MOLTEN SALT BATTERIES

Elton J. Cairns

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Elton J. Cairns
Lawrence Berkeley Laboratory, and
University of California
Berkeley, California 94720

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1. INTRODUCTION

This chapter deals with the use of molten salts in advanced batteries. Molten salts play an important role as electrolyte in several types of batteries that operate at elevated temperatures. They offer the opportunity to make use of highly-reactive electrode materials that cannot be used with aqueous electrolytes. This permits the development of batteries having very high specific energy (>100 Wh/kg). Molten salts also offer very high electrolytic conductivities, which permit the use of high current densities, and therefore the achievement of high specific power (>100 W/kg). These goals, plus others, and their implications, are listed in Table 1.

The implications listed in Table 1 can be translated into some reasonably specific guidelines for the selection of the constituents of electrochemical cells intended to meet the goals of high specific energy, high specific power, and long life. These guidelines are presented in Table 2. Notice that it is desirable to have a large electronegativity difference between the reactants. This is achieved by selection of reactants for the negative electrode from the left-hand portion of the periodic chart of the elements (groups IA and IIA, the alkali metals and alkaline-earth metals), and reactants for the positive electrode from the right-hand portion of the periodic chart (groups VA, VIA, and VIlA). The need for low equivalent weights of reactants focuses attention on the upper portion of the periodic chart. This set of guidelines, coupled with the desirability of dealing with reactants as liquids or solids (not gases), yields the following lists of elements for electrode reactants:

negative electrode reactants: Li, Na, Be, Mg, Ca.
positive electrode reactants: P, As, Sb, O, S, Se, F, Cl, Br.
Some of these reactants are impractical to handle as elements, and are therefore used in the form of compounds, as indicated by the specific reactants discussed below.

The electrolyte in a cell must have low reactivity with the electrodes (no spontaneous chemical reactions), yet must support high rates of the desired electrochemical reactions, and must have high electrolytic conductivity, yet very low electronic conductivity (for negligible self-discharge rates). Molten salts can be used as the sole electrolyte, or as a combination auxiliary electrolyte and reactant, used in conjunction with a solid electrolyte as the main electrolyte. Examples of each will be given below.

Of the many possible combinations of negative electrode reactants, electrolytes, and positive electrode reactants that could be listed, only a relatively small number of them have been investigated. The ones that are under current investigation, or hold promise for the future include:

\[
\begin{align*}
\text{LiAl/LiCl-KCl/FeS} \\
\text{Li}_4\text{Si/LiCl-KCl/FeS}_2 \\
\text{Ca-Al-Si/LiCl-NaCl-CaCl}_2-\text{BaCl}_2/\text{FeS}_2 \\
\text{Li/Li}^+ \text{ solid/S} \\
\text{Na/Na}^+ \text{ solid/S} \\
\text{Na/Na}^+ \text{ solid/SCl}_3 \text{ AlCl}_4 \text{ in AlCl}_3-\text{NaCl} \\
\text{Na/Na}^+ \text{ solid/S}_2\text{Cl}_2 \text{ in AlCl}_3
\end{align*}
\]

These cells will be discussed below in terms of their characteristics, state of development, and areas requiring additional research.

2. CELLS WITH MOLTEN-SALT ELECTROLYTES.

The first three cells of the list presented above represent the main activity in this area of investigation. These cells can be used as primary (one discharge only) cells, or as rechargeable cells. There are other systems that have also been used as molten-salt primary cells, but these generally have poorer performance characteristics than the newer systems. Therefore, this discussion will be restricted to systems which have been reported during the last fifteen years.
Many of the rechargeable molten-salt electrolyte cells currently under investigation have been derived from the initial research on the Li/LiCl-KCl/S cell, in which both reactants and electrolyte were in the liquid state under operating conditions (375° C).(1-7)

The overall reaction for the cell is simply:

\[ 2\text{Li} + \text{S} \rightarrow \text{Li}_2\text{S} \]  

(1)

The theoretical specific energy for this reaction is 2600 Wh/kg, and the cell voltage is about 2.2 V\(^{(1,5)}\) at 375° C. Simple cells were prepared by holding the liquid reactants in porous current collectors of iron or steel for the lithium, and graphite or metal for the sulfur. These cells yielded very high performance, as indicated by the voltage vs. current density curve of Figure 1, and the voltage vs. capacity density curve of Figure 2. In each figure, the corresponding curve for a Pb/H\(_2\)SO\(_4\)/PbO\(_2\) cell is shown for comparison.

The high performance exhibited by the Li/LiCl-KCl/S cell was rather short-lived, and investigations showed that the relatively rapid loss of capacity was traceable to the appreciable solubility of sulfur-bearing species in the electrolyte, as shown in Figure 3.\(^{(1,5)}\) This solubility allowed the migration of sulfur to the lithium electrode where it reacted directly, forming Li\(_2\)S. This constituted a permanent loss of capacity, and ultimately rendered the cell useless. In addition, there were difficulties associated with retaining molten lithium in the pores of its current collector during repeated discharge and recharge cycles. Loss of lithium from the current collector was a second capacity-loss problem.

In order to improve the stability and lifetime of the lithium/sulphur cell, each reactant was "immobilized" by forming a solid compound which would still retain significant levels of activity and reactivity of the lithium and sulphur. These ideas gave birth to the LiAl/FeS cell and the Li\(_4\)Si/FeS\(_2\) cell which are discussed below.
2.1 The LiAl/LiCl-KCl/FeS Cell

The LiAl/FeS cell has shown a very significant increase in stability of performance and lifetime over the Li/S cell, but at the cost of a much lower specific energy, as expected. The overall cell reaction is:

\[ 2\text{LiAl} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe} + 2\text{Al} \] (2)

All reactants and products are solids at the cell operating temperature of about 450°C, and the solubility of all of these materials in the LiCl-KCl electrolyte is acceptably low for long cell life.

The LiAl has a weight of 1.266 g/Ah vs. 0.259 g/Ah for lithium, and the reversible electrode potential for the \( \alpha + \beta \) phase region of Figure 4(8) where the electrode is operated, is about 0.3 V positive with respect to lithium. The FeS active material has a weight of 1.640 g/Ah, as compared to 0.598 g/Ah for S, and the potential for its reaction in the cell is about 1.63 V vs. Li, compared to about 2.2 V for S vs. Li. The combination of the greater reactant weights and lower cell potential (1.33 V vs. 2.2 V) brings the theoretical specific energy for Reaction 2 to 458 Wh/kg.

