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RECHARGEABLE HIGH-TEMPERATURE BATTERIES

Elton J. Cairns

January 1981

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RECHARGEABLE HIGH-TEMPERATURE BATTERIES

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in

COMPREHENSIVE TREATISE ON ELECTROCHEMISTRY, VOLUME VII

J.O'M. Bockris, B.E. Conway, E.B. Yeager, eds.

Plenum Publishing Corporation
New York, NY

(in press)
1. INTRODUCTION

Since the mid-1960's there has been a growing research and development effort in the area of high specific energy, high specific power rechargeable batteries for use in electric vehicles, electric utility networks, and solar- and wind-powered electric generator systems. For a variety of reasons, including scientific, technological, and economic, high-temperature, non-aqueous systems have been found to be the most attractive candidates for the above relatively large-scale applications. Only the high-temperature cells offer the attractive combination of features sought for the cited applications: a specific energy above 100 W-h/kg, a specific power above 100 W/kg, a cycle life in excess of 500 cycles (at 100% depth of discharge), and a projected cost of less than $50* per kWh of energy storage capability.

Some perspective regarding the relative specific energies of various electrochemical cells can be gained by studying Figure 1, which shows the theoretical specific energy of various cells, plotted against the equivalent weights of the reactants (or products). The theoretical specific energy is defined as the Gibbs free energy change for the overall cell reaction, divided by the corresponding weights of the reactants.

\[
\text{Theoretical Specific Energy} = \frac{-\Delta G}{\sum v_i M_i}
\]

where \(v_i\) is the number of moles of reactant \(i\)

\(M_i\) is the molecular weight of reactant \(i\)

It is evident from Figure 1 that the higher theoretical specific energy values correspond to cells with low-equivalent-weight reactants, and with large electronegativity differences between the reactants. The alkali metals are very attractive reactants for the negative electrodes, and the chalcogens and

*1979 dollars

This manuscript was printed from originals provided by the author.
halogens (and some compounds containing them) are very attractive reactants for the positive electrodes. Notice that most of the high-specific-energy couples involve reactants that are incompatible with aqueous electrolytes. Among the non-aqueous electrolytes, only those that are used at elevated temperatures have high conductivities (>0.1 Ω⁻¹cm⁻¹), consistent with specific power values above 100 W/kg. A summary of other desirable characteristics for cell reactants and electrolytes is given in Table 1. (1)

The electrolytes which are most useful in high-temperature cells are solid ionic conductors (either ceramics or glasses) or molten salts. These electrolytes must be chemically stable in contact with both the negative and positive electrode reactants, and must have a decomposition potential safely above the maximum operating voltage of the cell (unless a component of the electrolyte is a cell reaction product). The above considerations significantly narrow the field of choices, so that high-temperature cells with sodium electrodes now must use solid electrolytes (because sodium is soluble in its molten halides, yielding an electronically conductive electrolyte), and cells with lithium (and some other) electrodes now must use molten salt electrolytes (because there are no solid lithium ion conductors sufficiently stable to lithium). Therefore, there is a natural grouping of high-temperature cells which will be followed in the discussion below: sodium cells with solid electrolytes, and lithium (and calcium) cells with molten-salt electrolytes.

2. CELLS WITH SOLID ELECTROLYTES

All of the high-temperature cells with solid electrolytes under current development contain molten sodium as the negative electrode, and rely upon sodium ion conduction in the electrolyte. The positive electrodes for these cells may be sulfur, a sulfide, or a halide. These cells operate at temperatures in the range 200-400°C.
### TABLE 1
DESIRABLE CHARACTERISTICS OF SYSTEMS FOR HIGH-PERFORMANCE ELECTROCHEMICAL CELLS

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Anode reactant</th>
<th>Cathode 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$^{-6}$)</td>
<td>High (&gt;10$^{-4}$)</td>
</tr>
</tbody>
</table>

*A more important criterion for the electrolyte is low density.*
2.1. The Sodium/Beta-Alumina/Sulfur Cell

The heart of the Na/β-Al₂O₃/S cell is the ceramic electrolyte, called beta alumina. Actually, the electrolyte is a sodium aluminate of the composition Na₂O·11Al₂O₃, consisting of hexagonal layers of spinel-like blocks containing aluminum and oxygen atoms, the layers being spaced apart by aluminum-oxygen bridges. The sodium ions are located in planes perpendicular to the C axis of the crystals, and are mobile in these planes. The conductivity is about 0.3Ω⁻¹cm⁻¹ at 300°C for single-crystal β-Al₂O₃, and 5 to 20 times lower for polycrystalline material. A related form of this material, β⁴-Al₂O₃, with a greater C axis spacing, has a higher conductivity of 0.3Ω⁻¹cm⁻¹ for the polycrystalline form at 300°C. A typical composition for β⁴Al₂O₃ is Na₂O·6Al₂O₃ with up to 2 w/o MgO and/or Li₂O to stabilize the structure.

The beta-alumina electrolyte for Na/S cells is prepared (usually by pressing and sintering) in a tubular form, with a wall thickness of 1-2 mm. The original form of the cell, reported by Kummer and Weber, is shown schematically in Figure 2, with sodium inside the electrolyte tube, and sulfur outside. The molten sodium, being an excellent electronic conductor, acts as its own current collector, and makes contact with the sodium container, which serves as the negative terminal of the cell. The sulfur and the polysulfides which form during discharge are poor electronic conductors, so a current collector network of graphite fibers (e.g., in the form of a felt matting) is used in the sulfur electrode, providing an electronically conductive pathway from the positive terminal through the metal cell case, to the sites of electrochemical reaction near or at the surface of the electrolyte.

