

Overview of high-temperature batteries for geothermal and oil/gas borehole power sources

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Abstract

Batteries currently used as power supplies for measurement while drilling (MWD) equipment in boreholes for oil and gas exploration use a modified lithium/thionyl chloride technology. These batteries are limited to operating temperatures below 200 °C. At higher temperatures, the batteries and the associated electronics must be protected by a dewar. Sandia National Laboratories has been actively engaged in developing suitable alternative technologies for geothermal and oil/gas borehole power sources that are based on both ionic liquid and solid-state electrolytes. In this paper, we present the results of our studies to date and the directions of future efforts.

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1. Introduction

A number of halide–electrolyte systems have been developed for use with the Li(Si)/FeS₂ and Li(Si)/CoS₂ couples that are used in thermally activated (“thermal”) batteries for weapons and missile applications. The batteries are inert until the electrolyte becomes molten when an electrical or mechanical signal initiates the burning of an internal pyrotechnic. By changing the composition of the electrolyte, the electrical conductivity and thermal operating window can be varied over a wide range for the different requirements of the various applications [1–3]. Thermal batteries typically operate over an internal temperature range of 350–600 °C. Sandia initially examined various halide compositions with the aim of lowering the operating temperature range to make such a system suitable for use in a geothermal borehole, where temperatures can be 300 °C or more. The goal was to eliminate the expensive dewar and internal pyrotechnic and use the heat of the borehole to maintain the electrolyte in the molten state [4]. Modeling efforts showed such an approach had promise under certain conditions [5]. The use of an internally powered heater was also examined but was found impractical due to the high power requirements.

Other non-halide molten salts were also examined during the course of the study, with the major emphasis on eutectic

molten nitrates. Several so-called room temperature molten salts were evaluated for possible borehole use. In addition, screening studies of a number of organic electrolytes were performed to determine their suitability for use in the liquid state at elevated temperatures in potential borehole applications. More recently, the use of ionically conducting solid electrolytes was reevaluated for a low-current so-called “keep-alive” application for memory retention in the MWD data logger.

Each technological approach that was explored had certain limitations. The paper will discuss the various approaches and the potentials and problems associated with each. Areas for future work will also be presented.

2. Experimental

2.1. Materials preparation and characterization

The candidate halide- and nitrate-eutectic electrolytes were prepared by fusion of the appropriate amounts of vacuum-dried, reagent-grade ingredients in a quartz crucible at 400–600 °C and then quenching on an Inconel® tray. The electrolytes were then ground and blended with 25–35% MgO (Merck Maglite ‘S’) and fused at 400 °C for 16 h to form the separator material. After grinding, the powders were pressed into 31.8 mm diameter discs at 72–75% of theoretical density. The pyrite cathodes for the halide systems were prepared by blending 25% separator and 1.5% Li₂O with acid-purified FeS₂ (–325 mesh) and then pressed

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into pellets as for the separator. The anodes were similarly pressed from 44% Li/56% Si material (−100 + 325 mesh) and 25% electrolyte.

The cathode used with the nitrate eutectic was primarily Ag_2CrO_4 blended with 20% electrolyte and 10% graphite (Lonza KS-6) to impart electronic conductivity. The anodes for the nitrate-based cells were based on 20% Li/80% Al alloy (−100 + 200 mesh) or 44% Li/56% Si alloy (−100 + 325 mesh) and contained 20 and 25% electrolyte, respectively.

Liquid organic electrolytes that were screened were based on propylene carbonate (PC). In some cases, ethylene carbonate (EC) was added (1:1, w/w) to improve the high-temperature stability. Supporting electrolytes that were evaluated included LiBr, LiBF_4 , lithium trifluoromethanesulfonimide [$\text{LiN}(\text{CF}_3\text{SO}_2)_2$ or “Li imide”], and lithium trifluoromethanesulfonate [$\text{Li}(\text{CF}_3\text{SO}_3)$ or “Li triflate”].

All handling and preparations were conducted in a dry room maintained at <3% relative humidity. In the case of the solid-electrolyte sulfide glasses, fusion of a blend of the appropriate amounts of constituent materials was carried out in a graphite crucible at 900–1000 °C in a glovebox under high-purity argon containing <1 ppm each of O_2 and H_2O . The glasses were quenched on an Inconel® tray and were then ground to make the solid electrolytes.