Reaction 2 is a simplification of the actual cell reaction, as can be seen by the phase diagram shown in Figure 5.(9) The line C-D in Figure 5 is the path followed by the composition of the FeS electrode during discharge. During the first stage of the discharge, two additional solid phases (Li\(_2\)FeS\(_2\) and Fe) form, according to the reaction:

\[ 2\text{FeS} + 2\text{Li} \rightarrow \text{Li}_2\text{FeS}_2 + \text{Fe} \] (3)

As the discharge continues into the X-Fe-Li\(_2\)S field of the phase diagram, Li\(_2\)S and more Fe are formed as follows:

\[ \text{Li}_2\text{FeS}_2 + 2\text{Li} \rightarrow 2\text{Li}_2\text{S} + \text{Fe} \] (4)

Reaction 4 continues until point D is reached, representing complete discharge. There is little difference in the potentials at which Reactions 3 and 4 take place, so the discharge curve has the appearance of a single plateau.
In the LiCl-KCl electrolyte, it has been found that the KCl can react with the positive electrode reactants to form a solid phase of the composition LiK₆Fe₂₄S₂₆Cl, which has the djerfischasite structure, and is therefore called J phase. The recharge process is slowed down by the difficulty of converting J phase to FeS. The formation of J phase can be minimized or avoided by increasing the LiCl content of the electrolyte (decreasing the KCl concentration) and by increasing the operating temperature. (10)

Lithium-aluminum/iron monosulfide cells of several different designs have been operated for significant periods of time (hundreds of cycles and thousands of hours). A drawing of a typical cell design is shown in Figure 6. Note that sets of like electrodes are connected in parallel within the cell case to build up the desired capacity. The electrodes are prepared by pressing mixtures of powdered reactant (FeS or LiAl) with powdered electrolyte to form plaques which are assembled in intimate contact with thin metal sheet current collectors (usually of iron). Fibrous boron nitride mat or powdered magnesium oxide serves to prevent the electrodes from contacting one another. Fine-pored screen-like sheets on the faces of the electrodes prevent loss of reactant powders and/or extrusion of the active material as the volume changes accompanying phase transformations occur. The negative electrodes are connected to the cell case, which may serve as the negative terminal. The positive electrodes are connected to a leak-tight electrical feedthrough, which is the positive cell terminal. Cells of more than 300 Ah capacity have been constructed according to this design.

Sample discharge curves for a cell of the type described above are presented in Figure 7. (11) As is to be expected, the higher-current discharges result in slightly lower voltages and capacities. The specific energy of three multiplate LiAl/FeS cells of 320 Ah capacity is plotted against the cycle number in Figure 8. (12) There is a gradual decline in specific energy with continued cycling. The most common failure mode for these cells is the decline in coulombic efficiency caused by internal shorts. These shorts are usually the result of the extrusion of active material from the electrodes, forming electronically-conductive fingers which reach across to the opposite electrode. The extrusion is caused by swelling of the active materials during repeated cycling. The forces accompanying the swelling are
sufficiently large that the cells must be operated under external restraint to prevent them from bulging.

A cause of gradual capacity loss is the slow agglomeration of the LiAl particles into larger, denser forms, reducing the accessibility of the lithium in the interior of the LiAl. This problem is currently under detailed investigation. Various alloying agents are being examined for their ability to reduce the rate and extent of agglomeration.(13)

The specific power of these cells has been lower than would be expected based on the conductivities of the materials involved. This has been the case partly because of poor wetting of the BN felt separator by the LiCl-KCl electrolyte. This wetting has been improved by sprinkling small amounts of LiAlCl₄ (20 mg/cm²) into the separator during cell assembly, or depositing MgO on the surface of the BN fibers before cell assembly. There are current efforts to replace the expensive BN felt (which doesn’t wet well enough) with very inexpensive MgO powder. Initial experiments yielded lower specific energy, but this should improve with modifications in cell design and assembly. Optimization of the current collector design for minimum resistance per unit current collector weight is also improving the specific power.

A few batteries of the 320 Ah LiAl/FeS cells have been constructed and tested. Typically, these contain about 10 cells, and store about 3.5 kWh. Some of these batteries have surpassed 100 cycles and are still operating. As larger batteries are built, they will be operated in enclosures that use very low conductivity insulation (such as vacuum multifoil), designed to pass heat at a rate equal to its average generation rate in the battery, so that the system will be thermally self-sustaining. Under normal circumstances, the batteries would be kept at operating temperature, but they probably could be cooled and reheated as necessary. Recent work with freeze-thaw cycling of single cells has shown no performance change after more than 60 such cycles.(14) Successful operation of batteries of cells could logically lead to demonstration in electric vehicles. A convenient summary of the status for this cell is presented in Table 3.
2.2 The Li₄Si/LiCl-KCl/FeS₂ Cell

A close relative of the LiAl/FeS cell, the Li₄Si/FeS₂ cell, has the advantage of a higher theoretical specific energy of 944 Wh/kg, corresponding to the overall cell reaction:

\[ \text{Li}_4\text{Si} + \text{FeS}_2 \rightarrow 2\text{Li}_2\text{S} + \text{Fe} + \text{Si} \]  

This reaction yields more than twice the theoretical specific energy of Reaction 2 primarily because Li₄Si weighs only 0.521 g/Ah (vs. 1.266 g/Ah for LiAl), and FeS₂ weighs 1.119 g/Ah (vs. 1.640 g/Ah for FeS). In addition, there is a higher voltage plateau (about 1.8 V) for the first half of the discharge.

The Li₄Si electrode behaves in accordance with the phase diagram of Figure 9.(15) Starting with an overall composition of Li₄Si, four plateaus are expected in the discharge curve of this electrode, ending with Si. Five plateaus are shown in Figure 10, for the charging of a Li-Si electrode at a current density of 1mA/cm², starting in the Li₂Si-Si field, progressing across the phase diagram, and extending into the Li-Li₂₂Si₅ field.(15,16) The potentials for the five two-phase fields (vs. Li) at 450°C are 326, 277, 150, 42, and 0 mV.