The overall cell reaction is the conversion of sodium and sulfur to sodium sulfides at about 350°C:
FIGURE 2

SEALS

MILD STEEL CONTAINER

SULFUR/CARBON

ALPHA ALUMINA

BETA ALUMINA

SODIUM

XBL 802-8067
2Na + xS → Na₂Sₓ 

The phase diagram showing the coexistence of two immiscible sulfur-rich liquid phases is presented in Figure 3. (4) Starting with the cell in the fully charged state at 350°C, the positive electrode is essentially pure liquid sulfur, with a potential of 2.1-2.2 V vs. the Na electrode. As the cell is discharged, a sodium polysulfide is formed according to Equation 2. When the amount of polysulfide formed exceeds the solubility limit in sulfur (a fraction of a percent), a separate polysulfide phase forms, having a composition (at 350°C) of Na₂Sₕ₂, comprised largely of Na₂S₅ and Na₂S₆. This phase has a high electrolytic conductivity. The amount of polysulfide phase increases at the expense of the sulfur phase as discharge continues. The reversible cell potential remains 2.07-2.08 V so long as the two phases coexist (see Figure 4).

When all of the sulfur is converted into polysulfide, the overall composition of the positive electrode is Na₂Sₕ₂. Further discharge is proposed by Ludwig (5) to take place as follows:

\[
\begin{align*}
\bar{S}₃ - S_2^- + e^- & \rightarrow \bar{S}₃ \cdots \bar{S}₂^- \\
\bar{S}₃ \cdots \bar{S}₂^- + e^- & \rightarrow S_3^- + S_2^- \\
2S_3^- & \rightarrow S_2^- + S_4^- \\
S_2^- + 2S_5^- & \rightarrow 3S_4^-
\end{align*}
\]

Reactions 3 and 4 are electrochemical, and are followed by chemical reactions 5 and 6, resulting in the conversion of the polysulfide phase to the overall composition Na₂S₄ (comprised of a mixture of Na₂S₂, Na₂S₄, and Na₂S₅). As discharge continues, a similar mechanism operates on Na₂S₄:

\[
\begin{align*}
\bar{S}₂ - S_2^- + e^- & \rightarrow \bar{S}₂ \cdots \bar{S}₂^- \\
\bar{S}₂ \cdots \bar{S}₂^- + e^- & \rightarrow 2S_2^-
\end{align*}
\]
FIGURE 4

Na/Na$_2$O - II Al$_2$O$_3$/Na in S
T = 350°C

EMF, volts
X$_{Na}$

L$_1$  L$_1$ + L$_2$  L$_2$  L$_2$ + Na$_2$S$_2$(S)
Na₂S₂ accumulates in the polysulfide melt until its solubility limit is reached, and solid Na₂S₂ precipitates at the electrolyte surface, preventing further reaction at a significant rate. The overall composition at this point is Na₂S₃ (at 350°C).

As the cell is recharged, the polysulfide phase is converted to sulfur which tends to form insulating layers, wetting and coating the graphite current collectors, preventing further reaction. This problem has resulted in a great deal of effort on improving the electronic conductivity of sulfur (by addition of such materials as C₆N₄), using specially shaped graphite felt current collectors, and by tailoring the conductivity of the graphite current collector, in order to provide an optimized current distribution in the sulfur electrode, avoiding the blockage of the recharge process by insulating sulfur layers.

Most of the early Na/S cells were relatively small (tubes ~1 cm dia x 10-15 cm long, <15 Ah), and many had glass housings and seals. The problems of corrosion and impurities were studied in terms of their influence on cell resistance and lifetime. High purity sodium, free of potassium and other alkali metals is needed, to avoid cation exchange and cracking of the β-Al₂O₃. Impurities in the sulfur, such as Fe, Ni, etc., from corrosion of the steel cell case were found to cause problems with the sulfur electrode due to metal sulfide precipitation, blocking access of sulfur to the electrolyte. The corrosion of metal containers by sulfur remains a serious problem. Many coatings have been tested; chromium and molybdenum are among the best. Some borides are promising.

In spite of the various materials problems associated with the Na/β-Al₂O₃/S cell, the simplicity of the basic cell design and the low cost of the reactants have resulted in a wide-spread interest in this cell. Major
efforts exist in the U.S., England, France, Germany, and Japan. In the last few years, progress has been good, and a number of approaches are being taken to the problems. Cells of significantly more than 100 Ah capacity (typically, 165 Ah) have been tested, having electrolyte tubes of up to 3 cm diameter and 45-60 cm long. A recent design of a 168 Ah cell used by General Electric is shown in Figure 5. This cell has sodium inside of the electrolyte tube, as do the Ford and Brown-Boveri cells. The cells of British Rail and Chloride Silent Power have sulfur inside the \( \beta''-\text{Al}_2\text{O}_3 \) tube, and sodium outside. This approach was taken to minimize the problem of corrosion by sulfur. Of course, the central current collector for the sulfur electrode must be corrosion resistant, but coatings are easier to apply to the outer surface of a current collector than to the inner surface of a cell case.

In all sodium/sulfur cells, the electrolyte tube is sealed to an alumina collar by a glass seal. This seal has been a cause of failure. Another difficult seal problem for this cell is that of the metal cell container to the alumina collar. Various gasketed seals with bolts have been used, but these are too heavy and expensive. Recently, emphasis has been placed upon thermocompression bonded seals, which appear to be more practical.

