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ABSTRACT

The chemistry and the state of development of rechargeable molten salt cells and batteries of current interest are reviewed in this chapter.

INTRODUCTION

Molten-salt cells offer the most attractive combination of high specific energy (100-200 Wh/kg), high specific power (50-200 W/kg), and long cycle life (300-1500 cycles) of any rechargeable cells under investigation at this time. It is these important features that justify the development and application of cells that have the disadvantages of operation at elevated temperatures, and difficult materials problems.

There are two major categories of molten-salt cells: those in which the molten salt is the sole electrolyte, and those in which the molten salt serves as a reactant and as an auxiliary electrolyte (the main electrolyte is a solid). In the first category are such cells as LiIA/LiCl-KCl/FeS, LiIA/LiCl-KCl/FeS2, and Li4S1/LiCl-KCl/FeS2; in the second category are Na/Na2O-xAl2O3/Na2S-hS, Na/Na+ glass/Na2S-hS, Na/Na2O-xAl2O3/SC13AlC14 in NaCl-AlCl3, and Li/Li2O/LiNO3-KNO3/V2O5. These cells have operating temperatures ranging from 150 to 475°C, and all must be sealed from the atmosphere because of the alkali metal reactants and hydrolytic degradation of molten salt electrolytes.

In this chapter, we will review the relevant chemistry of several of the systems mentioned above, and the state of development of rechargeable cells and batteries based on those systems.

CELLS WITH MOLTEN SALTS AS THE SOLE ELECTROLYTE

The LiIA/LiCl-KCl/FeS Cell:

This cell makes use of a solid lithium-aluminum alloy as the negative electrode. It supplies lithium as the reactant; the aluminum serves primarily to immobilize the lithium and store it in a solid form at cell operating temperature (450-475°C). The most recent phase diagram of the Li-Al system indicates that at the cell operating temperature (400-460°C) the solubility limit of lithium in aluminum is 10 at.%, which is the boundary of the a-Al phase field. The β-Li-Al field has a composition width of 9 at.% lithium (47-56 at.%). The electrode is normally cycled across the two-phase region between 10 and 47 at.% lithium, within which the emf of the electrode at 450°C is constant at 292 mV relative to lithium. (2,3) As the lithium content is increased above 47 at.% into the β-phase, the potential decreases steeply and approaches that of lithium. (3,4)

The positive electrode of this cell is iron monosulfide. The chemistry of the FeS electrode has been the subject of considerable research, much of it focused at Argonne National Laboratory (ANL). Recently, Tomczuk et al., (3) published a definitive paper on the phases formed in the electrode, the phase sequence during charge and discharge, and the thermodynamics of the electrochemical and chemical reactions occurring in the electrode, as well as electrolyte effects on such reactions. As much of the earlier work was discussed and cited in this paper, it was used as the principal source of information for this review, unless stated otherwise.

Five phases have been identified in the FeS electrode when operated in LiCl-KCl electrolyte: FeS, LiFeS2, Li2S (α-phase), Li2S2 (β-phase), Li2S and Fe. The FeS phase corresponds to a fully charged cell, the J- and X-phases are present at intermediate states of charge and discharge, and the Fe and Li2S phases are present in the fully discharged state. Figure 1 shows the ternary Li-Fe-S phase diagram for 450°C, on which all of the phases just mentioned (except J-phase) can be located. Line H-M of Figure 1 represents the pathway of the overall electrode composition as the cell is discharged.

Using the Gibbs phase rule for condensed systems and the fact that all the FeS electrode phases can be prepared from five components: LiCl, KCl, Li2S, Fe and FeS, it was found that for a given Li2+/K+ ratio in the electrolyte and a given temperature, only two sulfide phases can be in equilibrium; therefore, six such combinations of four sulfide phases result in six possible electrode discharge reactions. These reactions are as follows:
In an actual electrode, different regions are not always in equilibrium with one another. For example, it will occasionally be necessary to consider mixtures of three sulfide phases with iron. Such mixtures can be at equilibrium in a given electrolyte at only one temperature. At other temperatures in the same electrolyte, the three sulfide phases are not in equilibrium, and a chemical reaction tends to consume one of them. The four possible chemical reactions are:

\[
\begin{align*}
26\text{FeS} + \text{Li}^+ + 6\text{K}^+ + \text{Cl}^- + 6\text{e}^- & + \text{J} + 2\text{Fe} & [1] \\
\text{J} + 25\text{Li}^+ + 20\text{e}^- + 13\text{X} + 11\text{Fe} & + 6\text{K}^+ + \text{Cl}^- & [2] \\
\text{J} + 51\text{Li}^+ + 46\text{e}^- & + 26\text{Li}_2\text{S} + 24\text{Fe} & + 6\text{K}^+ + \text{Cl}^- & [3] \\
2\text{FeS} + 2\text{Li}^+ + 2\text{e}^- + \text{X} & + \text{Fe} & [4] \\
\text{FeS} + 2\text{Li}^+ + 2\text{e}^- & + \text{Li}_2\text{S} & + \text{Fe} & [5] \\
\text{X} & + 2\text{Li}^+ + 2\text{e}^- & + 2\text{Li}_2\text{S} & + \text{Fe} & [6]
\end{align*}
\]

In their work, Tomczuk, et al., used extensive emf and cyclic voltammetric measurements combined with metallographic examinations of the electrode to determine the electrode phase sequence during charge and discharge.