As might be expected from the discussion of the FeS electrode reaction above, the FeS₂ electrode reaction is also complex, and involves a number of solid phases. The reactions take place in accordance with the path AZXB in Figure 5. The steps involved in the reaction are proposed to be:(17)

\[ 2\text{FeS}_2 + 3\text{Li} \rightarrow \text{Li}_3\text{Fe}_2\text{S}_4 \quad E = 2.04 \text{ V vs. Li} \]  

\[ \text{Li}_3\text{Fe}_2\text{S}_4 + \text{Li} \rightarrow \text{Fe}_1-x\text{S} + \text{W}^* \quad E \sim 1.90 \text{ V} \]  

\[ \text{Fe}_1-x\text{S} + \text{W} + \text{Li} \rightarrow 2\text{Li}_2\text{FeS}_2 \quad E = 1.90-1.64 \text{ V} \]  

\[ 2\text{Li}_2\text{FeS}_2 + 4\text{Li} \rightarrow 4\text{Li}_2\text{S} + 2\text{Fe} \quad E = 1.64 \text{ V} \]  

Reaction 6 corresponds to the line AZ in Figure 5, Reaction 7 corresponds to the dashed line between Z and the intersection of the dashed line with the line W-Fe₁₋ₓS, Reaction 8 corresponds to the next line segment up to point X,

*See Figure 5 for composition of W phase, approximately Li₁₂Fe₄S₁₁.*
and Reaction 9 corresponds to the line segment X-B. It can be seen from the potentials listed next to Reactions 6-9 that two major voltage plateaus are present for the FeS\textsubscript{2} electrode: one near 2 V vs. Li, and one near 1.6 V vs. Li.

A number of light-weight laboratory cells of the Li\textsubscript{4}Si/FeS\textsubscript{2} type have been operated, using the LiCl-KCl eutectic (mp = 352°C) as the electrolyte. A drawing of the cross section of a typical cell is shown in Figure 11.(18) There are general similarities between the cell of Figure 11 and the one of Figure 6. In Figure 11, the central electrode is comprised of FeS\textsubscript{2} particles mixed with graphite (for current collection) and electrolyte, and pressed against molybdenum expanded metal mesh current collectors. The molybdenum mesh current collectors are fastened to a molybdenum rod which serves as the positive terminal and is sealed by a compression feedthrough. There are two Li\textsubscript{4}Si powder electrodes with porous nickel current collectors in intimate contact with the stainless-steel cell case, which serves as the negative terminal. The powdered electrode materials are contained by fine-pored cloth or mesh. Between the electrodes is a boron nitride felt or cloth separator. Electrolyte fills the pores of the separator and electrodes.

Some discharge curves for a cell of the design shown in Figure 11 are presented in Figure 12.(18) These cells were about 11 cm dia and weighed about 0.57 kg. Typical specific energies were 120-130 Wh/kg at 25 W/kg, and 180 Wh/kg at 10 W/kg. Specific power values up to about 100 W/kg were obtained. As shown in Figure 13,(18) cycle lives of up to 700 cycles have been demonstrated, corresponding to over 10,000 hours of operation.

Additional investigations have included the design and operation of light-weight bipolar cells, for series stacking to form compact batteries.(19) These cells also delivered about 700 cycles and 11,000 hours of operation, along with high specific energy. Recent experiments with various LiCl-KCl electrolyte compositions seem to indicate that the eutectic composition (58 m/o LiCl) is best.(20)

The items requiring additional attention include lower-cost sulfur-resistant current collector materials for the positive electrode, light-weight, low-cost feedthroughs, and low-cost separators (BN felt is still very expensive). There is a tendency for the FeS\textsubscript{2} electrode to swell during
cycling, so mechanical restraint of the cell and the positive electrode are required. There is a low solubility of sulfur-bearing species in the electrolyte, which contributes to a gradual loss of capacity. The seriousness of this problem requires further evaluation; a means for reducing this solubility may be necessary (e.g. change of electrolyte composition and/or operating temperature). As these cells are refined, additional scale-up to 100-300 Ah is appropriate. Of course, modules of cells and full batteries should be operated in a thermally self-sustaining mode within a high-quality thermal jacket, to demonstrate thermal regulation.

The Li$_4$Si/LiCl-KCl/FeS$_2$ cell is in an earlier stage of development than the LiAl/LiCl-KCl/FeS cell, but it has already demonstrated much higher specific energy (180 vs. 100 Wh/kg) and similar lifetime (several hundred cycles). The status of the Li$_4$Si/FeS$_2$ cell is summarized in Table 4.

2.3 The Ca-Al-Si/LiCl-NaCl-CaCl$_2$-BaCl$_2$/FeS$_2$ Cell

The issues of sufficient availability and acceptable cost of lithium have been raised with regard to cells using lithium as a reactant. If it should develop that there is a problem with lithium availability or cost, then a substitute material will be needed. Calcium has been suggested as such a substitute, and investigations of a Ca alloy/FeS$_2$ cell have been carried out.\(^{(21)}\) The overall reaction of this cell is as follows:

$$\frac{5}{2}\text{CaAl}_{1.2}\text{Si}_{0.4} + \text{FeS}_2 \rightarrow 2\text{CaS} + \text{Fe} + 2\text{Al} + \frac{1}{2}\text{CaAl}_2\text{Si}_2$$  (10)

During discharge, the reversible potential declines from 2.0 to 1.2 V, with two major plateaus. The theoretical specific energy is about 610 Wh/kg at 460°C. This means that with good cell design, it may be possible to achieve a specific energy about 140 Wh/kg (20-24% of the theoretical value is typical for well-designed cells).

In changing from a lithium-containing electrode to a calcium-containing electrode, several modifications are necessary. The electrolyte must contain calcium ions in sufficient concentration to support reasonable current densities (\(-0.1\ A/cm^2\)), and must have a melting point well below the operating temperature. The calcium-containing electrode must be capable of high utilization at high current densities (\(-80\%\ at\ 0.1\ A/cm^2\)), and must have a low
equivalent weight (high Ah/g). The electrolyte must also have a low solubility for the cell reactants and products.