The internal resistance of the cells has a strong influence on the efficiency of operation, and the heat generation rate. In the interest of lowering the internal cell resistance to a value below 2 \( \Omega\text{-cm}^2 \), a new sodium-ion electrolyte is being evaluated. This electrolyte, called NASICON, has an advantage of having high sodium ion mobility in all three crystallographic directions, rather than just two, as for \( \beta-\text{Al}_2\text{O}_3 \). The general formula for the family of NASICON compositions is \( \text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_3-x\text{O}_{12} \). Resistivities in the range of 2-4 ohm-cm have been reported at 300-350°C. Another problem with internal resistance in sodium/sulfur cells relate to the existence of a...
resistance associated with the sodium/β"Al₂O₃ interface, which increases as cell cycling continues. (7) There is no general agreement on the precise source of this interfacial resistance, or means for eliminating it. The sulfur electrode, as one would expect, is a significant source of resistance. Various designs of graphite fiber current collectors have been investigated in attempts to reduce the cell internal resistance. Currently, the best values are about 2 Ω·cm², and 1.2 Ω·cm² may be achievable with present approaches (and electrolyte thicknesses near 1.5 mm).

Sodium/β-alumina/sulfur cells are typically operated at 350°C, a current density of 0.1 A/cm² or less, and have capacity densities of 0.2–0.4 Ah/cm², based on the area of the electrolyte. The resistance-area product for well-built cells is 2 ohm·cm² at 350°C. The specific energy values achieved by the best-designed cells are near 150 Wh/kg, at about 40 W/kg. There is a great deal of variation in the reported lifetimes of individual cells, but the better ones operate for more than 200 deep cycles; some have achieved about 1500 deep cycles.

A few multi-kilowatt-hour sodium/sulfur batteries have been tested, but their lifetimes have been very short, due to the variability of characteristics of the individual cells. The voltage-current curve for a 96-cell battery having a design capability of 10 kWh is shown in Figure 6. (8) The cells were arranged in four parallel strings, giving 50 V and 177 Ah. Currently, most of the sodium/sulfur battery programs are placing emphasis on semi-pilot production of cells having capacities of 100–200 Ah, the life-testing of these cells, and the preparation of batteries. The problems of thermal management and optimum interconnection of cells to form batteries are in the early stages of investigation. In the period 1980–82, a number of demonstration batteries for electric vehicles will be constructed and tested.
FIGURE 6

-80 -60 -40 -20 0 20 40 60 80 A 100 120

CHARGE

DISCHARGE

$R_{\text{battery}} = 196 \text{ m}\Omega$

$R_{\text{cell}} = 32.7 \text{ m}\Omega$

CURRENT

BATTERY VOLTAGE

XBL 802-8071
Table 2 summarizes the present state of sodium/sulfur cell research and development. To put the status data into perspective, the best of the specific energy and specific power values are acceptable for energy storage and vehicle propulsion applications, as is the longest cycle life. The lifetime necessary for most applications is at least 3 years (26,000 h), and the cost should be below $100/kWh.

2.2 The Sodium/Sodium Glass/Sulfur Cell

This interesting cell operates according to the same principles as the sodium/beta alumina/sulfur cell. The beta alumina electrolyte, however, is replaced by a sodium-ion-conducting glass. This glass electrolyte has a much higher resistivity than beta alumina ($10^4 \Omega\text{-cm} \text{ vs. } 3-20 \Omega\text{-cm} \text{ at } 300-350^\circ \text{C}$). It is necessary, therefore, to use a much thinner layer of electrolyte between the electrodes, and to operate the cell at much lower current densities in order to have an acceptably small voltage loss due to the cell resistance. This is accomplished by using hollow fibers of glass electrolyte, 70 µm O.D., and 50 µm I.D., with a 10 µm wall thickness.

The design of the sodium/sodium glass/sulfur cell, using thousands of hollow glass fibers is shown in Figure 7. The fibers have one end sealed, and the other (open) end bonded to a glass tubesheet, providing communication between the insides of the fibers and the sodium reservoir. The sulfur is on the outsides of the hollow fibers. Current collection in the sulfur electrode is provided by a carbon- or molybdenum-coated aluminum foil which is spirally wound among the glass fibers (a simple operation performed by rolling the fibers together with the Al foil before sealing into the tubesheet). Typically, the distance between fibers is 200 to 500 µm, and the distance from a fiber to the Al current collector is 20 µm. Because of the very large total electrolyte area offered by the fibers, the operating current density
TABLE 2
Na/β-Al₂O₃/S
2Na + 3S → Na₂S₃
$\bar{E} = 2.0$ V; 758 Wh/kg Theoretical

<table>
<thead>
<tr>
<th>Status</th>
<th>50-200 Ah</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Size</td>
<td>85-150 Wh/kg @ 30-40 W/kg</td>
</tr>
<tr>
<td>Specific Energy</td>
<td>60-130 W/kg peak</td>
</tr>
<tr>
<td>Specific Power</td>
<td>200-1500</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>3000-15,000 h</td>
</tr>
<tr>
<td>Lifetime</td>
<td>&gt;$1000/kWh</td>
</tr>
</tbody>
</table>

Recent Work
- Batteries, ~10 kWh
- C₆N₄ additive to S
- Ceramic (TiO₂) electronic conductors
- Shaped current collectors
- Tailored resistance current collectors
- Sulfur-core cells
- Na₁⁺ₓZr₂Si₁₋ₓP₃₋ₓO₁₂
- Thermocompression bonded seals

Problems
- High Na/β'-Al₂O₃ interfacial resistance
- Corrosion of materials in contact with S
- High cost seals
- High cost electrolyte
- Thermal cycling causes failure
- Thermal control of batteries
- Cell mismatch in batteries
SODIUM LEVEL FULLY CHARGED