Metallographic examinations of the electrodes showed that during the first discharge, when large particles of FeS are present, the discharge of the particle proceeded in four successive stages: (1) FeS on the surface discharged to J-phase and iron, (2) FeS in the core discharged to X-phase and iron, (3) X-phase in the core discharged to Li$_2$S and iron, and (4) J-phase on the surface discharged to Li$_2$S and iron. Because the formation of J-phase was limited by diffusion and the discharge of J-phase was found to be a slow, lower-voltage reaction, suppressing these reactions and accentuating the X-phase reaction seemed desirable.

One method found and implemented to decrease the stability of J-phase was to increase the Li$^+/K^+$ ratio of the electrolyte, which tends to drive the chemical reactions [7]-[9] to the left. (6,7) Saboungi, et al., investigated the stability of J-phase and the effect that the Li$^+/K^+$ ratio has on the stability of J-phase, using both an electrochemical titration method (6) and a metallographic reaction product-examination method. (7)

A first discharge of FeS in LiCl-saturated (68 mol % LiCl) electrolyte at 425°C indicated the J-phase surface layer generated under these conditions was only one fifth as thick as the surface layers generated under similar conditions in the eutectic (58 mol % LiCl) electrolyte. (5) Vissers, et al., (9) in tests of small FeS cells found the active material utilization of FeS electrodes improved markedly as the LiCl content of electrolyte was increased above that of the eutectic. From these cell studies, it was apparent that the LiCl-rich electrolyte (68 mol % LiCl-32 mol % KCl) permitted recharge of the electrode at a low voltage (-1.55 V, IR-included) and discharge of the electrode at high current densities (50-100 mA/cm$^2$). Consequently, this electrolyte composition was taken to be an optimum and it is referred to as LiCl-rich electrolyte. This electrolyte is now routinely used in 300 Ah cells.

To determine the phase sequence in the FeS electrode during charge and discharge, cyclic voltammetric, emf, and metallographic studies were conducted on the FeS electrode both in the eutectic and in the LiCl-rich electrolytes. (5) These studies were conducted with well-cycled electrodes where the particle size of the active electrode material was <20μm.

The phase sequence determined for the electrode during charge and discharge in the eutectic and LiCl-rich electrolytes is summarized in Figure 2. In this figure, the Roman numerals indicate the sequence of electrochemical reactions, while the broad arrows indicate the chemical reactions.

In the eutectic electrolyte, the charge sequence found was L$_2$, Li$_2$S + X; II$_C$, X + FeS; chemical reactions [7] X + J + Li$_2$S, [8] FeS + X + J and III$_C$, J + FeS. The X + J + Li$_2$S chemical reaction is believed to be minimal. On discharge, the sequence was I$_D$, FeS + J; II$_D$, X + Li$_2$S; IV$_D$, J + Li$_2$S; V$_D$, X + J + Li$_2$S; VI$_D$, X + J + Li$_2$S, which indicate that each phase discharge by multiple pathways. The chemical reactions [7] and [8] or X + Li$_2$S and J, and FeS + X + J are superimposed on the electrochemical discharge pathways.

In the LiCl-rich electrolyte, the phase sequence during charge is very similar to that in the eutectic electrolyte, except that the chemical reactions forming J-phase are greatly reduced. The result is an electrode that is much more readily charged. On discharge, the electrochemical phase sequence is similar to that found in the eutectic electrolyte, except that J-phase may now react chemically with Li$_2$S to form X-phase, a material with fast electrochemical kinetic properties.

Phase transition potentials were measured in an investigation on the thermodynamic properties of the FeS electrode system in LiCl-KCl eutectic electrolyte. (5) For three of the phase transitions: E$_5$(J - X), E$_4$ (J - Li$_2$S) and E$_7$ (X + Li$_2$S), the emf of the FeS electrode was measured at appropriate states of charge and discharge. In making such measurements, an emf value was extracted from such data only when certain reversibility criteria were satisfied. For example, the J + X (E$_4$) data were obtained at both 20% discharge and 80% charge, which are equivalent states of charge approached from different directions. The agreement in these measurements is an indication of reversibility. To obtain the other three phase-transition potentials, the
emf of the FeS + Li2S transition was calculated from the available free energy values for (a + β)-Li-Al, FeS and Li2S; the FeS + X and FeS + J values were then calculated from the thermodynamic interdependence that exists between the potentials. The potentials E2, E4, and E9, which are dependent on electrolyte composition, were then calculated for the LiCl-rich (67 mol % LiCl) electrolyte from the reaction stoichiometry and the changes in the activity of LiCl and KCl with electrolyte composition. The regions of phase stability and emf values for the respective transitions in the two electrolyte systems (eutectic and LiCl-rich) are summarized in Figures 3 and 4.