Melting points of the various candidate electrolytes were determined by differential scanning calorimetry (DSC) with a TA Model DSC 2920 (New Castle, DE). This was also used for materials-compatibility screening. Samples were sealed in the glovebox in an Al pan. For materials not compatible with Al, a Mo liner was used. Samples were generally heated at 10 °C/min to the upper test temperature (generally, 700 °C). Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed with a TA TGA/TDA Model SDT 2960.

2.2. Single-cell testing

Single cells were discharged in the glovebox under constant current under computer control at a temperature of 200–500 °C between heated platens at a constant applied pressure of 55.2 kPa. Steady-state loads of 30–125 mA (3.8–15.2 mA/cm², respectively) were used for the lower-temperature molten salt cells. This was increased to 63 mA/cm² for some of the cells with the higher-melting halides. The loads were doubled for 1 s every 30 or 60 s, to measure the cell polarization during discharge. The cell discharge was terminated when the voltage dropped below 1.00 V.

3. Results and discussion

3.1. Molten bromide salts

In geothermal applications, the borehole temperatures can reach 400 °C. There are a number of halide-based sys-

tems that have melting points under 350 °C. One electrolyte is the LiBr–KBr–LiF eutectic that melts at 324.5 °C [6]. This electrolyte has the composition 57.33% LiBr–42.0% KBr–0.67% LiF. (All compositions are reported as weight percentage.) A separator with 25% MgO was evaluated with the Li(Si)/FeS₂ couple. At 400 °C under a steady-state load of 63 mA/cm², the bulk of the cell polarization was Ohmic and cathode related. The cell voltage transitions that were observed were associated with phase changes in the cathode [7]. The performance of the LiBr–KBr–LiF eutectic decreased dramatically at lower temperatures. When the temperature was lowered to 350 °C from 400 °C, the run time at a current density of 63 mA/cm² dropped by a factor of four to only 600 s (1 g cathode and 0.9 g anode).

To improve the lower-temperature performance, a similar eutectic electrolyte with the composition 42.75% CsBr–39.08% LiBr–18.17% KBr was examined. This electrolyte has a melting point of 228.5 °C [7]. A separator with 30% MgO was evaluated with the Li(Si)/FeS₂ at temperatures of 300 and 250 °C. The lifetimes showed similar declines with temperature for the same mass of anode and cathode, dropping from 80 s at 300 °C to only 20 s at 250 °C at a much-reduced current density of only 16 mA/cm². The predominant polarization losses were Ohmic in nature and cathode related. The conductivity of the CsBr–LiBr–KBr-based separator is only about 1/4 of that of the LiBr–KBr–LiF-based separator, which is the main reason for the higher impedance in the former case. Thus, the lifetime dropped almost an order of magnitude for the Li(Si)/CsBr–LiBr–KBr/FeS₂ cell at 300 °C at only 1/4 the current density of that for the Li(Si)/LiBr–KBr–LiF/FeS₂ cell at 350 °C. This dramatically shows how the sustained current density is critically dependent on the temperature and electrolyte composition.

The use of the Li(Al)/Ag₂CrO₄ couple with the CsBr–LiBr–KBr eutectic electrolyte was briefly explored, in hopes of increasing the open circuit voltage to slightly over 3.0 V versus a nominal 2.0 V for the Li(Si)/FeS₂ couple under the same conditions. Unfortunately, the cathode was not chemically compatible with bromide above 200 °C [8].

3.2. Molten iodide salts

The use of iodide-based halide eutectics was next examined, as they are known to form lower-melting eutectics than the corresponding bromide or chloride analogs. For example, a ternary LiI–LiCl–LiF eutectic melts at 334.3 °C and there are several quaternaries based on LiI–LiBr–LiCl–LiF and melt between 325.4 and 326.1 °C [9].