MOLten SODIUM REServoir

ANODE

CERAMIC INSULATOR

SODIUM FILLING TUBE

ALUMINUM

SODIUM LEVEL AT DISCHARGE

GLASS TUBE SHEET

SULFUR FILLING TUBE

SULFUR LEVEL FULLY CHARGED

GLASS FIBERS PENE- TRATE TUBE SHEET COMMUNICATE WITH THE SODIUM RESERVOIR

MOLten S-$Na_2S_4$ CHAMBER

ALTERNATE LAYERS OF SODIUM FILLED GLASS FIBERS & ALUMINUM FOIL

GLASS FIBERS ARE CLOSED AT THE BOTTOM

FOIL TO CONTAINER WALL

CATHODE LEAD WILL BE ATTACHED TO CASE AT POINT OF CONVENIENCE

XBL 7912-13726
is only 0.002 A/cm², yielding a low resistance loss (0.1 V), and a high efficiency (typically, 90% overall). This cell is designed to operate at 300°C between the composition limits Na₂S₂₀ (charged) and Na₂S₃.₅ (discharged), with a theoretical specific energy of 691 Wh/kg. A sulfur utilization of 90% (based on Na₂S₃.₅) is achieved. As expected, the cell resistance rises rapidly toward the end of the charging process. Many small cells (0.5 to 6 Ah*) have been tested, and lifetimes up to about 9000 hr, and 500 cycles have been achieved with stable performance. A small number of 40 Ah cells (with 13,000 fibers) have been tested also.

The current problems with the glass fiber cell include fracture of the fibers near the tubesheet, gradual sagging of the glass tubesheet, and undesirable interaction between the two glass compositions making up the fibers and the tubesheet. When a number of fibers fail, the exothermic reaction between sodium and sulfur can cause thermal runaway. This safety problem is currently receiving attention. Thermal control must be reasonably precise for these cells because the cell resistance (mostly glass fiber resistance) has a high temperature coefficient. Cooldown of cells after startup is not permitted, because of excessive fiber breakage.

Recent work with 40 Ah cells is encouraging, and development of these cells continues, with emphasis on increasing cell lifetime and improved safety. Table 3 presents a summary of the status of this cell.

2.3 The Sodium/Beta-Alumina/Antimony Trichloride Cell

This cell is a relative of the sodium/sulfur cells. It uses a molten salt mixture of SbCl₃ in NaCl-AlCl₃ in place of sulfur as the positive electrode reactant. The melting point of NaCl-AlCl₃ mixtures is low enough that cell operation can be carried out at 200°C. It was claimed by the

*The 6 Ah cells contain about 2000 fibers.
### TABLE 3

<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><strong>Cell Sizes</strong></td>
<td>0.5, 6, 40 Ah</td>
<td>n.a.</td>
<td>500</td>
<td>9000 h</td>
<td>&gt;$1000/kWh</td>
</tr>
</tbody>
</table>

#### Recent Work

- 40 Ah Cells
- Mo coating on Al
- New glass for tubesheet

#### Safety

#### Problems

- Breakage of fibers near tubesheet
- Thermal runaway on failure
- Sagging of tubesheet
- Compatibility of fibers and tubesheet
- Impurities attack fibers
- High temperature coefficient of resistance
- Thermal cycling

![Image](image-url)
TABLE 4

Na/β"-Al₂O₃/SbCl₃ in AlCl₃

3Na + SbCl₃ + 3AlCl₃ → 3NaAlCl₄ + Sb

\[ \bar{E} = 2.8 \text{ V}; \ 328 \text{ Wh/kg Theoretical} \]

<table>
<thead>
<tr>
<th>Status</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy (projected)</td>
<td>90 Wh/kg @ 12 W/kg</td>
</tr>
<tr>
<td>Specific Power (projected)</td>
<td>30 W/kg</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>100 @ 100% DOD</td>
</tr>
<tr>
<td>Cost</td>
<td>too early</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>210°C</td>
</tr>
</tbody>
</table>

Recent Work

- Tubular cells
  - 6 Ah, 30 Ah
- Improved electrode designs

Problems

- Wetting of β"-Al₂O₃ by Na
- Current collectors (W or Mo)
- Seals
- Low current density (7.5mA/cm²)
- Degradation of β"-Al₂O₃
- Slow recharge (14 h)
- Low specific energy
investigators (10,11,12) that the lower operating temperature would permit	polymeric materials to be used as insulators and seals, however, these were
not satisfactorily developed and demonstrated.

The overall cell reaction is as follows:

$$3\text{Na} + \text{SbCl}_3 + 3\text{AlCl}_3 \rightarrow 3\text{NaAlCl}_4 + \text{Sb}$$  \hspace{1cm} (9)

With an average cell potential of 2.8 V, the theoretical specific energy is
328 Wh/kg.

Small cells, up to 6Ah, were operated at current densities up to
7.5 mA/cm$^2$. These cells used graphite powder and molybdenum or tungsten as
the current collector in the positive electrode. Cycle lives of about 100
have been demonstrated. Problems encountered in the work on this cell have
included difficulty of wetting of the $\beta''$-$\text{Al}_2\text{O}_3$ by sodium, inadequate seals,
low current density, and degradation of the $\beta''$-$\text{Al}_2\text{O}_3$.

The status of this cell is shown in Table 4 where a projected specific
energy of 90 Wh/kg is given. This value is low, compared to the values
already demonstrated for the Na/S cell (150 Wh/kg).

2.4 The Sodium/Beta-Alumina/Sulfur Chloride Cell

The newest cell of the sodium/beta alumina family of cells uses SCl$_4$ in
NaCl-AlCl$_3$ as the positive electrode reactant.\(^{(13)}\) Again, a lower operating
temperature is offered by the NaCl-AlCl$_3$ mixture: temperatures of 130 to
255°C have been used.

The overall cell reaction for reduction to S$^0$ is:

$$4\text{Na} + \text{SCl}_3\text{AlCl}_4 + 3\text{AlCl}_3 \rightarrow \text{S} + 4\text{NaAlCl}_4$$ \hspace{1cm} (10)

The cell voltage is impressively high: 4.2 V; yielding a theoretical specific
energy for Reaction 10 of 563 Wh/kg.

Some glass laboratory cells have been operated according to Reaction 10,
having a capacity of 4 Ah at 255°C.\(^{(13)}\) These cells have used tungsten
spiral current collectors, and have operated for at least 45 cycles before failure of the $\beta''$-Al$_2$O$_3$ electrolyte.