The initial work on the related Ca$_2$Si/FeS$_2$ cell involved a LiCl-NaCl-CaCl$_2$ electrolyte, but relatively low utilizations of the active material were obtained. It was found that the addition of BaCl$_2$ improved performance and utilization of the reactants. Calcium silicide proved to be very corrosive toward the boron nitride separator, and didn't maintain high calcium utilization. The addition of aluminum to the calcium-silicon alloy has had a beneficial effect on performance and utilization. The currently-used composition is CaAl$_{1.2}$Si$_{0.4}$.

Sample discharge and charge curves for a CaAl$_{1.2}$Si$_{0.4}$/FeS$_2$ cell similar to the design in Figure 5 are shown in Figure 14.(21) There are two major plateaus, reflecting the behavior of the FeS$_2$ electrode. Note that this cell was operated at currents corresponding to discharge times of 8 hr and 19 hr, which represent specific powers of about 9 and 4 W/kg respectively.

The capacity, coulombic efficiency (Ah efficiency), and specific energy for the cell of Figure 14 are shown in Figure 15 for each cycle, up to the 50th cycle. Other cells have operated up to 102 cycles.(21)

Recent work has also included addition of 7% cobalt to the positive electrode, to improve current collection and utilization of the FeS$_2$, because of the importance of increasing the specific power and specific energy. The questionable stability of the boron nitride separator with the calcium-containing electrodes makes it important to examine other candidate separator materials.

As can be seen from the summary presented in Table 5, this cell is in the earliest stage of investigation of all of the cells of this general family using metal sulfides as the positive electrode and alkali-halide containing electrolytes as the sole electrolyte.
3. CELLS WITH MOLTEN-SALT REACTANTS

The use of molten-salt reactants in rechargeable cells is made convenient by combining them with solid electrolytes. This concept is very appealing because it leads to relatively simple cell designs, and provides the opportunity for complete separation of the reactants, with no cross-diffusion. At the same time, however, there are stringent requirements that must be fulfilled, including no electronic conductivity, high purity with regard to the ion transported (e.g., no K in the Na if Na⁺ is the mobile ion in the electrolyte), very good stability in the presence of the reactants, a transport number of 1.000 (to a high accuracy), high strength, and others.

There has been a long-standing search for a lithium-ion conducting solid electrolyte which is stable to lithium, and stable to a high-electronegativity positive electrode reactant such as a sulfur-polysulfide mixture. Such an electrolyte would provide an opportunity to take advantage of the Li/S couple and its very high specific energy. If only 20 percent of the theoretical value could be obtained, then a cell of over 500 Wh/kg would be available (compared to 30-40 Wh/kg for Pb/PbO₂).

Unfortunately, the known lithium-ion solid electrolytes are not stable to lithium (e.g., lithium-oxide glasses), are not stable to sulfur, or have too low a lithium-ion conductivity at temperatures below about 450°C (sulfur boils at 444°C). This situation presents a challenging and important opportunity for the synthesis of new lithium-ion conducting solid electrolytes.

The situation with regard to sodium-ion conducting solid electrolytes is much better. There are available several of these, both crystalline ceramics and glasses, which are stable in the presence of sodium, and are of acceptably high ionic conductivity at reasonable temperatures (below 400°C). Resistivities of 3 to 20 ohm-cm are typical for the sodium-ion-conducting ceramics at 350°C, and 10³ to 10⁴ ohm-cm for the glasses at 350°C. These electrolytes permit the development of cells with sodium negative electrodes, and various positive electrodes containing molten-salt reactants. The more prominent of these are discussed below.
3.1 The Na/Na$_2$O$\cdot$xAl$_2$O$_3$/S Cell

The sodium/sulfur cell with an electrolyte of Na$_2$O$\cdot$xAl$_2$O$_3$ ($x = 5$ to $11$) was the first of this type to be reported.\(^{(22-24)}\) The electrolyte is called beta alumina, and it possesses a high sodium-ion conductivity in crystallographic planes perpendicular to the C axis. The sulfur electrode obeys the phase diagram shown in Figure 16.\(^{(26)}\) It is evident from this phase diagram that as soon as a fraction of a percent of sodium reacts with sulfur at 350°C, a separate sodium polysulfide-rich liquid phase forms, so that the two liquid phases co-exist. The polysulfide-rich phase is a good electrolyte, and provides for the complete utilization of the sulfur through the following sequence of reactions:\(^{(27)}\)

\begin{align*}
2\text{Na} + 5\text{S} & \rightarrow \text{Na}_2\text{S}_5 \\
\text{S}_5^- + e^- & \rightarrow \text{S}_3^- \ldots \text{S}_2^- \\
\text{S}_3^- \ldots \text{S}_2^- + e^- & \rightarrow \text{S}_3^- + \text{S}_2^- \\
\text{S}_2^- + 2\text{S}_3^- & \Rightarrow 3\text{S}_4^- \\
2\text{S}_3^- & \rightarrow \text{S}_4^- + \text{S}_2^- \\
2\text{S}_2^- + \text{S}_4^- & \rightarrow 2\text{S}_5^- \\
2\text{S}_2^- + \text{S}_6^- & \rightarrow 2\text{S}_5^- \\
2\text{S}_4^- + \text{S}_2^- & \rightarrow 2\text{S}_5^-
\end{align*}

After the sulfur-rich phase is consumed, there exits a single sodium polysulfide phase of overall composition Na$_2$S$_5$, which is at once a good electrolyte and the reactant used in the continuing discharge process:

\begin{align*}
\text{S}_2^- - \text{S}_2^- + e^- & \rightarrow \text{S}_2^- \ldots \text{S}_2^- \\
\text{S}_2^- \ldots \text{S}_2^- + e^- & \rightarrow 2\text{S}_2^-
\end{align*}
When the phase boundary located near Na$_2$S$_3$ is reached, solid Na$_2$S$_2$ precipitates from the liquid. Because it is difficult to recharge the cell if solid Na$_2$S$_2$ is allowed to form, Na$_2$S$_3$ is the overall composition defined to correspond to the 100% discharged condition. The overall cell "reaction" is therefore written as:

$$2\text{Na} + 3\text{S} \rightarrow \text{Na}_2\text{S}_3 \quad (21)$$

The reversible voltage followed by the Na/S cell during discharge is shown in Figure 17,(1) and it ranges from 2.08 to 1.75 V at 350°C. This corresponds to a theoretical specific energy of 758 Wh/kg, or an anticipated achievable specific energy of 160-180 Wh/kg.