The melting points for these are still too high for the envisioned geothermal or oil/gas borehole applications. A pentanary iodide-based electrolyte shows promise, however. It has the composition 45.09% LiI–32.07% CsI–16.75% KI–5.14% KBr–0.95% LiCl and melts at 151 °C. Single-cell tests were conducted at 200 °C and 8 mA/cm² with the Li(Si)/FeS₂ couple using nominal 1 g anodes and cath-

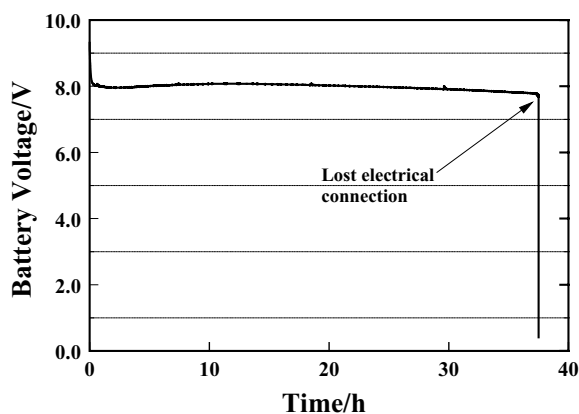
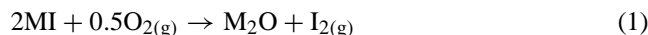


Fig. 1. Discharge characteristics of Li(Si)/Li–CsI–KI–KBr–LiCl (MgO)/FeS₂ battery made up of two 5-cell parallel stacks and discharged at 3.8 mA/cm² total current density at 200 °C.

odes and 35% MgO in the separator made with this electrolyte. The initial results were promising, in that the performance under these conditions was superior to that observed at a higher temperature of 240 °C for the Li(Si)/CsBr–LiBr–KBr/FeS₂ couple at the same current density. Follow-on tests were carried out with much larger anodes and cathodes (~5 g) in two 5-cell parallel stacks, each discharging at 1.9 mA/cm², for a total current density of 3.8 mA/cm². Under these conditions, the battery ran for 37 h before loss of the internal electrical connection occurred (see Fig. 1).

There are practical difficulties, however, in utilizing any iodide-based system. Melting of the electrolytes must be conducted in an oxygen-free environment, such as a glove-box. Similar conditions are necessary for preparation of the separator mixes. This makes processing much slower and more expensive. The battery mixes containing iodide must also be stored under Ar or N₂, to prevent oxidation that continues to occur even at room temperature



Processing conditions must be controlled very carefully. We found that it was difficult to replicate the initial favorable performance that was observed with the multi-stack battery due to changes in the chemical and electrochemical properties of the pentanary iodide salt. This lack of reproducibility makes the pentanary iodide electrolyte unattractive from a commercialization perspective.

3.3. Molten nitrate salts

Another category of molten salts that appears usable is based on molten nitrates. One nitrate eutectic has the composition 66.79% KNO₃–33.21% LiNO₃ and melts at 124.5 °C. This electrolyte has been examined previously for possible use in reserve thermal batteries by Giwa [10,11]. The basic electrochemistry of nitrate-containing molten salt systems has also been studied by Miles [12]. We decided to study this

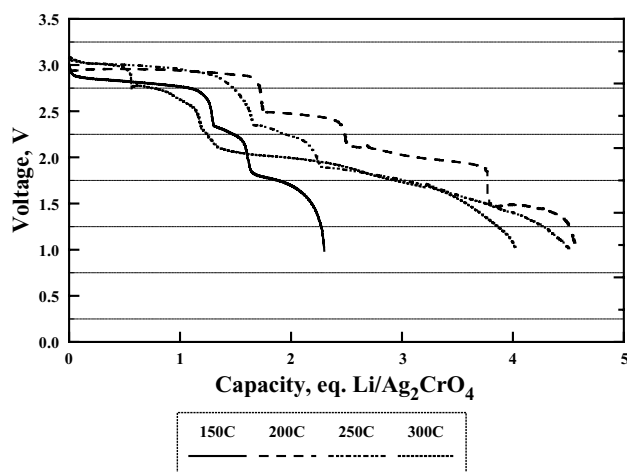


Fig. 2. Discharge of Li(Al)/KNO₃–LiNO₃ (MgO)/Ag₂CrO₄ single cells at 7.8 mA/cm² as a function of temperature.

eutectic in greater detail, because of a number of promising features of the system. We have studied a number of anodes, including Li, Li(Al), Li(Si), Ca, Mg, Zn, and Al. Cathodes that we have examined include Ag₂CrO₄, LiMn₂O₄, MnO₂, CrO₂, and LiCoO₂. The work reported here used the Li(Al)/Ag₂CrO₄ couple with 10% graphite and 20% electrolyte in the cathode; the anode contained 20% electrolyte.