Using the emf equations and the activities of LiCl and KCl, Tomczuk, et al., calculated the temperature at which the emf curves intersect in LiCl-saturated electrolyte. The intersection of E2*, E4*, and E9, which occurs at 621°C in eutectic electrolyte, was calculated to occur at 481°C in electrolyte saturated with LiCl [75.2 mol % LiCl(11)]. This temperature is in excellent agreement with the thermodynamically determined temperature of 481°C ± 5°C(7). Similar calculations for the intersection of E2, E4*, and E9 (which occurs at 473°C in eutectic electrolyte) provided a value of 429°C in LiCl-saturated electrolyte [68.4 mol % LiCl(12)], which is in reasonable agreement with the 419°C ± 5°C temperature determined in the metallographic studies. (7) The above temperature calculations rely on the reaction stoichiometries and certain emf differences, while the metallographic studies only require the presence or absence of phases. The good agreement between these independent methods tends to confirm the emf equations and the reaction stoichiometries. Therefore, the free energy changes of the chemical reactions can be calculated with a reasonable degree of confidence.

The free energy changes of the four chemical reactions were calculated from the thermodynamic relationships between the six electrochemical transition potentials and the free energies. The free energy changes of the chemical reactions are:

\[
\begin{align*}
\Delta G^0_1 &= 322.6 + 0.682 T \\
\Delta G^0_2 &= -236 + 0.380 T \\
\Delta G^0_3 &= -223 + 0.336 T \\
\Delta G^0_{10} &= 4.32 - 0.015 T \\
\end{align*}
\]

where the temperatures are in °C and free energy changes are in kJ.

In a more recent study, Tomczuk, et al.,(12) determined the phase transition potentials of the FeS electrode from similar studies in LiF-LiCl-LiBr, where the only phase transitions are FeS + X and X + Li2S. The results of these emf measurements were:

*Indicates the emf has been calculated.

These values are in good agreement with their earlier values.(5)

Thermodynamically, one would predict that the principal overcharge reactions of the FeS electrode are as follows:

FeS + Fe+S + x Fe2+ + 2xe- 
2FeS + FeS2 + Fe2+ + 2e- 

The calculated voltages for these reactions vs. (a + β)-Li-Al at 450°C are 1.86 and 2.17 V, respectively; studies of overcharged FeS electrodes by Tomczuk, et al., confirm the proposed overcharge reactions.(13)

A large number of LiAl/LiCl-KCl/FeS cells of various sizes and designs have been built and operated. A typical cell design is shown in Figure 5. The electrodes are pressed plaques of electrode reactant and powdered electrolyte; the electrolyte between the electrodes is usually held in a boron nitride felt (but sometimes in used in a paste form using MgO powder).(14) Cells of the type shown in Figure 5 having capacities up to about 350 Ah have been tested, and they have demonstrated cycle lives of 250-400, with a few cells surpassing 1000 deep cycles. Specific energy values up to about 100 Wh/kg have been achieved.

A few batteries of LiAl/FeS cells have been tested in sizes up to about 6 kWh. The lifetimes, as is to be expected, have been shorter than for single cells. These batteries have shown cycle lives up to about 275.(15) The main cause of failure is the extrusion of the pasty positive electrode active material out of the positive electrode. This extruded material bridges access to the negative electrode, shorting the cell.

Table 1 summarizes the status of cell performance, lifetime, and other features. The recent cell development activities are also summarized, including work on 10-cell batteries, as are the remaining problem areas.

The Li-Si/LiCl-KCl/FeS2 Cell:

This cell is closely related to the one discussed just above. It makes use of electrodes that have a much lower equivalent weight, and therefore has a significantly higher specific energy.

The negative electrode of this cell is a solid lithium-silicon alloy, which operates very effectively at practical current densities, and can store up to about four lithium atoms per silicon atom. The Li-Si phase diagram has been subject of several investi-
The positive electrode of this cell is solid FeS$_2$. This is an attractive material because it is plentiful, has good electronic conductivity, a reasonably low equivalent weight, rapid reaction rates at cell operating temperature (450°C), and has a sulfur activity such that good potentials are achieved (1.6-2.1 V vs. Li).

The most extensive study of the high-temperature phases in the Li-Fe-S system was conducted by Martin(22,23) who employed metallography to establish the number and identity of the phases and X-ray diffraction to support the phase identification. In his work, Martin developed the Li$_2$S-FeS-FeS$_2$ section of the Li-Fe-S phase diagram, which provides an excellent guide for electrolytic investigations. Tomczuk, et al.,(24) have subsequently updated this work on the phase relationships of the FeS$_2$ electrodes and elucidated their role in the chemistry of the electrode. The updated phase diagram is shown in Figure 1. The major ternary phases in the diagram are indicated by the point F, which is the compound Li$_2$FeS$_2$ (or Li$_{1.7}$FeS$_3$), and the field C-D-E, which is a solid solution whose composition can be approximated by Li$_{2+2x}$Fe$_{1-x}$S$_2$. This field is quite narrow and is best approximated in the diagram by a line, although, of course, it must have some finite width. At X = 0 (point E), this phase has the composition Li$_2$FeS$_2$ and it is a major phase in FeS electrodes. At X = 0.2 (point D), the composition is approximately Li$_{2.2}$Fe$_{0.8}$S$_2$; this composition is in equilibrium with Li$_3$Fe$_2$S$_4$. At X = 0.33 (point C), the composition is Li$_{2.33}$Fe$_{0.67}$S$_2$, and the material of this composition is in equilibrium with Li$_2$S and FeS$_2$.

