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THEIR APPLICATIONS

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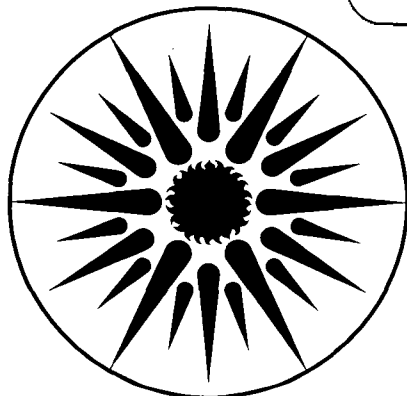
**ENERGY
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HIGH SPECIFIC ENERGY SECONDARY BATTERIES AND THEIR APPLICATIONS

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to be presented at

HIGH SPECIFIC ENERGY SECONDARY BATTERIES AND THEIR APPLICATIONS

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INTRODUCTION

The electronics and computer industries are enhanced by the availability of secondary (rechargeable) batteries, which can increase the attractiveness and capabilities of their products. Rechargeable batteries can provide for portability of many electronic devices, and can provide continuous (uninterrupted) electrical power in the event of a utility power failure. There are many different types of rechargeable batteries. Several are available now in the marketplace, others are in various stages of research and development. The characteristics of the many rechargeable cells are highly varied, making it useful to provide information on those systems available now, and what may be developed in the future.

In order to simplify the discussion, it is appropriate to classify rechargeable cells according to the type of electrolyte used, and the temperature of operation. Table 1 shows the classifications, and examples of cells in each classification.

Table 1. Classifications of Batteries

	Ambient Temperature	High Temperature (>200°C)
Aqueous Electrolyte	$Pb/H_2SO_4/PbO_2$ $Zn/KOH/NiOOH$	none
Non-aqueous Electrolyte	$Li/LiClO_4$ in Dioxolane/TiS_2	$Na/Na_2O \cdot 11Al_2O_3/S$ $Li_4Si/LiCl-KCl/FeS_2$

In general, electrochemists searching for new electrochemical couples to be used as rechargeable batteries take into consideration a number of guidelines.[1] Two of the main guidelines are those of electronegativity and equivalent weight. Elements of low electronegativity are selected as reactants for the negative electrodes because they readily give up electrons; correspondingly, elements of high electronegativity (and their compounds) are selected as reactants for the positive electrodes because they have a strong affinity for electrons. A large electronegativity difference between the electrodes corresponds to a large cell voltage. The elements of low electronegativity are found on the left-hand side of the periodic chart of the elements; those having high electronegativity are found on the right-hand side of the periodic chart. In many applications, the weight of the battery is to be minimized. This calls for the use of low-equivalent-weight reactants, which are found at the top of the periodic chart. These simple guidelines focus attention on such elements as H, Li, Na, Be, and Mg for the negative electrode, and O, S, F, and Cl for the positive electrode. Other considerations and compromises result in the use of heavier metals such as Zn, Cd, and Pb as the negative electrode in some cells, and various oxygen-or sulfur-containing compounds such as NiOOH, PbO_2, AgO, FeS_2 and TiS_2 as the positive electrode reactant.

Of course, the electrode materials selected for use in a cell must be compatible with the chosen electrolyte. For example, Li and Na react with water, so they must be used with non-aqueous electrolytes. Some of the results of selecting compatible electrodes and electrolytes are summarized

in Table 2, which lists a number of rechargeable cells, their voltages, theoretical specific energies, and overall reactions. The theoretical specific energies were calculated using the overall reactions and cell voltages shown in Table 2. Practical specific energies obtained from real cells are 20 to 25 percent of the theoretical values given in Table 2 (see below).

In the next section, the state of development, problems, and possible applications will be discussed for a number of rechargeable cells.