Various designs of sodium/sulfur cells with beta-alumina electrolytes have been constructed and tested in several countries. A typical "sodium-core" cell is shown in Figure 18(28). The ceramic electrolyte is glass-sealed to an alpha-alumina insulating collar, which in turn is thermocompression bonded to the metal cell cases which contain the sodium reservoir and the sulfur electrode. The sulfur electrode is comprised of a compressible graphite fiber mat containing sulfur. The graphite serves as the current collector for the sulfur electrode, because of the poor electronic conductivity of sulfur and sodium polysulfides.

Earlier in the development of Na/S cells, there was great difficulty in obtaining full sulfur utilization and full recharge of the sulfur electrode because of the segregation of the sulfur and polysulfide immiscible liquid phases, and their very different wetting properties. In attempts to maintain good electronic contact between the current collector and the two liquid phases, and good electrolytic contact between the beta alumina and the two liquid phases, various current collector designs, wetting agents, surface treatments, and other approaches were investigated. Some of the more successful ideas have been the use of graded-resistance graphite fiber current collectors (to distribute the reaction zone),(28) and the use of a layered current collector consisting of alternating layers of alumina cloth and graphite felt so that both the sulfur-rich and the polysulfide-rich phases are wicked to and from the reaction sites near the beta alumina surface.(29)
In recent years, cells of the 120 Ah size have been common to most of the development efforts. These cells use electrolyte tubes about 3 cm dia and 30-50 cm long, with 1-2 mm wall thickness. A battery of about 25 parallel-connected cells has yielded the discharge and recharge curves shown in Figure 19. Individual cells have been cycled up to about 2500 times in some cases, but there is a large scatter (lack of reproducibility) of cell lives, even for "identical" cells. Cycle lives of 300-1000 are most common. A typical capacity vs. cycle number plot for a single cell is shown in Figure 20. In terms of time, the longer-lived cells last 1-2 years.

The specific energy of Na/S cells has been improving, and some cells now deliver up to 180 Wh/kg, but 140 Wh/kg is more common. The peak specific power is in the range 60-130 W/kg, typically. This performance is adequate for a number of applications, and is similar to that available from the Li alloy/metal sulfide cells.

A major problem has been the corrosion of metallic components (cell case, terminals) by the sulfur. Various coatings have been investigated, but with little success. The few metals that resist sulfur attack (Mo, Cr, W) are too expensive for use in large amounts. A recent interesting approach is the mechanical "bonding" of graphite paper to aluminum. Other approaches to this materials problem include electronically conductive ceramics (such as doped TiO₂).

Other problems include the high mortality of cells on freeze-thaw cycling, and the failure of the α-alumina-glass-β-alumina seal. The major economic issue is the cost of the solid electrolyte, which remains very high, partly because of the use of high-purity starting materials, and partly because of the rigorous sintering conditions, requiring high temperatures and very close control. The overall status of Na/β-Al₂O₃/S cells is summarized in Table 6.

In spite of the problems discussed above, a number of Na/S batteries (~10 kWh) are under test in various laboratories, and the results are becoming more encouraging. The next few years of progress should be very interesting.
3.2 The Na/Na+ glass/S Cell

An alternative to the use of the ceramic electrolyte described above for the Na/S cell is the use of a sodium-ion conducting glass. Such glass has a relatively high resistivity (about $10^4 \, \Omega\cdot cm$ at 350°C), so it is necessary that the electrolyte be very thin for an acceptable resistance. This is accomplished by using thin, hollow glass fibers (80 μm OD, 50 μm ID), with sodium on the inside, and sulfur on the outside. These fibers are sealed into a glass tubesheet, as shown in Figure 21, and current collection for the sulfur electrode is provided by an aluminum foil spiral among the fibers. The aluminum foil is coated with graphite or molybdenum for corrosion protection. Because of the fact that thousands of the Na$_2$O–B$_2$O$_3$ glass fibers are used in each cell, there is a large, total electrolyte area, and the cell operates at a low current density (about 3 mA/cm$^2$ of electrolyte area). Because of the low current density, the efficiency can be high (85–90%).

Individual lab cells of 6 Ah–40 Ah have been tested extensively. A typical cycle life is 500 cycles, corresponding to about one year of operation. The lifetime has been highly variable, and failure is caused by a few common modes, including gradual sagging of the glass tubesheet, failure of the seal between the tubes and the tubesheet, and breakage of the fibers (apparently caused at least partly by micro-inclusions of foreign material in the fibers).

The status of the work on the glass hollow-fiber Na/S cell is summarized in Table 7. Some design projections indicate that the specific energy of full-sized cells may approach 200 Wh/kg.

3.3 The Na/Na$_2$O·xAl$_2$O$_3$/SCl$_3$AlCl$_4$ in AlCl$_3$–NaCl Cell

There has been some interest in reducing the operating temperature of high-temperature cells, but the phase diagrams and/or rates of the reactions have made that infeasible. Another approach to permitting operation at lower temperatures is to change the positive electrode reactant. Instead of sulfur, a solution of SC1$_3$AlCl$_4$ in a low-melting AlCl$_3$–NaCl mixture has been investigated.
The overall reaction for reduction of 4-valent sulfur to zero-valent sulfur is:

\[ 4Na + SCl_3AlCl_4 + 3AlCl_3 \rightarrow 4NaCl \cdot AlCl_3 + S \]  
(22)

The theoretical specific energy corresponding to this reaction is 563 Wh/kg; the reversible voltage is 4.2 V. This high cell voltage is a specific advantage for this cell. High cell voltages are attractive because fewer series-connected cells are needed to satisfy a given voltage requirement, as compared to cells with lower voltages (say 1-1.5 V).