The active reducing anodes are stable in contact with the molten oxidizing nitrates only because of the formation of a passivation layer of Li₂O. If that layer is disrupted for various reasons, a violent exothermic reaction can occur. DSC tests with the Li(Al) anode showed it to be stable near 315 °C during ramp heating at 10 °C/min. Because of this, we targeted a conservative working temperature range of 150–300 °C for possible borehole use. The performance of Li(Al)/KNO₃–LiNO₃/Ag₂CrO₄ single cells are shown in Fig. 2 for this temperature range at a discharge current density of 7.8 mA/cm². The corresponding total polarization (Ohmic plus concentration) is shown in Fig. 3.

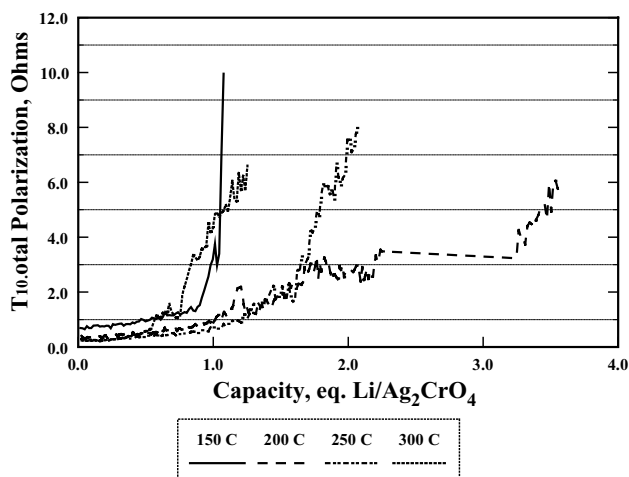


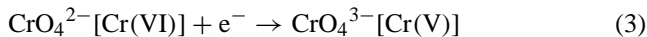
Fig. 3. Total polarization during discharge for the cells of Fig. 2.

The discharge time increased at 200 °C relative to 150 °C. However, at 250 °C, the cell lifetime dropped. At 300 °C, the performance dropped to below what was observed at 150 °C. This behavior is believed to be due to self-discharge reactions that become increasingly more important at the higher temperatures. Apparently, the passivation layer on the Li(Al) anode becomes less protective under these conditions.

Three distinct discharge plateaus were generally evident during discharge, with a fourth plateau shown by the cell discharged at 200 °C. The first plateau is due to Ag⁺ reduction

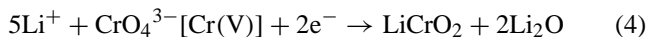


Two equivalents of charge are associated with this reaction per mole of Ag₂CrO₄. The next reduction step is believed to involve reduction of Cr(VI) to Cr(V), as postulated by Giwa [11].



Giwa then proposes a second one-electron reduction to form Cr(IV). However, it was not possible to verify this due to the lack of starting weights for his discharge traces. There was some evidence for the presence of Li₂O in those tests late in discharge. (A similar discharge mechanism was proposed by Mesinna and Perichon for discharge of Ag₂CrO₄ in propylene carbonate [13].)

The formation of Cr(V) is likely associated with the second voltage plateau observed in the discharge traces in this work. However, a more likely scenario is offered here for the third discharge plateau. It involves a two-electron reduction to form Cr(III), suggested by the reaction of Eq. (4), which also involves Li₂O formation.



A two-electron reduction is more reasonable and is consistent with what has been observed during the discharge of Ca/CaCrO₄ cells in molten LiCl–KCl eutectic [14]. Thus, one would expect to realize a total of five equivalents of Li per mole of Ag₂CrO₄ based on the above reactions.

The mass (thickness) of the anode and cathode pellets had a dramatic impact on the electrochemical performance. When the thickness was increased by a factor of five, one should theoretically obtain five times longer life. In practice, however, <50% of this capacity was realized. This indicates that there are severe mass-transport limitations of Li ions through such thick electrodes, which then gives rise to severe Li⁺ concentration gradients that progressively increase during discharge (Fig. 2).

The results of the single-cell tests are promising enough that tests are underway with multiple 5-cell battery stacks connected electrically in parallel to boost the current output to obtain about 60 mA at 12–15 V. Rather than a single stack with 5 g anode and cathode masses, each stack will use 1 g pellets and then five stacks will be electrically paralleled to obtain the same capacity. This arrangement would be ade-

quate for many oil/gas borehole applications for powering the electronics drilling package.