Table 2. Some Rechargeable Cells

Cell	Voltage	Theoretical Specific Energy Wh/kg	Overall Reaction
Ambient-Temperature, Aqueous:			
$Pb/H_2SO_4/PbO_2$	2.095	175	$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$
$Cd/KOH/NiOOH$	1.3	210	$Cd + 2NiOOH + 2H_2O \rightleftharpoons Cd(OH)_2 + 2Ni(OH)_2$
$Fe/KOH/NiOOH$	1.37	267	$Fe + 2NiOOH + 2H_2O \rightleftharpoons Fe(OH)_2 + 2Ni(OH)_2$
$Zn/KOH/NiOOH$	1.73	326	$Zn + 2NiOOH + H_2O \rightleftharpoons ZnO + 2Ni(OH)_2$
$H_2/KOH/NiOOH$	1.3	380	$H_2 + 2NiOOH \rightleftharpoons 2Ni(OH)_2$
$Zn/ZnCl_2/Cl_2 \cdot 8H_2O$	2.12	461	$Zn + Cl_2 \cdot 8H_2O \rightleftharpoons ZnCl_2 + 8H_2O$
$Zn/ZnBr_2/Br_2$	1.8	430*	$Zn + Br_2 \cdot Q \rightleftharpoons ZnBr_2 + Q$
High-Temperature, Non-aqueous:			
$Na/Na_2O \cdot 11Al_2O_3/S$ (350°C)	2.1–1.75	758	$2Na + 3S \rightleftharpoons Na_2S_3$
$Li_4Si/LiCl-KCl/FeS_2$ (450°C)	1.8–1.3	944	$Li_4Si + FeS_2 \rightleftharpoons 2Li_2S + Fe + Si$
Ambient-Temperature, Non-aqueous:			
$Li/LiClO_4$ in Dioxolane/TiS_2	2.2 (avg)	490	$Li + TiS_2 \rightleftharpoons LiTiS_2$

*The weight of the complexing agent Q is not included.

STATUS OF ADVANCED RECHARGEABLE BATTERIES

The Lead/Lead Dioxide Cell.

This cell, also known as the lead-acid cell, is usually taken as the standard of comparison for rechargeable cells because it has been available for a long time, is well known, and is the most widely used rechargeable cell, by a considerable margin. The lead-acid cell is available in a wide range of sizes, from about one ampere-hour to thousands of ampere-hours. Another paper in this conference discusses this cell in detail, so it is brought in here primarily as a basis for comparison of the other cells discussed below. Table 3 summarizes the pertinent information on this system.[2]

Recent advances in the development of lead-acid cells include the development of completely sealed cells for applications such as portable tools and

appliances, and some portable electronics uses. Larger cells and batteries are used for uninterruptable and emergency power supplies for computers and other electronic equipment. Lead-acid cells are particularly well suited to stand-by applications when kept in the fully-charged state. They should not be used when long stand periods in the discharged state are necessary. For some applications, a major disadvantage is the large weight per unit of energy stored. A significant advantage is the cost effectiveness in many applications.

Table 3. Summary of $Pb/H_2SO_4/PbO_2$ Cell

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

$$E = 2.095 \text{ V}; \ 175 \text{ W·h/kg Theoretical}$$

Status

Specific Energy	30-40 W·h/kg @ 10 W/kg
Specific Power	50-100 W/kg @ 10 W·h/kg
Cycle Life	400+ @ 10 W/kg, 70% DOD
Cost	$50-150/kWh

Recent Work

Replace Sb with Ca in positive current collector
Maintenance-free cells
Use $4PbO·PbSO_4$ instead of $PbO + Pb_3O_4$ in positives
Redesign of current collectors for low resistance
Small sealed cells
Circulating electrolyte for EV cells

Problems

Sealing of large cells
Positive current collector corrosion
Cohesion and adhesion of PbO_2
High internal resistance
Heavy

The Cadmium/Nickel Oxide Cell.

This cell is very widely used in many applications, especially in portable systems such as communications equipment, portable appliances, aerospace power systems, and others in which long cycle life, ruggedness, and high reliability are important. The cadmium/nickel oxide cell is more widely used than any other rechargeable cell, except lead-acid. The overall cell reaction is shown in Table 4. The electrodes are based upon a porous, sintered metal matrix, and are therefore very rugged. The electrolyte is a concentrated aqueous solution of KOH ($\sim$30 w/o).

Both the cadmium electrode and the nickel oxide electrode are well-behaved; the oxidized and reduced forms of both electrodes are essentially in-soluble in the electrolyte, and their electrochemical reactions are rapid, with very little tendency toward undesired side-reactions. This behavior results in the ability to construct cells that can be discharged and recharged thousands of times before failure.