The dashed lines A-L and H-M are given in Figure 1 to indicate the equilibrium phase progressions in FeS$_2$ and FeS electrodes, respectively. These progressions are only valid, of course, in the absence of phases like LiK$_6$Fe$_2$S$_4$Cr (which would require a quinary diagram). Thus, the dashed line H-M gives FeS - Li$_2$FeS$_2$ and Fe - Li$_2$S and Fe as the predicted phase progression in the FeS electrode, but, as noted before, more complex phase progressions are also known. The dashed line A-L gives as the predicted phase progression in FeS$_2$ electrodes:

$$\text{FeS}_2 \rightarrow \text{Li}_2\text{Fe}_{1-x}\text{S}_2 \rightarrow \text{Fe}_1\text{S} \rightarrow \text{Li}_2\text{FeS}_2 \rightarrow \text{Li}_2\text{S} + \text{Fe}$$

The arrows on the above phase progression are a shorthand notation used by Tomczuk, et al.,(24) for the cell reactions.

The phase found in the room-temperature examinations of the FeS$_2$ electrodes were FeS$_2$, KFeS$_4$, Li$_3$Fe$_2$S$_4$, Li$_{2.33}$Fe$_{0.67}$S$_2$, Li$_2$FeS$_2$, Fe$_1$S, LiK$_6$Fe$_2$S$_4$Cr, Li$_2$S, and Fe. In metallographic examinations, these phases could be readily distinguished from one another by their color, isotropy, and crystal structure. The X-ray diffraction and crystal systems are presented in this work(24) for the respective phases. If the two potassium-containing compounds, which were present at low levels, are excluded from consideration, the phases identified by Tomczuk, et al.,(24) in the FeS$_2$ electrodes are in agreement with Martin's phase diagram.

Coulometric discharge data(24) obtained on the FeS$_2$ electrode also support Martin's phase diagram. The breaks in the discharge curve were located at 37.9, 42.6, and 50% of the total capacity. These values compare well with the breaks predicted by the phase diagram, namely 37.5, 41.8, and 50%, and they indicate that the phase sequence during discharge observed in the FeS$_2$ electrodes agrees with that predicted by the phase diagram if one neglects the potassium-containing compounds.

The phase sequence during charge was found by Tomczuk, et al.,(24) to be slightly different than that observed during discharge for the Li$_3$Fe$_2$S$_4$, FeS$_2$ phase transition. During discharge, the Li$_3$Fe$_2$S$_4$ formed on the FeS$_2$ during charge, the FeS$_2$ formed on the Fe$_1$S. The phases formed during charge are shown in Table 2. Cyclic voltammetry studies(25) have shown that the discharge begins very near 1.76 V vs. (a + b)-Li-Al, but the charge reaction occurs at 1.82 V; these observations are also supported by the cell data.(24) A nonequilibrium soluble electrode species also seemed to be formed in this transition region during charge,(24) which further suggests that the charge and discharge reactions for this transition must be quite different.

The principal overcharge reaction(25) of the FeS$_2$ electrode occurs at -2.4 V vs. (a + b)-Li-Al and is:

$$\text{FeS}_2 + 2\text{Cl}^- + \text{FeCl}_2 + 2\text{S} + 2e^- \quad [13]$$

where the formation of sulfur and ferrous chloride increases the porosity of the electrode and decreases the coulombic efficiency of the cell.

A number of Li/Si/FeS$_2$ cells of various designs have been built and operated at Argonne National Laboratory, and General Motors Research Laboratories. The GM cell was disk-shaped and had the construction shown in Figure 5. Cells of this type had a capacity of about 70 Ah, and had voltage vs. capacity curves as shown in Figure 7.
These cells had lifetimes of up to 16,000 h, and cycle lives of up to about 700 cycles. Only a small amount of work has been performed on batteries of Li-Si/FeS₂ cells. This system is in an earlier stage of development than LiAB/FeS₂, but offers the possibility of twice the specific energy, as shown in Table 3, which summarizes the status of the Li-Si/FeS₂ cell.

**CELLS WITH MOLLEN SALTS AS REACTANT AND AUXILIARY ELECTROLYTE**

The Na₂S₉₀ₓ•xAl₂O₃/Na₃Sn-S Cell:

This cell makes use of a molten sodium negative electrode; a solid tubular electrolyte of beta alumina (Na₂S₉₀ₓ•xAl₂O₃, x = 5 to 11) which conducts sodium ions; and a molten sulfur-sodium polysulfide positive electrode with graphite felt as the current collector. The operating temperature is 350°C. The overall cell reaction can be represented by

\[ 2Na + xS \rightarrow Na₂S\_x \]  
\((x = 2 \rightarrow 5)\)

[14]

The reaction at the sulfur electrode

\[ (x-1)S\_x^x + 2e^- \rightarrow xS\_x^{x-1} \]  
\((x = 3 \rightarrow 5)\)

[15]

is followed by equilibration with the free sulfur phase

\[ xS\_x^{x-1} + S \rightarrow xS\_x^x \]

[16]

as long as free sulfur exists.

This overview will discuss the Na₂S₂-S phase diagram, some of the properties of sodium polysulfides and the electrochemical reactions at the electrode interface including diffusion and subsequent chemical reactions. Only highlights can be given of facts that are well established and of important questions that are still open.