The status of the work on the Na/$\beta''$-Al$_2$O$_3$/SCl$_4$ in NaCl-AlCl$_3$ cell is shown in Table 5. The high cell voltage offers the possibility of high efficiency. If the $S^0$ can be reduced to $S^\pm$ by deeper discharge at a voltage above about 3 V, the specific energy in practical cells could be well above 100 Wh/kg.

3. CELLS WITH MOLTEN SALT ELECTROLYTES

All of the rechargeable cells with molten salt electrolytes currently under development make use of solid electrodes. These cells are an outgrowth of earlier work on cells with liquid electrodes and molten salt electrolytes. The forerunner of the present Li alloy/molten salt/FeS$_x$ cells was the Li/LiCl-KCl/S cell, which was very attractive because of its high theoretical specific energy (2600 Wh/kg) and attractive cell potential (~2.4 V). Significant problems with the solubility of polysulfides in the electrolyte, and the retention of liquid lithium in its current collector caused attention to be focused upon immobilization of lithium in the form of a solid alloy (of relatively high lithium activity) and the insolubilization of sulfur and polysulfides by using transition metal sulfides (which have a very low solubility). These measures cause a significant decrease in the specific energy of the cell and a moderate decrease in voltage, but a great increase in cell lifetime.

In principle there are many lithium alloys that can be used as the negative electrode, but only a few of them have an acceptable combination of low weight per electrochemical equivalent, low cost, ability to be recharged many times, high exchange current density, and high lithium diffusion coefficient. The alloys that have been investigated most are Li-Al and Li-Si.
**TABLE 5**

Na/Na$_2$O$\cdot$xAl$_2$O$_3$/SCl$_3$AlCl$_4$ in AlCl$_3$-NaCl \( T = 250^\circ C \)

\[
4\text{Na} + \text{SCl}_3\text{AlCl}_4 + 3\text{AlCl}_3 \rightarrow 4\text{NaCl} \cdot \text{AlCl}_3 + \text{S}
\]

\[ E = 4.2 \text{ V}; 563 \text{ Wh/kg Theoretical} \]

**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>45 @ 100% DOD</td>
</tr>
<tr>
<td>Cost</td>
<td>too early</td>
</tr>
</tbody>
</table>

**Recent Work**

- Larger cells - 4 Ah
- Less expensive current collectors

**Problems**

- Sodium wetting
- Vapor pressure
- Corrosion of metals and some electrolytes
- Electrolyte cracking
- Overcharge ?
Some recent work has been performed with Ca-Si and other calcium alloys.\(^{(21,22)}\)

The metal sulfides that have been investigated as positive electrodes include the iron sulfides, nickel sulfides, cobalt sulfides, copper sulfides, and molybdenum sulfide.\(^{(23)}\) The ones receiving the most emphasis are FeS and FeS\(_2\).

From the several negative and positive electrode materials indicated above, a long list of cells can be made, however only two of these have been receiving a significant amount of research and development effort. These are LiAl/LiCl-KCl/FeS, Li\(_4\)Si/LiCl-KCl/FeS\(_2\). Another system of interest is Ca\(_2\)Si/LiCl-NaCl-CaCl\(_2\)-BaCl\(_2\)/FeS\(_2\).

3.1 The Lithium-Aluminum/Lithium Chloride-Potassium Chloride/Iron Monosulfide Cell

This electrochemical system has shown itself to be very stable in operation, with relatively few serious operating and materials problems. The overall cell reaction is:

\[
2\text{LiAl} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe} + 2\text{Al} \tag{11}
\]

This cell is usually operated at 450°C, and exhibits a single voltage plateau near 1.3 V, as shown in the constant current discharge curves of Figure 8.\(^{(24)}\)

The overall reaction given above, and the single voltage plateau are, however, misleadingly simple. Detailed investigations of the phase transformations occurring during charge and discharge of the FeS electrode have led to the establishment of the phase diagram shown in Figure 9.\(^{(22)}\)

The dashed line C-D in Figure 9 shows the path followed by the composition of the FeS electrode from the fully charged condition (point C) to the fully discharged condition (point D). Starting at point C, as lithium is added to the FeS electrode by electrochemical reaction, two new phases, Li\(_2\)FeS\(_2\) and Fe, are formed:
FIGURE 8

CELL R-2
Li-Al/LIQKO/FeS
Positive Electrode Area = 278 cm²
Negative Electrode Area = 323 cm²
Cell Temperature = 450°C

LEGEND
• = 10 A - Discharge
○ = 15 A - Discharge
△ = 20 A - Discharge
+ = 30 A - Discharge

Cell Voltage, V

Cell Capacity, A-hr
A-B: Discharge path of FeS₂ electrode

\[ Z = Li_3Fe_2S_4 \]

\[ X = Li_2FeS_2 \]

X-W-Y = Solid solution field

C-D: Discharge path of FeS electrode
Additional discharge beyond the point where line C-D crosses the X-Fe line in Figure 9 results in a new phase, \( \text{Li}_2\text{S} \), being formed:

\[
2\text{FeS} + 2\text{Li} + \text{Li}_2\text{FeS}_2 + \text{Fe}
\]

Reactions 12 and 13 occur at essentially the same potential, near 1.6 V vs. reversible lithium, so the voltage vs. capacity curve for the discharge from point C to point D shows only one plateau.

Depending on the temperature of operation, and the composition of the LiCl-KCl electrolyte, another phase, called djerfischerite, may form, having the composition \( \text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl} \). This material tends to reduce the rate at which the recharge reactions can be carried out, hence its formation is undesirable. The extent of formation of \( \text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl} \) can be minimized by using an electrolyte that has more LiCl than the eutectic composition, and by operating at temperatures above 450°C.