3.4. Room temperature molten salts

The use of an electrolyte that is liquid at room temperature and thermally stable to 300 °C or higher appears to offer the most promise for an ideal power source for oil/gas borehole applications. Paired with an appropriate electrochemical couple, such a system would be usable at ambient conditions as well as at the elevated temperatures in the borehole. The essential feature for the success of this approach will be a suitable room temperature molten salt (RTMS) that is chemically stable with the anode and cathode materials. One candidate RTMS that was explored was 3-ethyl-1-methylimidazolium tetrafluoroborate (EMIBF₄). The EMIBF₄ has been reported to be thermally stable to 300 °C [15].

The chemical compatibility of the EMIBF₄ with Li(Si) and Li(Al) alloy powders (–100 + 325 mesh) and with Ca-metal foil was examined by contact in sealed glass tubes at temperatures of 100, 150, and 200 °C over a period of several weeks [16]. Changes in color or melting point were noted to follow any degradation during these tests. Detailed quantification of the degradation was measured by changes in the nuclear magnetic resonance (NMR) spectra. The EMIBF₄ was found to react significantly with the Li(Al) and the Li(Si) alloys at 150 °C in less than an hour. The extent of reaction with Ca was considerably less, due to its lower chemical activity and reduced surface area. Because of the measurable reactivity of the EMIBF₄ with these typical anode materials, subsequent electrochemical tests were not performed because of the material incompatibilities.

The major contribution to the incompatibility was thought to be the anion composition. To address this, tests are underway with a modified imidazolium derivative that has been coupled to an imide [N(CF₃SO₂)₂]¹⁻ anion. Initial TGA tests indicate that this material is thermally stable alone up to over 400 °C. Anode compatibility tests are current underway with this new imide.

The organic cation that makes up the RTMSs allows some engineering options in terms of substituent groups. However, there will be tradeoffs among the key physical and chemical properties desired for use in borehole power sources: low electrolyte viscosity, high ionic conductivity, high thermal stability, good chemical compatibilities, and a wide operating voltage window.

3.5. Organic electrolytes

PC has been used in Li ambient-temperature cells and has a boiling point of 240 °C at 1 atm. A co-solvent also used in Li-ambient cells is ethylene carbonate (EC), which has an even higher boiling point. At temperatures of under 250 °C, solutions of PC and EC might be usable, with the proper supporting electrolyte. This option is currently being

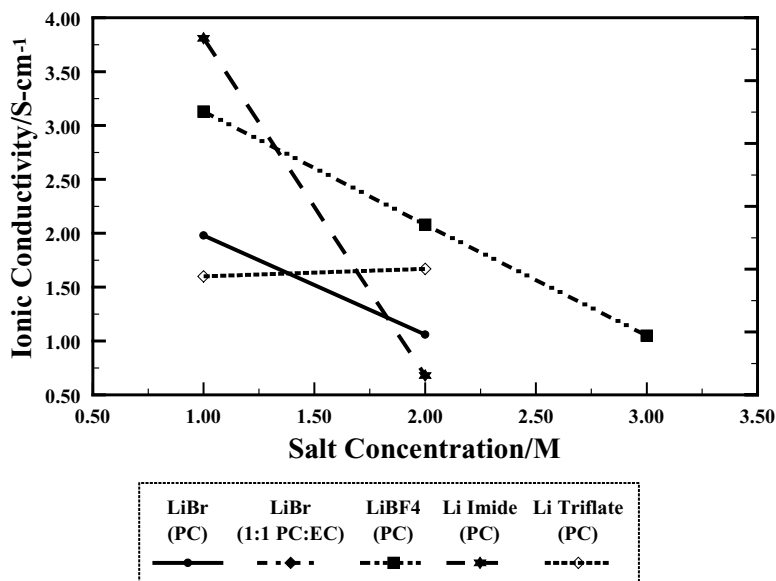


Fig. 4. Ionic conductivity at room temperature of PC and PC–EC solutions with various concentrations of supporting electrolytes.

explored with solutions of PC and EC with supporting electrolytes of LiBr, LiBF₄, Li imide, and Li triflate. The ionic conductivity at room temperature of a number of test solutions is summarized in Fig. 4. In general, the conductivities decreased at levels above 1 M, monotonically in the case of LiBF₄. The best overall results were obtained with 1 M Li imide. The values observed with the PC solutions are much less than the 10–15 mS/cm typical of standard electrolytes used in Li-ambient cells (e.g., 1 M LiPF₆ in EC/dimethyl carbonate).