The phase diagram (Figure 8) has been investigated numerous times. (32-36) The main difficulty in such investigations is that in this system equlibria are established slowly and that sodium polysulfides tend to undercool and solidify as glasses. (31) If the glass is subsequently crystallized, the resulting crystals are not necessarily in equilibrium with the melt at the liquid line. The salient features of the phase diagram are the existence of the three polysulfides Na₂S₂, Na₃S₄, and Na₃S₅, and a miscibility gap with liquid sulfur and Na₂S₅ saturated with sulfur in equilibrium. This miscibility gap plays an important role in electrode kinetics and consequently in cell performance. Na₂S₅ is stable at room temperature, but decomposes above 100°C into Na₂S₄ and Na₃S₆, which of course does not preclude its existence in the melt. (32, 33)

Attempts have been made to interpret the dependence of the open circuit voltage of the cell on melt composition thermodynamically. (34-36)

One difficulty in analyzing the kinetics in this system is our limited knowledge of the exact composition of the melt, i.e., of the nature of the ions present. However, it has been established that uncharged sulfur is present in the polysulfide melt only in the form of polysulfide ions. (36)

The propensity of polysulfide melts to solidify as glasses was used to advantage in Raman spectroscopy. (33) Investigations at the temperature of the melt gave little insight, because of the coexistence of a series of polysulfides, (37) whereas with glasses interpretable results were obtained. The presence of the ions S²⁻, S⁴⁻, and S⁶⁻ in melts of the appropriate composition was confirmed, but the existence of S⁷⁻ in the melt is still controversial.

Another difficulty in analyzing the kinetics is the problem of defining diffusion in a pure melt. Earlier approaches used in other systems have been applied here successfully. (38, 39) Also, it must be kept in mind that in electrochemical measurements in pure melts without solvent, migration of reactant ions is not negligible, and diffusion coefficients obtained are only effective values. However, these values (around 10⁻⁸ cm²/s) agree quite well with those determined by tracer studies. (40) Activation energies are in agreement with those found for melt viscosity. (41-43)

The rate of the interfacial reactions at practical current densities is clearly determined by diffusion. Exchange currents are extremely high. Relaxation methods have yielded values of 1 A/cm² with steps up to 400 mV and of more than 10 A/cm² with steps of a few millivolts. This may be understood as measuring one and in the former case both of two consecutive steps in the two electron reaction. (38, 39)

Kinetics have been investigated by potential sweep chronamperometry, (38, 39) by chronopotentiometry, (44) and by the rotating disc method. (45, 46)

The kinetics of the cell reactions are illustrated by Figure 9 of a cyclic potential sweep with melt resistance measured concurrently. Neither anodically nor cathodically do we see a limiting current. On both sides the reaction peak (A, P) is followed by an abrupt decrease
In current caused by an insoluble reaction product: solid Na$_2$S$_2$ on the cathodic side (8) and liquid sulfur on the anodic side. The conductance decreases correspondingly. The formation of insoluble products necessitates the use of expanded electrodes in all but very thin layers of polysulfide electrolyte. The reduction peak A has been identified as a superposition of two consecutive one electron reaction peaks. On the return sweep, the current always passes through zero at the potential of a melt saturated with Na$_2$S$_2$.

It has been suggested that the Randles-Sevcik equation cannot be applied because of formation of these blocking surface layers. However, careful analysis has shown that the influence of layer formation becomes noticeable only after the peak has been reached, and the consistent results obtained with Randles-Sevcik analysis bear this out.

The formation of solid Na$_2$S$_2$ does not pose a problem in cell operation, especially since the layers seem to be crystalline and not very dense; they in fact inhibit overdischarge. The influence of sulfur formation at the anode depends on the nature of the electrode material, i.e., on its preferential wettability. Carbon and many other materials are preferentially wetted by sulfur. When the melt composition reaches Na$_2$S$_2$ and becomes saturated with sulfur, there is no longer a mechanism for the removal of the adsorbed insulating sulfur layer. Current flow is blocked, and the cell cannot be recharged beyond this point. Fortunately there are means of modifying the surface so that it becomes preferentially wetted by polysulfide and permits charge into the two phase region of the phase diagram. Certain metal surfaces (e.g., those of chromium steels) will not block anodic current at all. These surfaces (covered by a corrosion layer) are clearly preferentially wetted by polysulfide. Unfortunately they are not stable enough for use in practical cells.

Basic research stimulated by the invention of the sodium/sulfur cell has established many facts that are essential for the development work. But there are still a few important questions to be solved:

1) the distribution of ion species $S_x^a$ (x = 2 to 6) in sodium polysulfide melts;
2) the actual values of the very high exchange currents at the electrode;
3) the role of migration in the transport process.

Even though there are some unanswered questions about the sulfur-sodium polysulfide electrode, there is enough known to allow high-performance, long-lived cells to be built in significant quantities. Cells of various sizes, recently 65-200 Ah, have been operated, and have demonstrated specific energies of 120-160 Wh/kg, peak specific power values of 100-200 W/kg, and cycle lives of 300-1500. A typical cell design is shown in Figure 10.