The negative electrode for the LiAl/FeS cell is the intermetallic compound LiAl, which has a potential 0.3 V positive with respect to a reversible pure lithium electrode. The phase diagram of Figure 10 shows that there is a broad composition range (from 10% to 45% Li in Al) over which there is a two-phase mixture (\( \beta+\alpha \)), yielding a single voltage plateau (0.3 V vs. reversible Li). This feature makes the Li-Al electrode attractive.

Lithium/iron monosulfide cells of various designs have been constructed and tested. A multiplate cell with two positive (FeS) and three negative (LiAl) electrodes is shown in Figure 11. The electrodes for such cells may be prepared by various techniques, including cold or hot pressing of mixed powders of reactant and electrolyte (with or without a current collector powder such as graphite for the FeS added), or by using a conductive carbon cement (the so-called carbon bonded structure). Various
(\(\alpha = \text{Al}, \beta = \text{LiAl}, \gamma = \text{Li}_3\text{Al}_2, \delta = \delta' = \text{Li}_9\text{Al}_4\))

XBL 801-7726
FIGURE 11

- FEEDTHROUGH
- POSITIVE CURRENT COLLECTOR
- STRAP
- CERAMIC BAR
- INSULATION STRIP
- CELL CAN
- RETAINER
- COVER
- POSITIVE PLAQUE
- SEPARATOR
- NEGATIVE WITH METAL FRAME

XBL 802-8073
additives to the FeS electrode have been used to improve the utilization and current collection, including Cu₂S (about 6 m/o). The current collectors are made of corrosion-resistant metals such as iron, iron alloys, stainless steels, etc. The electrolyte is soaked into a porous boron nitride mat, which may be a woven cloth or a felt. The boron nitride is not readily wetted by the LiCl-KCl electrolyte. Wettability is improved by the addition of LiAlCl₄ to the BN mat (~20 mg/cm²).

Cells of the general multiplate type described above have been evaluated with regard to performance and lifetime. Figure 12(27) shows the specific energy vs. cycle number data of some 300 Ah cells designed for use in electric vehicles. Specific energies near 100 Wh/kg were achieved early in life (vs. 458 Wh/kg theoretical). Cycle lives of over 300 were achieved before 40% of the initial specific energy was lost.

Failure modes for these cells include shorting due to active material from the positive electrode extruding through openings in the structure, and touching the negative electrode. The gradual loss of capacity is to some degree associated with morphological changes in the Li-Al alloy (an agglomeration of the initially finely divided structure).

Cells of the multiplate type (300 Ah) have been assembled into batteries, including a module for a fork-lift truck, and 20 kWh modules for electric van testing. Initial results for the 10 cell* fork-lift battery are shown in Figure 13. (27) The 20 kWh modules have had start-up problems; more will be tested. Experience with batteries and their thermal control is needed very much.

Table 6 summarizes the status of the LiAl/FeS cell. The current problems include a relatively low specific energy, internal cell shorting and

*Two parallel strings of 5 ladder-connected cells.
TABLE 6

LiAl/LiCl-KCl/FeS

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

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

<table>
<thead>
<tr>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Size</td>
</tr>
<tr>
<td>Specific Energy</td>
</tr>
<tr>
<td>Specific Power</td>
</tr>
<tr>
<td>Cycle Life</td>
</tr>
<tr>
<td>Lifetime</td>
</tr>
<tr>
<td>Cost</td>
</tr>
</tbody>
</table>

Recent Work

- Multielectrode cells
- LiCl-rich electrolyte
- BN felt separators
- Batteries of 320 Ah cells
- Charging equipment

Problems

- Low specific energy
- Low voltage per cell
- Cell shorting major failure made
- Electrolyte leakage
- Agglomeration of Li-Al with cycling
- High separator cost
- Leak-free feedthroughs
- Thermal control
FIGURE 12

TEMPERATURE RANGE 450-475°C
DISCHARGE VOLTAGE CUTOFF RANGE 0.89-0.94V
CHARGE VOLTAGE CUTOFF RANGE 1.57-1.62V
DISCHARGE CURRENT RANGE 50-71A

SPECIFIC ENERGY, W-hr/kg

No. OF CYCLES

XBL 801-7729
high cost of BN separators. Sufficient promise has been shown by the results that industrial organizations are constructing pilot quantities of cells for testing and demonstration, under government sponsorship. This system may be the first to achieve commercial status among the rechargeable cells with molten salt electrolyte.

3.2 The Lithium-Silicon/Lithium Chloride-Potassium Chloride/Iron Disulfide Cell

This electrochemical cell is very closely related to the one described immediately above and operates at the same temperature (450°C). The main difference is that both the positive and the negative electrode reactants have significantly lower weights per electrochemical equivalent than those of the LiAl/FeS cell. The theoretical specific energy is 944 Wh/kg vs. 458 Wh/kg. The overall cell reaction is:

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

Reaction 14 actually takes place in stages, as indicated by the path A-Z-X-B in Figure 9. Starting at point A, representing the fully-charged positive electrode, FeS\textsubscript{2} reacts with lithium as follows:

\[ 2\text{FeS}_2 + 3\text{Li} \rightarrow \text{Li}_3\text{Fe}_2\text{S}_4 \quad E=2.04 \text{ V} \] (15)

This is followed by a reaction involving only a few percent (~4.5%) of the total charge of Reaction 14:

\[ \text{Li}_3\text{Fe}_2\text{S}_4 + \text{Li} \rightarrow \text{Fe}_{1-x} + \text{W-phase} \quad E=1.9 \text{ V} \] (16)

Reaction 16 is not balanced; its meaning is best seen by examination of Figure 9. W-phase is a solid solution having the composition range shown in Figure 9. The next stage of reaction also involves only a small portion (~8.25%) of the charge associated with Reaction 14:

\[ \text{Fe}_{1-x}\text{S} + \text{W} + \text{Li} \rightarrow \text{Li}_2\text{FeS}_2 \quad E=1.9-1.64 \text{ V} \] (17)

The final step is:
Note that out of an overall 8-electron process for Reactions 15 through 18, only one electron is associated with the sum of Reactions 16 and 17. The reaction scheme above, proposed by Tomczuk and Martin (27) is based upon extensive phase diagram work, voltage sweep experiments, and metallographic work on electrodes operated under well controlled conditions, as well as electrodes from engineering cells.