Emphasis on light-weight cells for space applications has yielded cells that have specific energies of 40 Wh/kg, and somewhat higher, at a high cost. The peak specific power of Cd/NiOOH cells can be hundreds of watts per kilogram of cell weight, because of the high-conductivity sintered-metal electrodes, and close electrode spacing. The use of improved, porous separators permits sealed operation, because oxygen produced at the NiOOH electrode during recharge can diffuse rapidly through the separator to react with the

3

cadmium. Recent work on the NiOOH electrode to reduce the tendency to swell after being cycled is providing for even longer cycle lives.

The problems that prevent wider application of Cd/NiOOH cells include the relatively low specific energy (traceable to the low cell voltage and the high equivalent weights of the electrodes), and the high cost of cad-

mium (a relatively rare element in the earth's crust). Another feature that limits the utility of this cell is the low recharge efficiency of the nickel oxide electrode at elevated temperatures (e.g. 50°C). Instead of converting $Ni(OH)_2$ to NiOOH, the recharge current is consumed by the oxygen evolution reaction ($2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$). Table 4 summarizes the information for this cell.[3,4]

Table 4. Summary of Cd/KOH/NiOOH Cell

$$Cd + 2NiOOH + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$$

$$E = 1.3 \text{ V}; \ 210 \text{ Wh/kg Theoretical}$$

Status

Specific Energy	25-40 Wh/kg
Specific Power	100+ W/kg
Cycle Life	500-5000 @ 100% DOD
Cost	>$1000/kWh

Recent Work

Lightweight sealed cells
Improved NiOOH electrodes
Improved separators

Problems

Low specific energy
Expensive (Cd)
Low cell voltage
Poor charge acceptance above 50°C

The Hydrogen/Nickel Oxide Cell.

A relatively recent development which significantly increases the specific energy to about 60 Wh/kg is the hydrogen/nickel oxide cell. Here, the heavy cadmium electrode is replaced by a light-weight hydrogen fuel-cell electrode. The cell voltage is 1.3 V, the same as for the Cd/NiOOH cell. Since the reactant at the negative electrode is hydrogen gas, a leak-tight storage arrangement is necessary. In most designs, the hydrogen is stored as a pressurized gas in the cell case. Storage of hydrogen as a metal hydride is also being investigated, but this usually decreases the specific energy because of the added weight of the metal reactant.

Space power systems have been the main area of application for H_2/NiOOH cells, because of the fact that this

cell has an extremely long cycle life, making it very desirable, and because its high cost (~$10,000/kWh) makes it prohibitively expensive for most other applications. Lower-cost versions could find other specialty applications.

The fact that the hydrogen pressure in the cell is an accurate state-of-charge indicator enhances its attractiveness. Also, this cell is electrochemically very robust, and is able to tolerate extensive overcharge and overdischarge. Table 5 gives a summary of information on the H_2/NiOOH cell.[5,6]

The Iron/Nickel Oxide Cell.

This electrochemical cell has existed in various designs for a long time; it has been known as the Edison cell, and has been used in a number of

heavy-duty applications such as electric vehicles, and stationary stand-by power. The overall reaction is shown in Table 6, along with the cell voltage and theoretical specific energy. This cell is very robust, and is able to tolerate extensive overcharge and overdischarge without permanent damage. It can also be left standing fully discharged without harm.

Table 5. Summary of H_2/KOH/NiOOH Cell

$$H_2 + 2NiOOH \rightarrow 2Ni(OH)_2$$

$$E = 1.3 \text{ V}; \ 380 \text{ W·h/kg Theoretical}$$

Status

Specific Energy	60 W·h/kg @ 20 W/kg
Specific Power	60 W/kg @ ~50 W·h/kg
Cycle Life	1000-2000 @ 20 W/kg, 60% DOD
Cost	~$10,000/kWh

Recent Work

Life tests of separators
AgO electrodes being evaluated
Metal hydrides

Problems

Bulky
Expensive
High self-discharge rate (50% in 8 days)

Table 6. Summary of Fe/KOH/NiOOH Cell

$$Fe + 2NiOOH + 2H_2O \rightarrow Fe(OH)_2 + 2Ni(OH)_2$$

$$E = 1.370 \text{ V}; \ 267 \text{ W·h/kg Theoretical}$$

Status

Specific Energy	40-50 W·h/kg @ 10 W/kg
Specific Power	50-100 W/kg @ 10 W·h/kg
Cycle Life	300-600 @ 10-25 W/kg, 80% DOD
Cost	>$100/kW·h

