initially attractive, but their safety concerns make them less than desirable for battery applications. Most of the work that has been done with these materials has been strictly in small laboratory cells.

Cells using Ca anodes with  $\text{LiNO}_3\text{-KNO}_3$  eutectic have been examined.<sup>24</sup> These were designed to operate between 250° and 400°C but at relatively low current densities (<10 mA/cm<sup>2</sup>). Open-circuit voltages of between 2.5 V and 2.8 V were reported with power densities of 200 mW/cm<sup>2</sup> at a current density of 10 mA/cm<sup>2</sup>.

In related work, cathodes of  $\text{Ag}_2\text{CrO}_4$  and  $\text{V}_2\text{O}_5$  were used with a  $\text{Li}(\text{Al})$  anode in a cell based on a  $\text{LiNO}_3\text{-KNO}_3$  melt.<sup>25</sup> Current densities of 10 - 100 mA/cm<sup>2</sup> were reported at 160°C - 215°C. The high

electrical conductivity of the elemental silver that formed accounts for part of the good performance.

In molten-nitrate cells, the active anode is in direct physical contact with the cathode (molten-nitrate). This combination is thermodynamically unstable; the primary reason that rapid exothermic reactions do not occur is that a protective, passivating film of  $\text{Li}_2\text{O}$  forms on the anode surface— $\text{Li}_2\text{O}$  on Li alloys and  $\text{CaO}$  on Ca. (This is similar to the film of  $\text{LiCl}$  that forms on the surface of the Li anode in  $\text{Li}/\text{SOCl}_2$  cells.) As long as the film remains intact, the cell will function. As the temperature is increased, however, film rupture can occur, resulting in a violent exothermic chemical reaction. Unfortunately, the conditions under which this can occur are very unpredictable.

#### Results of Single-Cell Tests

**LiBr-KBr-LiF Eutectic** – The LiBr-KBr-LiF eutectic has a melting point of only  $324.5^\circ\text{C}$  but has not been examined in detail in the past at temperatures below  $400^\circ\text{C}$ .<sup>26</sup> For this work, tests were conducted at a temperature of  $350^\circ\text{C}$ , to test the rate capability of the system. A typical discharge trace is shown in Figure 4 for  $\text{Li}(\text{Si})/\text{FeS}_2$  cells for current densities of 16 and 32  $\text{mA}/\text{cm}^2$  and a temperature of  $350^\circ\text{C}$ . (The MgO content of the separator was 25%.)

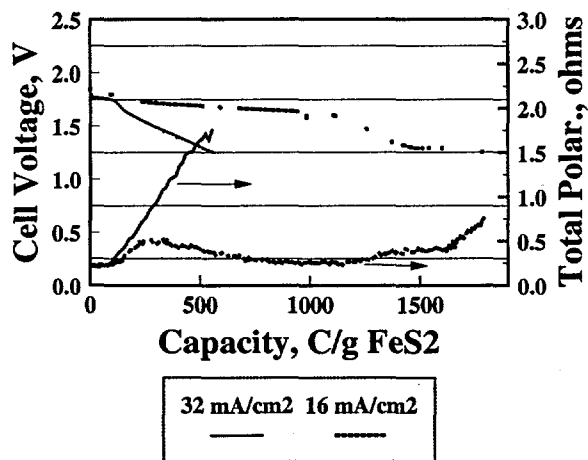


Figure 4. Discharge of  $\text{Li}(\text{Si})/\text{LiBr-KBr-LiF}/\text{FeS}_2$  Cells at  $350^\circ\text{C}$  and 16 and 32  $\text{mA}/\text{cm}^2$ .

There was a rapid drop in life when the current density was doubled and a concomitant rapid rise in polarization. The hump in the cell polarization (resistance) near 250 coulombs/g  $\text{FeS}_2$  is due to a cathode phase transition. A second hump is also

evident near 1,300 coulombs/g  $\text{FeS}_2$ . At this temperature, the cell is only  $25^\circ\text{C}$  above the melting point of the electrolyte. This can lead to significant  $\text{Li}^+$  concentration gradients at the anode-separator interface. The resulting solids precipitation is responsible for the rapid rise in polarization.