The negative electrode, Li-Si, operates according to the phase diagram of Figure 14. (20) This electrode is operated between the extremes of silicon and Li₄Si. The phases encountered at 450°C are: Si, Li₂Si, Li₂₁Si₈, Li₁₅Si₄, and Li₂₂Si₅, and the voltage plateaus (vs. reversible lithium) are given in Table 7. (20)

It is obvious that the combination of the FeS₂ electrode with two major plateaus and the Li-Si electrode with perhaps three major plateaus will yield a complex voltage vs. capacity curve for the complete cell showing several plateaus.

A cross-section of a typical light-weight development cell using Li₄Si and FeS₂ electrodes is shown in Figure 15. (23) This cell is in the form of a circular disc, with a central positive electrode, and two negative electrodes. The electrodes are separated by a BN cloth or felt. The electrodes may be prepared by various techniques, including pressing of powder mixtures into the desired shapes. The specific energy vs. specific power curves for two cells of this type are shown in Figure 16. (23) Note that specific energies above 180 Wh/kg have been achieved at low specific power, and that specific powers up to about 100 W/kg have been demonstrated also. This is in contrast to the lower specific energy of the LiAl/FeS cell (~100 W/kg).

Life testing of Li₄Si/FeS₂ cells has shown that cycle lives of 700
TABLE 7

EMF Values for the Li-Si Electrode at 725°K

<table>
<thead>
<tr>
<th>Phases in Equilibrium</th>
<th>EMF vs. Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Li$_2$Si</td>
<td>0.326</td>
</tr>
<tr>
<td>Li$<em>2$Si-Li$</em>{21}$Si$_8$</td>
<td>0.277</td>
</tr>
<tr>
<td>Li$_{21}$Si$<em>8$-Li$</em>{15}$Si$_4$</td>
<td>0.149</td>
</tr>
<tr>
<td>Li$_{15}$Si$<em>4$-Li$</em>{22}$Si$_5$</td>
<td>0.042</td>
</tr>
<tr>
<td>Li$_{22}$Si$_5$-Li (Sat. with Si)</td>
<td>0.001</td>
</tr>
</tbody>
</table>
FIGURE 14

- Federov & Ioffe
- Böhm
- Obinata, et al.
- Present Data

Temperature (K)

453 ± 2K
789 ± 5K
813 ± 5K
906 ± 5K
908 ± 5K

39.4 ± 0.5 at. %

Atom Percent Silicon

Li

XBL 801-7727
cycles and lifetimes of over 15,000 h can be achieved (see Figure 17). Even though good progress has been made in developing long-lived, high specific energy Li₄Si/FeS₂ cells, there are some significant problems requiring additional effort, as indicated in Table 8.

This cell has somewhat more severe materials problems than the LiAl/FeS cell, because the FeS₂ electrode presents a higher sulfur activity to the current collector, narrowing the selection of current collector materials. Presently, molybdenum is used in conjunction with graphite powder. There is some degree of concern with the formation of slightly-soluble sulfur-containing species which can migrate gradually through the electrolyte toward the negative electrode. A full assessment of this problem has not been completed. In any event, the performance and lifetime data reported are encouraging.

The Li₄Si/FeS₂ cell is in an earlier stage of development than the Na/S or LiAl/FeS cells, but it is clear that the main problems have to do with materials, as is the case for those other cells. Electrochemical kinetics and transport processes are sufficiently rapid in all of these systems that rate processes, properly taken into account in the designs, will not present formidable barriers to the development of cells with performance capabilities appropriate for such applications as vehicle propulsion and off-peak energy storage.

3.3 The Calcium-Silicon/Molten Halide/Iron Disulfide Cell

An interesting variant of the cell just described is obtained by replacing the lithium with calcium. The negative electrode becomes a calcium-silicon alloy, which can be operated over the range Ca₂Si to at least CaSi₂. The electrolyte must contain calcium ions, of course, and the most effective electrolyte investigated is a mixture of 29% LiCl-20% NaCl-35% CaCl₂-16% BaCl₂,
TABLE 8

Li₄Si/LiCl-KCl/FeS₂
Li₄Si + FeS₂ → 2Li₂S + Fe + Si
E = 1.8, 1.3 V; 944 Wh/kg Theoretical

<table>
<thead>
<tr>
<th>Status</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Size</td>
<td>70 Ah</td>
</tr>
<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>~15,000 h</td>
</tr>
<tr>
<td>Cost</td>
<td>&gt;$1000/kWh</td>
</tr>
</tbody>
</table>

Recent Work

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

Problems

- Materials for FeS₂ current collector
- Leak-free feedthroughs
- High internal resistance
- Low-cost separators needed
- Thermal control
Cells similar in structure to LiAl/FeS and Li4Si/FeS2 cells have been operated, but only at low current densities. A cell voltage vs. capacity curve for a 100 Ah cell is shown in Figure 18.27 The voltage range over which this cell operates is similar to that for Li4Si/FeS2, and there is the possible advantage of being able to use the more abundant, lower-cost calcium instead of lithium.

The status of the work on this system is shown in Table 9. Note the low specific power and specific energy. These need improvement in order to make this system sufficiently interesting to work on extending the life to significantly longer values. Successful improvement in the cell performance and lifetime could yield a system of significant practical interest.