Simple glass-cased cells, with a $\beta''$-Al$_2$O$_3$ electrolyte and a tungsten-wire spiral current collector have been operated at current densities of 10-20 mA/cm$^2$, and 255$^\circ$C. Sample discharge and recharge curves are shown in Figure 22. A cell of this type has operated for about 475 cycles. Failure commonly involves cracking of the electrolyte or a glass seal to the tungsten current collector lead.

Recently, some cells have been operated such that the $S^0$ is reduced to $S^-$ on a lower-voltage plateau. Also, cells as large as 10 Ah have been tested, and substitute materials for tungsten are being evaluated. Some forms of carbon may be acceptable. Table 8 summarizes the work on this cell. It is too early to access the specific power and specific energy capabilities of this cell; a more practical cell design is a prerequisite.

3.4 The Na/Na$_2$O-$x$Al$_2$O$_3$/S$_2$Cl$_2$ in AlCl$_3$ Cell

A variant on the cell discussed immediately above uses S$_2$Cl$_2$ dissolved in molten AlCl$_3$ as the positive electrode reactant. The first discharge of the cell shows plateaus at 3.65 V, 3.55 V, and 2.65 V, but only the 2.65 V plateau is available for many cycles. The proposed reaction for the 2.65 V plateau is:

\[ 2Na + 2[S] + NaCl + NaAlCl_4 \rightarrow [S] + 3NaCl + NaAlSCl_2 \]  
(23)

The theoretical specific energy is somewhat less than 400 Wh/kg.
Several simple, small (~0.15 Ah) cells, using tubular \( \beta''\)-Al\(_2\)O\(_3\) electrolyte, and a graphite felt current collector operating at 175°C have delivered 200 cycles in stable operation. These cells have advantages of lower-temperature operation and less severe corrosion (because of the basic AlCl\(_3\) melt). It is too early in the work on this system to assess with confidence the specific energy and specific power likely to be achieved, but 80–100 Wh/kg may be feasible.

4. CANDIDATE APPLICATIONS

Molten-salt batteries were shown in the previous sections of this chapter to have the capability of storing 180–200 Wh/kg, and operating at specific power levels above 100 W/kg. This performance can be maintained for several hundred deep cycles. These properties raise several interesting possibilities that have not heretofore seemed realistic. The most interesting possibility appears to be that of high-performance electric vehicles with a long range between recharges. It can be estimated by well-known methods (37) that an electric vehicle with a 200 Wh/kg battery occupying 30% of its weight can be expected to have an urban driving range of 400 km between recharges. A specific power of 120 W/kg will yield acceleration similar to that of a small, 4-cylinder automobile.

A second major candidate application for molten-salt batteries is stationary energy storage.(38,39) For this application, the attractive features of these batteries are their compactness and high efficiency. Example stationary energy storage applications are the storage of off-peak energy in electric utility systems, or electrical energy generated by solar- or wind-powered generators. There are many other possible applications, but none has the possible impact of those just mentioned.

In all of the above applications, cost is a very important factor. None of the molten-salt batteries has reached the stage of development where costs can be estimated accurately. Appropriate cost goals are less than $100/kWh for vehicle batteries and other relatively small (multi kWh) batteries, and less than $50/kWh for electric utility batteries. These costs must be combined with lifetimes of at least three, and perhaps five years for vehicle batteries, and longer for utility batteries.
5. SUMMARY AND CONCLUSIONS

A comparison of several of the batteries discussed here is given in Table 9.

From the material presented, the following conclusions can be drawn.

1. Lithium alloy/iron monosulfide cells are ready for testing in modules and batteries. They are the most advanced of the cells using metal sulfide electrodes.

2. Lithium alloy/iron disulfide cells have demonstrated 180 Wh/kg and over 700 cycles. They promise very high performance, but are at an earlier stage of development (single cells).

3. Calcium-containing negative electrodes offer a possible alternative if lithium cost or availability presents a problem.

4. Sodium/sulfur cells with 8\(^{-\text{th}}\)-Al\(_2\)O\(_3\) electrolyte are entering the battery testing stage, with 10 kWh (and larger) batteries. Cell reproducibility and electrolyte cost need attention.

5. New lower-temperature cells with AlCl\(_3\)-containing positive electrodes may offer advantages for certain applications.

6. For all of these high-temperature systems, the development of low-cost materials will probably set the pace for advancement into commercialization.

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REFERENCES


Table 1

General Goals for Batteries

<table>
<thead>
<tr>
<th>Goal</th>
<th>Implication</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Specific Energy</td>
<td>High cell voltage</td>
</tr>
<tr>
<td></td>
<td>Low equivalent weight</td>
</tr>
<tr>
<td></td>
<td>High utilization of active material</td>
</tr>
<tr>
<td>High Specific Power</td>
<td>High cell voltage</td>
</tr>
<tr>
<td></td>
<td>Rapid reactions</td>
</tr>
<tr>
<td></td>
<td>Rapid mass transport</td>
</tr>
<tr>
<td></td>
<td>Low internal resistance</td>
</tr>
<tr>
<td>Long Life</td>
<td>Reversible reactions</td>
</tr>
<tr>
<td></td>
<td>Low corrosion rates</td>
</tr>
<tr>
<td></td>
<td>Negligible rates of side reactions</td>
</tr>
<tr>
<td>Low Cost</td>
<td>Inexpensive, plentiful materials</td>
</tr>
<tr>
<td></td>
<td>Simple manufacturing processes</td>
</tr>
<tr>
<td></td>
<td>High efficiency</td>
</tr>
<tr>
<td></td>
<td>Little or no maintenance</td>
</tr>
</tbody>
</table>
Table 2
Desirable Characteristics of Systems for High-Performance Electrochemical Cells