Difficulty has been encountered in obtaining full recharge of the sulfur electrode because of the formation of an insulating layer of sulfur at the sites of the electrochemical reaction. Various schemes were devised for maintaining electrolytic and electronic contact between the solid electrolyte, the polysulfide phase, and the graphite current collector. Some useful approaches have included graded-resistance graphite felt current collectors (to distribute the reaction zone more widely), layered current collectors (graphite felt, well wetted by sulfur, in alternating layers with alumina cloth, well wetted by polysulfide), with the planes of the layers perpendicular to the axis of the electrolyte tube, and additives to sulfur, to improve its electronic conductivity.

A number of batteries of Na/Na$_2$S$_n$-S cells have been tested. Figure 11 shows typical charge and discharge curves for a parallel-connected module of 25 cells(47). Most of the batteries have been able to store about 10 kWh, and a recent one has stored 100 kWh. One 25 kWh module of the latter battery has operated for over 600 cycles. This represents the largest and longest-lived high-temperature battery known to these authors.

The status of the work on this system is summarized in Table 4. The remaining problems include corrosion of the metals in contact with the electrolyte, the high cost of the electrolyte, seals, and failure of cells during freeze-thaw thermal cycling.

The Na/Na$_2$O-$x$Al$_2$O$_3$/SC$_3$AtC$_3$ in Al$\text{Cl}_3$-NaCl Cell:

This cell offers an unusually high voltage of 4.2 V, and a theoretical specific energy of 563 Wh/kg, corresponding to the reaction:

$$4\text{Na} + \text{SC}_3\text{AtCl}_4 + 3\text{AlCl}_3 + \text{S} + 4\text{NaAlCl}_4$$

It is also possible to discharge the sulfur to the minus-2 valence state. In this case, the reactions are:

$$4\text{Na} + \text{SC}_3\text{AtCl}_4 + 3\text{AlCl}_3 + \text{S} + 4\text{NaAlCl}_4$$

$$2\text{Na} + \text{S} + 2\text{AlCl}_3 + 2\text{AlSCl}_2 + 2\text{NaCl}$$

In addition, the operating temperature is in the range 180-250°C vs. 350°C for Na/Na$_2$S$_n$-S.

As discussed below, Reaction 17 proceeds through several intermediates. The evidence for the reactants, products and the intermediates may be summarized as follows:

1. The Raman spectrum of the melt in the positive electrode compartment of a fully charged cell(48) is a summation of the spectral features of $\text{Al}_2\text{Cl}_7^-$, $\text{AlCl}_4^-$ and SC$_3$At$^+$ (the presence of Na$^+$ ions is, of course, not detected by Raman spectroscopy). The fully charged state may be obtained either by a four electron oxidation of elemental sulfur in the melt or by the addition of the compound SC$_3$AtC$_4$(49) to an acidic (Al$\text{Cl}_3$/NaCl molar ratio > 1) melt.
2. Raman spectra taken at different stages of the first discharge plateau clearly show the disappearance of $\text{SCl}_4^-$, the increase of $\text{ACl}_4^-$, and the decrease of $\text{At}_2\text{C}_7^-$ bands.\(^{(48)}\) In fact, the melt compositions estimated from the intensities of the Raman bands of $\text{At}_2\text{C}_7^-$ and $\text{ACl}_4^-$ are in reasonable agreement with melt compositions calculated from the stoichiometry of the electrochemical process. Thus, the discharge corresponds to a decrease in the modified Lewis acidity of the melt in the positive electrode compartment, in agreement with Equations 17 and 18. Although no clearcut assignments of intermediate species could be made based on Raman spectra, UV-visible and electron spin resonance spectroelectrochemical and electrochemical studies\(^{(50-54)}\) of more dilute melt solutions provide evidence for monovalent sulfur species, present as $\text{S}_2\text{C}_2^2$ or possibly $\text{S}_4\text{C}_4^+$ and, in $\text{ACl}_3$-rich melts, for cations such as $\text{S}_8^{2-}$, $\text{S}_8^{2+}$ and $\text{S}_8^{3+}$\(^{(50,51)}\). Thus the overall reduction process of $\text{SCl}_4^+$ involves an increase in $\text{S}$-$\text{S}$ bonds and decreasing $\text{Cl}^-$ complexation.

3. The end of the first discharge plateau corresponds to the formation of elemental sulfur, present predominantly as $\text{S}_8$\(^{(48,55)}\). The solubility of sulfur in the melt increases with the melt acidity\(^{(55)}\) or, in other words, it decreases as the discharge proceeds. Thus, it is likely that in a cell most of the elemental sulfur is present as a suspension.

4. The product formed during the second discharge plateau depends on whether the melt is acidic or basic (this will usually correspond to NaAlCl\(_4\) saturated with NaCl\(^{(56)}\)). In acidic melts, polymeric (Al(In)Cl\(_4\)) is formed, while in basic melt polymeric (Al(Sn)Cl\(_4\)) is present.\(^{(48,57)}\) The values of $n$ are believed to be $3-4$ in dilute melts.\(^{(57)}\) There is no evidence for the formation of polysulfide ions in $\text{AtCl}_3$-$\text{NaCl}$ melts, although Raman evidence for the $\text{S}_8$ ion in basic $\text{ACl}_3$-$\text{CaCl}_2$ melts has been obtained.\(^{(58)}\)

The electrochemistry of sulfur oxidation and reduction has been investigated in very acidic ($\text{ACl}_3$-$\text{NaCl}$, 63/37 mole %) melts,\(^{(52)}\) melts of intermediate pCl (where pCl is defined as $-\log$ (Cl\(^-\))\(^{(54)}\)) and in $\text{ACl}_3$-$\text{NaCl}$ melts saturated with NaCl.\(^{(53)}\) These investigations, as well as spectroelectrochemical studies in 63/37 $\text{ACl}_3$-$\text{NaCl}$ melts,\(^{(51)}\) were performed in more dilute melts than is normally the case for cell studies.