Recent Work

Improved Fe and NiOOH electrodes
200-300 Ah cells and modules
Vehicle-size batteries

Problems

H_2 evolution during recharge; can't be sealed
Heat evolution
Low efficiency ~60%
Capacity loss at low temperature

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In recent years, there have been efforts to increase the specific energy and specific power, and decrease the cost without sacrifice of cycle life. The result has been specific energy values up to about 50 W-h/kg, and peak specific power values near 100 W/kg. The cost of the Fe/NiOOH cell, although reduced, is still high compared to that of Pb/PbO$_2$. The efficiency of this cell is low (about 60%), owing to hydrogen evolution at the Fe electrode during recharge. This hydrogen also presents a safety problem, and results in the need for water addition (costly maintenance).

Applications for the Fe/NiOOH cell in the electronics field are probably restricted to those of larger energy requirements (>1 kWh), such as power supplies for stationary equipment or large transportable equipment. Depending on the application, there may be a cost advantage over Cd/NiOOH. Table 6 summarizes the current information for the Fe/NiOOH cell.[7,8]

The Zinc/Nickel Oxide Cell.

This cell is a close relative of the Cd/NiOOH and Fe/NiOOH cells. It has the advantage of a higher specific energy, and lower cost, but suffers from a short cycle life. The Zn/NiOOH cell can be sealed, so is compatible with various electronics applications. It has been tested in various sizes from less than 1 Ah to at least 400 Ah. Because of its relatively high specific energy (60-80 Wh/kg vs. 30-40 for Pb/PbO$_2$), the Zn/NiOOH cell is attractive for use in portable electronic equipment and portable appliances. Other possible applications include electric vehicles and aerospace power.

The short cycle life of the Zn/NiOOH cell is caused by failure of the zinc electrode. This electrode can fail as a result of dendrite formation (which can short-circuit the cell), passivation, densification, or zinc redistribution. During the last several years, the severity of these problems has been reduced, but the problems have not been eliminated. As shown in Table 7, cycle lives of 100-300 have been achieved at 80% depth of discharge. For widespread application, it is likely that a minimum cycle life of 300 will be required. This is probably an achievable goal, but more research and development will be required. Current research on the zinc electrode includes the study of the effect of heavy-metal additions (e.g. Cd, Pb, In) on the rates of hydrogen evolution and zinc

Table 7. Summary of Zn/KOH/NiOOH Cell

$$Zn + 2NiOOH + H_2O \rightarrow ZnO + 2Ni(OH)_2$$

$$E = 1.735 \text{ V}; \ 326 \text{ W·h/kg Theoretical}$$

Status

Specific Energy	60-75 W·h/kg @ 30 W/kg
Specific Power	100-150 W/kg @ 35 W·h/kg
Cycle Life	100-300 @ 25-50 W/kg, 80% DOD
Cost	>$100/kW·h

Recent Work

Microporous separators
Sealed cells
Non-sintered electrodes
Modified Zn electrodes
100-400 Ah cells and modules
Modified charging methods

Problems

Sealing of cells - O$_2$ evolution and recombination
Zn redistribution
Separators

6

redistribution, the effect of alkaline-earth hydroxides on zincate solubility, and the effect of modified charging methods on zinc morphology. All of these investigations have the goal of increasing the cycle life of the zinc electrode.

In the sealing of Zn/NiOOH cells, it is necessary to provide for the recombination of the oxygen evolved at the NiOOH electrode during recharge. This is done by providing access to the Zn electrode, so that the $Zn + \frac{1}{2}O_2 \rightarrow ZnO$ reaction can take place. Hydrogen evolution is more difficult to accommodate, and therefore is avoided by the use of high-hydrogen-overvoltage metals added to the zinc electrode (1-2 w/o). See Table 7 for a summary of Zn/NiOOH work.[9,10]

The Zinc/Silver Oxide Cell.

The zinc/silver oxide cell is a close relative of the zinc/nickel oxide cell, but it has a higher specific energy. The cycle life is similar to that for the Zn/NiOOH cell because the zinc electrode is the life-limiting component. Because of the high cost of silver and short cycle life, this cell has been used primarily in applications that absolutely require a specific energy near 100 Wh/kg. These are primarily military (e.g. communications) and aerospace applications.