Tests with this system indicate that a limiting current density of between 15 and 20  $\text{mA}/\text{cm}^2$  should be possible at  $350^\circ\text{C}$ . However, much higher levels would be attainable at higher temperatures.

**CsBr-LiBr-KBr Eutectic** – Similar discharge tests were conducted with  $\text{Li}(\text{Si})/\text{CsBr-LiBr-KBr}/\text{FeS}_2$  cells. This electrolyte melts much lower, at  $228.5^\circ\text{C}$ . Figure 5 shows the results of discharge tests at  $300^\circ\text{C}$  at the same current densities used for the LiBr-KBr-LiF eutectic (Figure 4).<sup>27</sup> (The MgO content of the separator was 30%.)

The capacities of the cells were reduced by more than half at the lower temperature relative to the LiBr-KBr-LiF eutectic. The cell polarizations were comparable for the two systems at the beginning of discharge, with both showing rapid increases at the higher load. When the discharge temperature was reduced to  $250^\circ\text{C}$  (only  $21.5^\circ\text{C}$  above the melting point), the discharge capacity at 16  $\text{mA}/\text{cm}^2$  dropped by a factor of four. This parallels the effects of the LiBr-KBr-LiF eutectic near its melting point.

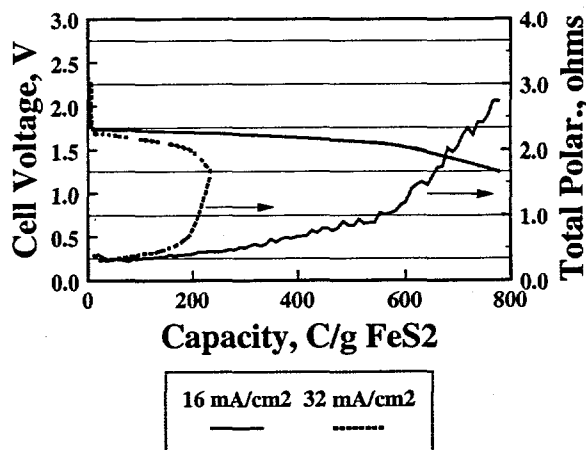


Figure 5. Discharge of  $\text{Li}(\text{Si})/\text{CsBr-LiBr-KBr}/\text{FeS}_2$  Cells at  $300^\circ\text{C}$  and 16 and 32  $\text{mA}/\text{cm}^2$ .

The maximum effective current density for the  $\text{Li}(\text{Si})/\text{CsBr-LiBr-KBr}/\text{FeS}_2$  system is of the order of

16 mA/cm<sup>2</sup> at 300°C, but this drops to half by 250°C. A long-term battery test was carried out with this system using ten times the normal cathode and anode masses. Discharge times in excess of 24 h were attained at 250°C at a nominal current density of 8 mA/cm<sup>2</sup> by paralleling two battery stacks. This demonstrates the feasibility of this approach for certain borehole environments.

#### LiNO<sub>3</sub>-KNO<sub>3</sub> Eutectic

An electrolyte with a lower melting point (150°C) is needed for oil/gas borehole applications. One promising candidate is the LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic that melts at 124.5°C. Nitrates are not chemically compatible with sulfides and react exothermically. Cathodes that are compatible include Ag<sub>2</sub>CrO<sub>4</sub> and LiMn<sub>2</sub>O<sub>4</sub>, among others. (Thermal stability was determined by differential scanning calorimetry of candidate catholyte mixes at temperatures up to 400°C.) The disadvantage of such cathode is that they are poor electronic conductors, so that conductive additives (e.g., graphite) must be added. This reduces the energy density and specific energy of the catholytes.

A representative voltage trace for a Li(Si)/LiMn<sub>2</sub>O<sub>4</sub> cell tested at 200°C in the nitrate melt at 32 mA/cm<sup>2</sup> is shown in Figure 6.