In very acidic melts the oxidation of sulfur to $\text{SCl}_4^+$ involves three voltammetrically distinguishable steps. The first of these steps results in $\text{S}_8^{2-}$ and probably $\text{S}_8^{3+}$ and $\text{S}_8^{4+}$\(^{(51)}\). The apparent $n$-value per sulfur atom ranges from 0.13 to 0.22 depending on the temperature (175-250°C) and the concentration of sulfur. The second step results in the formation of monovalent sulfur which is oxidized to $\text{SCl}_4^+$ in the third step. Spectroelectrochemical studies\(^{(51)}\) point to the formation of $\text{S}_8^{2+}$ and divalent sulfur as intermediates in the second and third oxidation steps. The low oxidation states of sulfur, such as $\text{S}_8^{2+}$ and $\text{S}_8^{3+}$, were found to be unstable in slightly acidic melts (pCl < 3.8);\(^{(54)}\) only two voltammetric steps are observed corresponding to the formation of $\text{S}_2\text{C}_2^2$ and $\text{SCl}_4^-$. In NaCl-saturated melts $\text{SCl}_4^+$ is unstable; the main oxidation product is $\text{S}_2\text{C}_2^2$.\(^{(51)}\)

A number of simple glass laboratory cells of up to twenty amperes capacity have been operated, and a few metal-cased cells have been tested.\(^{(59,60)}\) Some voltage vs. capacity curves for a cell employing both Reactions 17 and 18 above are shown in Figure 12. The upper plateau corresponds to Reaction 17; the lower plateau corresponds to Reaction 18. This cell used a reticulated vitreous carbon current collector in the positive electrode. Tungsten spirals have also been used.

Recent work with this cell has demonstrated that high power densities (up to 788 mW/cm\(^2\) at 360 mA/cm\(^2\) and 2.2 V) can be achieved. Some cells of this type have demonstrated cycle lives in excess of 400 cycles, and one small cell (0.56 Ah) was operated for 1370 cycles (with the positive electrode inside the $\text{Al}_2\text{O}_3$ tube).

Values for specific energy and specific power of complete cells cannot be quoted because no cells of practical design have been constructed yet. The status of this cell is summarized in Table 5. The problems include: highly corrosive positive electrode material; significant vapor pressure of $\text{ACl}_3$; seals; poor wetting of the electrolyte by sodium requires special start-up procedures.

**CONCLUSIONS**

Based upon the material presented in this paper, the following conclusions may be drawn.

1. Molten-salt rechargeable cells are making good progress in their evolution into high-performance, long-lived batteries.
2. The chemistry and electrochemistry of these systems are complex, but are reasonably well understood.
3. Materials problems are significant for these systems, and could well be the pace-setting issues in their development.
4. The field of molten salts offers interesting opportunities for the development of new electrochemical cells. More are sure to follow.
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Table 1. Summary of LiAt/LICl-KCl/FeS Cell

| Status            | Specific Energy | 60-100 Wh/kg @ 30 W/kg |
|-------------------|-----------------|------------------------|
| Specific Power    | 60-100 W/kg, peak |
| Cycle Life        | 300+ @ 100% DOD  |
| Lifetime          | 5000+ h          |
| Cost              | >$100/kWh        |

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

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

\[
2\text{LiAt} + \text{FeS} + \text{Li}_2\text{S} + 2\text{At} \rightarrow \]
\[
E = 1.33 \text{ V; 458 Wh/kg Theoretical} \]
\[
T = 450^\circ\text{C} \]
Table 2. Sulfide Phases During Charge of LiAl/FeS₂ Cells Operated at 410°C Using Eutectic Electrolyte

| Cell designation | Charge potential \(^b\) vs. (a + b) LiAl | X-ray findings | Metallographic findings |
|------------------|------------------------------------------|----------------|------------------------|
| Z-1              | 1.53                                     | Li₂FeS₂        | Li₂Fe₂S₄ + Fe₁₋₀S    |
| Z-9              | 1.64                                     | Li₂Fe₀.₈₇S₂ and Li₂FeS₂ | Li₂Fe₂S₄ + Fe₁₋₀S + Li₂.₃₃Fe₀.₆₇S₂ |
| Z-2              | 1.72                                     | Li₃Fe₂S₄       | Li₃Fe₂S₄ only         |
| Z-7              | 1.79                                     | Li₃Fe₂S₄       | Li₃Fe₂S₄ + 5% Fe₁₋₀S |
| Z-3              | 1.82                                     | Li₃Fe₂S₄       | Not examined           |
| Z-8              | 1.85                                     | FeS₂           | Fe₂S + Fe₁₋₀S         |

a The phases Li₂S and Fe are not shown in this table because they react at a much lower potential of 1.33V to yield Li₂FeS₂.