4. CONCLUSIONS

The discussion above, regarding various types of high-temperature cells in all stages of research and development, leads to the following conclusions:

• Sodium/sulfur cells with ceramic electrolytes (β- and β"-Al2O3) are in the most advanced state of development. Several more multi-kilowatt-hour batteries will be developed and tested, both in Europe, and in the U.S., during the early 1980's. These batteries may find application in vehicle propulsion and stationary energy storage. Thermal cycling remains a problem.

• Variants of the Na/S cell, such as the Na/SCl3AlCl4 cell may have advantages in certain applications where lower operating temperatures and higher cell voltages are important. This cell is still in research stages.

• Lithium alloy/iron sulfide cells are making good progress in both lifetime and performance. Full-scale cells are being tested, and...
TABLE 9

Ca$_2$Si/LiCl-NaCl-CaCl$_2$-BaCl$_2$/FeS$_2$

Ca$_2$Si + FeS$_2$ $\rightarrow$ 2CaS + Fe + Si

E = 2.0-1.2 V; $\sim$750 Wh/kg Theoretical

<table>
<thead>
<tr>
<th>Status</th>
<th>Specific Energy</th>
<th>Specific Power</th>
<th>Cycle Life</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 Wh/kg @ 8 W/kg</td>
<td>&lt;10 W/kg</td>
<td>60</td>
<td>too early</td>
</tr>
</tbody>
</table>

Recent Work

- BaCl$_2$ added to electrolyte
- Larger cells - 100 Ah

Problems

- Low specific power
- Low current densities
FIGURE 18

CELL CA-16
Ca$_2$Si/LiCl-NaCl-CaCl$_2$-BaCl$_2$/FeS$_2$
T-460°C
I-5A

CELL VOLTAGE, V

0 20 40 60 80 100
A-hr DISCHARGED

Ca$_2$Si/FeS$_2$
CaSi/FeS$_2$
CaSi/FeS
CaSi$_2$/FeS

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multi-kilowatt hour batteries will be tested in the early 1980's. These systems appear to have promise of being rugged and capable of thermal cycling.

- The calcium-silicon/iron disulfide system may offer a lower-cost option than lithium alloy/iron sulfide cells. This cell is in early stages of R&D.

- Overall, the pace-setting problems for high-temperature batteries are materials and materials-related problems. Major problem areas include sulfur and sulfide-resistant current collectors, corrosion resistant seals and feedthroughs, rugged solid electrolytes, including lithium ion conductors, and alkali metal resistant insulators.

The progress in the research and development of high temperature rechargeable cells and batteries in the last decade has been remarkably good. There are at least a few systems among which to choose, and at last performances and cycle lives greater than those for many, if not all high performance ambient-temperature systems are being realized. These systems have come a long way. Will they be made available commercially in the next decade? The probability is getting higher!
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Utility Application (May 16, 1979).


15. E. J. Cairns, J. P. Ackerman, P. D. Hunt, and B. S. Tani, The Thermodynamics and Electrochemistry of the Lithium/Sulfur Cell by EMF and Phase Equilibration Methods, presented at The Electrochemical Society Meeting, Cleveland, Ohio, Abstract No. 48 (October, 1971); See also Extended Abstracts, p. 118.


27. Argonne National Laboratory, Annual DOE Review of the Lithium/Metal Sulfide Battery Program (June, 1979).

FIGURE CAPTIONS

Figure 1  Theoretical specific energy (W-h/kg) for various electrochemical couples plotted against the sum of the molecular weights of the reactants times the number of moles of each involved in the balanced cell reaction. The straight lines are iso-EMF lines. A good approximation to practical specific energies is obtained by multiplying the values in the figure by 0.2-0.25 for couples with solid reactants, and 0.15-0.2 if gaseous reactants are involved.

Figure 2  Cross section of a sodium/beta-alumina/sulfur cell, using the sodium-core design.

Figure 3  The sodium-sulfur phase diagram, after Gupta and Tischer.\(^1\)

Figure 4  The reversible emf of the sodium/sulfur cell as a function of the sulfur electrode composition.\(^1\)

Figure 5  Exploded view of a 168 Ah sodium/sulfur cell of the sodium-core design.\(^7\)

Figure 6  Voltage-current curve of a 96-cell, 10 kWh sodium/sulfur battery.\(^8\) The cells were connected as four parallel strings of 24 cells each, with cross-connections between strings every 8 cells. Each cell was nominally 48 Ah. The battery yielded 177 Ah, with an energy efficiency of 61%.

Figure 7  Schematic cross section of the hollow glass fiber sodium/sulfur cell.\(^9\)

Figure 8  Voltage-capacity curve for a LiAl/FeS cell.\(^{24}\)

Figure 9  Isothermal section of the Li-Fe-S phase diagram at 450°C.\(^{22}\)

Figure 10  The lithium-aluminum phase diagram.\(^{26}\)
Figure 11  Multiplate LiAl/FeS cell design. (23)

Figure 12  Specific energy vs. cycle number for 300 Ah LiAl/FeS cells. (27)

Figure 13  Voltage vs. capacity curve for a 10-cell Li/AlFeS$_2$ battery, connected as two parallel strings, five cells each, with cross connections at each cell. (27)

Figure 14  The Lithium-Silicon phase diagram. (20)

Figure 15  Cross-section of a disc-shaped Li$_4$Si/FeS$_2$ cell, having about 70 Ah capacity. (28)

Figure 16  Specific power vs. specific energy curves for Li$_4$Si/FeS$_2$ cells. (28)

Figure 17  Specific energy vs. operating time curves for LiAl/FeS$_2$ and Li$_4$Si/FeS$_2$ cells. (28)

Figure 18  Voltage vs. capacity curve for a 100 Ah Ca$_2$Si/FeS$_2$ cell, operating at 460°C. (27)