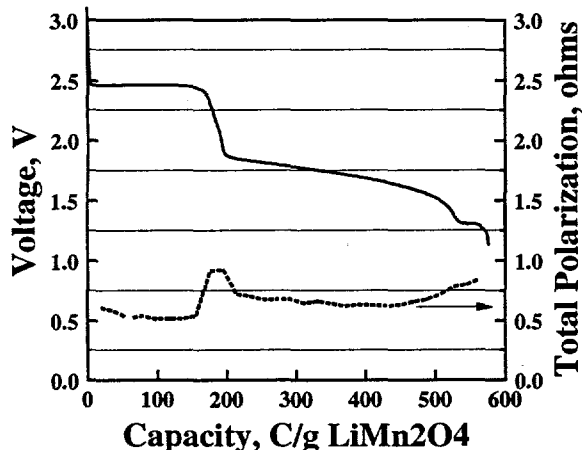


Figure 6. Discharge of Li(Si)/LiNO<sub>3</sub>-KNO<sub>3</sub>/LiMn<sub>2</sub>O<sub>4</sub> Cell at 200°C and 32 mA/cm<sup>2</sup>.

The performance was very good at this low temperature for this current density. This is especially notable when one compares the performance to the Li(Si)/FeS<sub>2</sub> cells in the halide systems at much higher temperatures. In one comparison test, the capacity was only 30 C/g LiMn<sub>2</sub>O<sub>4</sub> for a Li(Si)/LiMn<sub>2</sub>O<sub>4</sub> cell tested in the CsBr-LiBr-KBr eutectic at 250°C at half this current

density. This indicates that this cathode has good kinetic capabilities.

#### Future Work

Additional work is scheduled with the nitrate eutectic and various Li-alloy, Li, Ca, Mg, and Zn anodes, to study the kinetics of passive-film formation. This is crucial for proper operation of these reactive materials in a strong oxidizing electrolyte. Tests will include other promising candidate cathodes, such as Ag<sub>2</sub>CrO<sub>4</sub>, to optimize this system for possible use in low-temperature borehole environments. A number of room-temperature molten salts will also be evaluated, with initial emphasis on chemical compatibility over a wide temperature range. This will be followed by single-cell tests at varying current densities, to determine the rate-limiting processes for the various combinations of anodes and cathodes, as well as the ionic conductivities as a function of temperature.

#### Conclusions

The critical technological and engineering issues that must be overcome for successful deployment of various types of chemistries for power sources in a geothermal borehole environment have been reviewed. These include chemical compatibility issues, which will impact performance, especially as it relates to self discharge or heat generation from exothermic chemical reactions. Any potential anode or cathode materials must be kinetically stable in contact with the various separator materials that consist of molten salts immobilized with (typically) MgO. Electronic factors that will influence cell performance include the ionic conductivity of the separator, the potential of the electrochemical couple, and the electronic conductivities of the anode and cathode. The melting point of the electrolyte and the thermal stability of these materials alone or in combination established the thermal operating window for a cell.

Most of the candidate alkali-halide molten salts for separator use contain Rb, Cs, or Al. The latter is not chemically compatible with high-activity Li-alloy anodes. The LiBr-KBr-LiF eutectic works well above 400°C but concentration polarization limits its useful current density to only 15 – 20 mA/cm<sup>2</sup> at 350°C. The CsBr-LiBr-KBr electrolyte functions

well at 300°C and has a rate-limiting current density of about 15 mA/cm<sup>2</sup> at 250°C. The Li(Si)/CsBr-LiBr-KBr/FeS<sub>2</sub> system is a viable candidate for a geothermal borehole power supply that can function in excess of 24 hours.

The LiNO<sub>3</sub>-KNO<sub>3</sub> eutectic shows great promise as an electrolyte for lower-temperature boreholes as for oil/gas drilling. The Li(Si)/iNO<sub>3</sub>-KNO<sub>3</sub>/LiMn<sub>2</sub>O<sub>4</sub> couple shows reasonably good rate capabilities of at least 30 mA/cm<sup>2</sup> at 200°C with acceptable capacities. More work is needed over a wider temperature range with other Li-based alloys and other suitable anode materials, as well as other high-voltage cathodes, to better define the rate-limiting processes that take place. The stability of the passivation film that forms on the anode is crucial for proper operation of this system. This needs to be examined in greater detail.

The materials that have the best potential of being usable over a large operating temperature range are the so-called "room-temperature molten salts." With the proper composition and combination of electrochemical couples, it may be possible to operate such cells from ambient to as high as 300°C.

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