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Negative electrode reactant</th>
<th>Positive electrode reactant</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>Low (&lt;1)</td>
<td>High (&gt;1.5)</td>
<td>--</td>
</tr>
<tr>
<td>Equivalent Weight (g/g-equiv.)</td>
<td>Low (&lt;30)</td>
<td>Low (&lt;30)</td>
<td>Low* (&lt;30)</td>
</tr>
<tr>
<td>Conductivity (ohm$^{-1}$ cm$^{-1}$)</td>
<td>High (&gt;10$^4$)</td>
<td>High (&gt;10$^4$)</td>
<td>High (&gt;1)</td>
</tr>
<tr>
<td>Electrochemical reaction rate ($i_0$, A/cm$^2$)</td>
<td>High (&gt;10$^{-3}$)</td>
<td>High (&gt;10$^{-3}$)</td>
<td>High (&gt;10$^{-3}$)</td>
</tr>
<tr>
<td>Solubility in electrolyte (mol %)</td>
<td>Low (&lt;0.1)</td>
<td>Low (&lt;0.1)</td>
<td>--</td>
</tr>
<tr>
<td>Mass transport rate (equiv./sec·cm$^2$)</td>
<td>High (&gt;10$^{-4}$)</td>
<td>High (&gt;10$^{-4}$)</td>
<td>High (&gt;10$^{-4}$)</td>
</tr>
</tbody>
</table>

* A more important criterion for the electrolyte is low density.
Table 3

LiAl/LiCl-KCl/FeS

\[ 2\text{LiAl} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe} + 2\text{Al} \]

\[ E = 1.33 \text{ V}; \ 458 \text{ Wh/kg Theoretical} \]

\[ T = 450^\circ \text{C} \]

Status

<table>
<thead>
<tr>
<th>Specific Energy</th>
<th>60-100 Wh/kg @ 30 W/kg</th>
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</thead>
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<tr>
<td>Specific Power</td>
<td>60-100 W/kg, peak</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>300+ @ 100% DOD</td>
</tr>
<tr>
<td>Lifetime</td>
<td>5000+ h</td>
</tr>
<tr>
<td>Cost</td>
<td>&gt;$100/kWh</td>
</tr>
</tbody>
</table>

Recent Work

- Multielectrode cells
- LiX-rich electrolyte
- BN felt separators
- Wetting agent for separators
- Freeze-thaw cycling
- Powder separators-MgO
- Batteries of 320 Ah cells
- Improved current collectors

Problems

- Low specific energy
- Low voltage per cell
- Cell shorting major failure mode
- Electrode swelling and extrusion
- Agglomeration of Li-Al with cycling
- Capacity loss
- High separator cost
- Leak-free feedthroughs
- Thermal control
Table 4

\[ \text{Li}_4\text{Si/\text{LiCl-KCl/FeS}_2} \]
\[ \text{Li}_4\text{Si} + \text{FeS}_2 + 2\text{Li}_2\text{S} + \text{Fe} + \text{Si} \]
\[ E = 1.8, 1.3 \, \text{V}; \, 944 \, \text{Wh/kg Theoretical} \]
\[ T = 450^\circ\text{C} \]

**Status**

<table>
<thead>
<tr>
<th>Status</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>120 Wh/kg @ 30 W/kg</td>
</tr>
<tr>
<td></td>
<td>180 Wh/kg @ 7.5 W/kg</td>
</tr>
<tr>
<td>Specific Power</td>
<td>100 W/kg, peak</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>700 @ 100% DOD</td>
</tr>
<tr>
<td>Lifetime</td>
<td>( \sim 15,000 , \text{h} )</td>
</tr>
<tr>
<td>Cost</td>
<td>( &gt; $100/\text{kWh} )</td>
</tr>
</tbody>
</table>

**Recent Work**

- Bipolar cells
- Li-Si electrodes
- BN felt separators
- 70 Ah cells

**Problems**

- Materials for FeS\(_2\) current collector
- Leak-free feedthroughs
- High internal resistance
- Low-cost separators needed
- Thermal control
Table 5

\[
\text{CaAl}_{1.2}\text{Si}_{0.4}/\text{LiCl-NaCl-CaCl}_2-\text{BaCl}_2/\text{FeS}_2
\]

\[
5/2\text{CaAl}_{1.2}\text{Si}_{0.4} + \text{FeS}_2 \rightarrow 2\text{CaS} + \text{Fe} + 2\text{Al} + 1/2\text{CaAl}_2\text{Si}_2
\]

\[
E = 2.0-1.2\text{ V}; \sim 610\text{ Wh/kg Theoretical}
\]

\[
T = 480\text{°C}
\]

**Status**

- Specific Energy: 67 Wh/kg @ 13 W/kg
- Specific Power: 15 W/kg
- Cycle Life: 100
- Lifetime: 3000 H
- Cost: too early

**Recent Work**

- \(\text{BaCl}_2\) added to electrolyte
- Larger cells - 100 Ah
- Co added to \(\text{FeS}_2\)
- Ca-Al-Si electrode

**Problems**

- Low specific power
- Low current densities
- BN separator not stable with \(\text{Ca}_2\text{Si}\)
- Rapid capacity loss
- Increasing cell resistance
Table 6

<table>
<thead>
<tr>
<th>Status</th>
<th>Specific Energy</th>
<th>Specific Power</th>
<th>Cycle Life</th>
<th>Lifetime</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90–180 Wh/kg @ 30 W/kg</td>
<td>60–130 W/kg peak</td>
<td>300–1500</td>
<td>3,000–15,000 h</td>
<td>&gt;$100/kWh</td>
</tr>
</tbody>
</table>

Recent Work

- Batteries, ~10 kWh
- $C_6N_4$ additive to $S$
- Ceramic (TiO$_2$) electronic conductors
- Shaped current collectors
- Tailored resistance current collectors
- Sulfur-core cells
- Layered current collectors
- Graphite cladding
- Na$_{1+x}$Zr$_2$Si$_{3-x}$O$_{12}$
- Thermocompression bonded seals

Problems

- Low cost electrolyte
- Corrosion-resistant material for contact with $S$
- Thermal cycling
- Low cost seals
- Specific power is low
Table 7

\[
\text{Na/Na}^+ \text{ glass/S} \\
2\text{Na} + 3\text{S} \rightarrow \text{Na}_2\text{S}_3 \\
\bar{E} = 2.0 \text{ V; } 758 \text{ Wh/kg Theoretical} \\
T = 350^\circ\text{C}
\]

<table>
<thead>
<tr>
<th>Status</th>
<th>(6 Ah cells)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>n.a</td>
</tr>
<tr>
<td>Specific Power</td>
<td>n.a.</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>500 (75-100% DOD)</td>
</tr>
<tr>
<td>Lifetime</td>
<td>9000 h</td>
</tr>
<tr>
<td>Cost</td>
<td>&gt;$100/kWh</td>
</tr>
</tbody>
</table>