b Cells were constant-current charged at -18 mA/cm² to this potential and then constant voltage charged at this potential for periods in excess of 18hr. Current densities at the end of this time period were <2 mA/cm².
### Table 4. Summary of Na/Na⁺ Solid/S Cell

2Na + 3S + Na₂S₃  
E = 2.0 V; 758 Wh/kg Theoretical  
T = 350°C

| Status | Specific Energy | 90-180 Wh/kg @ 30 W/kg |
|--------|-----------------|------------------------|
|        | Specific Power  | 60-180 W/kg peak       |
|        | Cycle Life      | 300-1500               |
|        | Lifetime        | 3000-15,000 h          |
|        | Cost            | >$100/kWh              |

**Recent Work**
- Batteries, 10-100 kWh
- C₆H₆ additive to S
- Ceramic (TiO₂) electronic conductors
- Shaped current collectors
- Tailored resistance current collectors
- Sulfur-core cells
- Layered current collectors
- Graphite cladding
- Na₁₋₋₂Zr₂Si₂P₃₋₋₋₀₁₂
- Thermocompression bonded seals

**Problems**
- Low cost electrolyte
- Corrosion-resistant material for contact with S
- Thermal cycling
- Low cost seals
- Robust electrolyte seals

### Table 5

Na/Na₂OₓxAIₓO₃/SCI₃AICl₄ in AICl₃-NaCl  
E = 4.2 V; 563 Wh/kg Theoretical  
T = 250°C

| Status: laboratory cells only (4 Ah) |
|-------------------------------------|
| Current Density | 20 mA/cm² @ 3.5 V |
| Power Density   | 790 mW/cm² max. @ 2.2 V |
| Cycle Life      | 1370 @ 100% DOD    |
| Lifetime        | 7000 h             |
| Cost            | too early          |

**Recent Work**
- Larger cells - 20 Ah
- Less expensive current collectors
- Reduction to S⁺⁺

**Problems**
- Sodium wetting?
- Vapor pressure of AICl₃
- Corrosion of metals and some electrolytes
- Electrolyte cracking?
- Seals
PHASES IN THE Li-Fe-S SYSTEM AT 450°C

Figure 1. Isothermal section of the Li-Fe-S phase diagram at 450°C.

Figure 2. Summary of reaction assignments for two general cases (a) lower LiCl concentrations and temperatures and (b) higher LiCl concentrations and temperatures. Peak assignments from cyclic voltammetry (roman numerals) and the directions of chemical reactions (X ↔ J + Li₂S) and (X + FeS ↔ J) are shown, where X = Li₂FeS₂ and J = Li₅Fe₂S₄Cl₂.

PHASES IN THE Li-Fe-S SYSTEM AT 450°C

This region not investigated

A-L = DISCHARGE PATH OF FeS₂ ELECTRODE
F = Li₂FeS₄
C-D-E = Li₂Fe₁₋ₓS₂
H-M = DISCHARGE PATH OF FeS ELECTRODE

Figure 4. Regions of stability of FeS, LiFe₂S₄Cl₂ (J-phase), and Li₂S in LiCl-electrolyte. Note that Eₐ, E', and E'' are shifted from that of an a-electric. An asterisk indicates a calculated emf

Figure 3. Regions of stability of J-phase, LiFe₂S₄Cl₂ (J-phase), and Li₂S in the LiCl-electrolyte.
Figure 6. Cross section of a disk-shaped Li4Si/LiFeS2 cell, having a capacity of 70 Ah.

Figure 5. Design used for the immobilized electrolyte/powder separator cells. 802-8075

Figure 7. Typical voltage vs. capacity curves for constant current discharges of a Li4Si/LiCl-KCl/FeS2 cell like that of Figure 6.

CAPACITY, A-h

| 11.1 | 22.3 | 33.3 | 44.4 | 55.5 | 66.6 | 77.7 |
|------|------|------|------|------|------|------|
| 2.5  | 2.5  | 2.5  | 2.5  | 2.5  | 2.5  | 2.5  |
| 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  |
| 1.5  | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  |
| 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  |
| 0.5  | 0.5  | 0.5  | 0.5  | 0.5  | 0.5  | 0.5  |

UTILIZATION OF POSITIVE ELECTRODE, PERCENT OF THEORETICAL CAPACITY XRL 019-1872

Figure 8. Na2S2-S phase diagram according to Oei, Gupta, and Tischer; (27,28) solid circle, data from emf measurements; open circle, data from DTA measurements.
Figure 9. Cyclic sweep and melt conductance in Na$_2$S$_4$ at 300°C. Vitreous carbon electrode area is 0.0047 cm$^2$. Sweep is IR corrected. (37)

Figure 10. Exploded view of a 168-Ah sodium/sulfur cell of the sodium-core design.

Figure 11. Charge and discharge curves for a 25-cell parallel-connected Na/S battery.
Figure 12. Galvanostatic charge-discharge curve and potentials of sulfur and sodium electrodes vs. AI(III)/AI (in NaCt sat. melt) reference electrode at 200°C. Reticulated vitreous carbon used as positive current collector.
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