Single-cell tests are currently underway with the Li(Si)/FeS₂ couple in 1 M Li imide in PC at temperatures of 50, 100, and 150 °C. If favorable results are obtained in these tests, additional tests at 200 and 225 °C will be conducted.

3.6. Solid inorganic electrolytes

Solid inorganic (ceramic or glass) electrolytes offer some advantages over the various candidate liquid electrolytes for possible use in borehole power sources. The Li-ion conductors can be used from room temperature to well over 300 °C in many cases. This is especially true for the ceramic types. Recently, a patent has been issued for a cell based on the La/BiF₃ couple and a fluoride-ion conductor [17]. Being usable over the entire operating temperature range envisioned for borehole power supplies offers a real advantage, in that the battery could be checked out on the surface prior to insertion into the well.

However, all of these solid ionic conductors suffer from one main disadvantage: low ionic conductivity. Their conductivities are typically several orders of magnitude lower than the liquid electrolytes that average 10–15 mS/cm. The preliminary room temperature values for some of the glasses and glass-ceramic materials examined in this lab are listed

Table 1

Ionic conductivity of pressed discs of some experimental and commercial glasses and glass ceramics at 25 °C

Material composition (w/o)	Ionic conductivity (mS/cm)
34.10% P ₂ S ₅ /14.49% Li ₂ S/51.41% LiI [18]	0.0026
95.33% LaF ₃ /4.54% BaF ₂ /0.13% LiF [17]	0.0038
1.83% LiPO ₄ /45.72% Li ₂ S/52.44% SiS ₂ [19,20]	0.073
Ohara YC–LC Li-ion conductant glass/ceramic	0.0470

in Table 1. These low conductivities severely limit the power available from such devices. This type of battery would be best suited for a “keep-alive” memory application, where currents would be on the order of several milliamperes or less at 3–5 V.

To minimize Ohmic losses in such cells, it is imperative that the separator films be as thin as possible. Compaction of powders in discs poses challenges below 0.2 mm in thickness. Vapor deposition or sputtering are alternative processes. Currently, Sandia is exploring plasma spraying of the fluoride-ion separator and cathode to form a multilayered composite. This technique will provide good interfacial contact while minimizing the contribution of the resistance of the separator to the overall cell resistance. This technique should also facilitate the production of such cells in large commercial quantities.

4. Conclusions

A number of molten-halide systems were examined for possible use as electrolytes for borehole power supplies. A system based on the CsBr–LiBr–KBr eutectic that melts at 228.5 °C would be usable at temperatures as low as 250 °C with the Li(Si)/FeS₂ couple at current densities as high as

16 mA/cm². While there are iodide-based electrolytes with even lower melting points (e.g., the LiI–CsI–KI–KBr–LiCl eutectic that melts at 151 °C), their reactivity with atmospheric oxygen requires preparation under an inert gas with limited access to oxygen during processing. This makes them unlikely candidates for further consideration for borehole use.

The KNO₃–LiNO₃ eutectic that melts at 124.5 °C shows considerable promise for temperatures as low as 150 °C for possible use in a borehole power source based on the Li(Al)/Ag₂CrO₄ couple. This system should be able to function at 4–8 mA/cm² over a temperature range of 150–250 °C. However, issues of self discharge—especially under open-circuit conditions—and rechargeability still need to be addressed.

More work is merited with several derivatives of room temperature molten salts based on imidazolium salts. An imide analog shows thermal stability to over 400 °C and chemical compatibility studies with high-activity anodes are underway.

Organic electrolytes based on PC and EC with Li imide and LiBF₄ also show promise, but more work remains to determine the long-term stability with high-activity anodes (e.g., Li(Si)) at temperatures over 150 °C.

Solid Li⁺ and F[−] conducting electrolytes show the greatest promise for use in “keep-alive” batteries for memory retention in the drilling tool. Because of their very high resistivities, separators based on them must be fabricated in very thin films to minimize Ohmic losses. Plasma spraying is currently being evaluated with the La/LaF₃–BaF₂–LiF/BiF₃ system to determine overall electrochemical suitability and viability of this process for commercialization.

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