Recent Work

- Improved tube sheet and seal to tubes
- Mo coating on Al foil
- 40 Ah cells

Problems

- Sagging of tube sheet
- Seal to tubes
- Feedthroughs
- Coating on Al
- Compatibility of tubes and tube sheet
- Breakage of fibers.
Table 8

Na/Na$_2$O·xAl$_2$O$_3$/SCl$_3$AlCl$_4$ in AlCl$_3$–NaCl

4Na + SCl$_3$AlCl$_4$ + 3AlCl$_3$ → 4NaCl·AlCl$_3$ + S

E = 4.2 V; 563 Wh/kg Theoretical

T = 250°C

Status: glass lab cells only (4 Ah)

<table>
<thead>
<tr>
<th>Current Density</th>
<th>20 mA/cm$^2$ @ 3.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Density</td>
<td>150 mW/cm$^2$ max. @ 2.5 V</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>475 @ 100% DOD</td>
</tr>
<tr>
<td>Lifetime</td>
<td>7000 h</td>
</tr>
<tr>
<td>Cost</td>
<td>too early</td>
</tr>
</tbody>
</table>

Recent Work

Larger cells – 10 Ah
Less expensive current collectors
Reduction to S$^-$

Problems

Sodium wetting
Vapor pressure
Corrosion of metals and some electrolytes
Electrolyte cracking
Overcharge?
Table 9
High-Temperature Rechargeable Cells

<table>
<thead>
<tr>
<th>Cell</th>
<th>Volts</th>
<th>Theor. Wh/kg</th>
<th>T°C</th>
<th>Cell Size Wh/kg</th>
<th>W/kg</th>
<th>Cycle Life</th>
<th>Lifetime Hours</th>
<th>Battery Comments</th>
<th>Problems</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAl/LiCl-KCl/FeS</td>
<td>1.3</td>
<td>458</td>
<td>450</td>
<td>320, 60-100</td>
<td>60-100</td>
<td>300⁺</td>
<td>5000⁺</td>
<td>2.5 kWh</td>
<td>Cell shorting</td>
</tr>
<tr>
<td>Li₄Si/LiCl-KCl/FeS₂</td>
<td>1.8, 1.3</td>
<td>944</td>
<td>450</td>
<td>70, 120-180</td>
<td>100</td>
<td>700</td>
<td>15,000</td>
<td>2-cell FeS₂ current collector only</td>
<td></td>
</tr>
<tr>
<td>CaAl₁₂S₄O₄/MCl₂/FeS₂</td>
<td>2.0-1.2</td>
<td>750</td>
<td>480</td>
<td>100, 67°</td>
<td>15</td>
<td>100</td>
<td>3000</td>
<td>none</td>
<td>Separators</td>
</tr>
<tr>
<td>Na/Na₂O·xAl₂O₃/S</td>
<td>2.1-1.7</td>
<td>758</td>
<td>350</td>
<td>100-200, 90-180</td>
<td>60-130</td>
<td>300-1500</td>
<td>3000-15000</td>
<td>10 kWh</td>
<td>Seals, thermal cycling</td>
</tr>
<tr>
<td>Na/Na₂O·xAl₂O₃/SCl₃AlCl₄</td>
<td>4.2</td>
<td>563</td>
<td>250</td>
<td>10</td>
<td>--</td>
<td>--</td>
<td>475</td>
<td>none</td>
<td>Corrosion</td>
</tr>
</tbody>
</table>

\( ^a \)At 30 W/kg
\( ^b \)Peak sustained, or max. reported
\( ^c \)\( >80\% \) depth of discharge
\( ^d \)At 7.5 W/kg
\( ^e \)At 13 W/kg
Fig. 1. Voltage vs. current density for Pb/PbO₂ and Li/S cells.
Figure 2. Voltage vs. capacity density for Pb/PbO₂ and Li/S cells.
Figure 3. Pseudo-ternary phase diagram of the system $\text{Li}_2\text{S}-\text{S}-(\text{LiCl-KCl})$. (1,5)
Figure 4. The lithium-aluminum phase diagram. (8)
Figure 5. Isothermal section of the Li-Fe-S phase diagram at 450°C. (9)
Figure 6. Multiple LiAl/FeS cell design.
Figure 7. Voltage-capacity curve for a LiAl/FeS cell. (11)
Figure 8. Specific energy vs. cycle number for 300-Ah LiAl/FeS cells.\(^{12}\)
Figure 9. The lithium-silicon phase diagram. (15)
Counter Electrode: Li
Electrolyte: LiCl-KCl Eutectic
Temperature: 680 K
Current Density: 10 mA/10 cm$^2$

Figure 10. Slow-rate charge of a silicon electrode. (15,16)
Figure 11. Cross section of a disk-shaped Li₄Si/FeS₂ cell, having about 70-Ah capacity.
Figure 12. Typical voltage vs. capacity curves for constant current discharges of a Li₄Si/LiCl-KCl/FeS₂ cell like that of Figure 11. (18)
Figure 13. Specific energy vs. operating time curves for LiAl/FeS$_2$ and Li$_4$Si/FeS$_2$ cells. (18)
Figure 14. Typical charge and discharge voltage curves for a CaAl_{1.2}Si_{0.4}/FeS_2 Cell.\textsuperscript{(21)}
Figure 15. Operating history of Cell CA-24.
Figure 16. The sodium-sulfur phase diagram, after Gupta and Tischer. (26)
Figure 17. The reversible emf of the sodium/sulfur cell as a function of the sulfur electrode composition. (1)
Figure 18. Exploded view of a 168-Ah sodium/sulfur cell of the sodium-core design.
Figure 19. Charge and discharge curves for a 25-cell parallel-connected Na/S battery. (30)
Figure 20. Capacity vs. cycle number for a full-sized Na/S cell. (30)
Figure 21. Schematic cross-section of the hollow glass fiber sodium/sulfur cell. (31-33)
Figure 22. Galvanostatic charge-discharge curve for cycle # 17, a Na/SCl$_3$AICl$_4$ in AICl$_3$-NaCl Cell MM-4-78. Charge current density 10 mA/cm$^2$; discharge current density 20 mA/cm$^2$. 
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