The improvements that have been made in the zinc electrode and separators for the Zn/NiOOH cell are applicable to the Zn/AgO cell, so both systems are advancing at about the same rate. Table 8 summarizes the current situation for the Zn/AgO cell.[11,12]

The Zinc/Halogen Cells.

Zinc/halogen cells (Zn/Cl_2, Zn/Br_2) make use of flowing electrolytes to carry halogen/halide to and from the positive electrode. This feature makes these systems less versatile than those discussed above, because it is not practical to construct flowing-electrolyte systems in sizes smaller than about 1 kWh. Therefore, these cells are limited to applications that require relatively large power sources, such as stand-by power, power for remote systems or stand-alone systems, etc.

Zinc/halogen cells operate as follows: At the start of discharge, there is a full zinc deposit on the graphite negative electrode, and a fully-charged storage container of halogen ($Cl_2 \cdot 8H_2O$, an ice-like material, or $Q \cdot Br_n$, an organic oily liquid). Halogen from the storage area is carried by the flowing electrolyte to graphite positive electrodes in the cells, where it is reduced to form halide ions, which are soluble in the aqueous electrolyte. The zinc electrode reacts to form zinc ions which are also soluble in the electrolyte. At the end of discharge, all of the halogen has been converted to halide, and all of the zinc metal has been converted to zinc ions in the electrolyte. During recharge, these processes are reversed.

Table 8. Summary of Zn/KOH/AgO Cell

$$Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Ag$$

$$E = 1.86\text{-}1.55 \text{ V}; \ 434 \text{ Wh/kg Theoretical}$$

Status

Specific Energy	80-100 Wh/kg
Specific Power	100+ W/kg peak
Cycle Life	50-150
Cost	>$1000/kWh

Recent Work

Improved separators
Improved AgO electrodes
Modifications to the zinc electrode

Problems

High cost
Short cycle life

The performance figures which have been achieved by Zn/Cl_2[13] and Zn/Br_2[14,15] systems are given in Tables 9 and 10, respectively. The efficiencies for these systems are relatively low (60-70%) because of migration of halogen to the zinc electrode with direct chemical reaction, hydrogen evolution, and parasitic power requirements. Specific power tends to be low because the zinc halide electrolyte has a relatively high resistivity. In order to minimize dendrite formation during recharge, it is necessary to remove all of the zinc (complete discharge) every cycle or every few cycles. A potential advantage of zinc/halogen cells is

Table 9.   Summary of $Zn/ZnCl_2/Cl_2 \cdot 8H_2O$ Cell

$$Zn + Cl_2 \cdot 8H_2O \rightarrow ZnCl_2 + 8H_2O$$

$$E = 2.12 \text{ V}; \quad 405 \text{ W} \cdot \text{h/kg Theoretical}$$

Status

    Specific Energy   66+ W·h/kg @ 3-4 W/kg
    Specific Power   70 W/kg for seconds
    Cycle Life   1400*
    Cost   >$100/kW·h

Recent Work

    Additives for Zn deposition
    Recombination of H_2 and Cl_2
    35-50 kWh systems
    Systems components

Problems

    Complete discharge required
    Bulky
    Complex
    Low specific power
    Very sensitive to impurities
    Low efficiency

*1 kWh system only, with electrolyte maintenance

Table 10.   Summary of $Zn/ZnBr_2/Br_2$ Cell

$$Zn + Br_2 \rightarrow ZnBr_2$$

$$E = 1.85 \text{ V}; \quad 430 \text{ W} \cdot \text{h/kg Theoretical}$$

Status

    Specific Energy   40-60 Wh/kg @ 5-10 W/kg
    Specific Power   30-70 W/kg
    Cycle Life   700 @ 90-100% DOD
    Cost   >$100/kWh

Recent Work

    Prototype 2-20 kWh batteries
    Complexing of bromide
    Bipolar cell modules

Problems

    Complete Zn discharge required every few cycles
    Complex system - flowing electrolyte
    Low efficiency - 60-70%
    High self-discharge rate
    Poor Zn adherence; dendrites
    Recharge of Br_2 electrode

their low projected cost. The materials of construction (carbon, graphite, polymers) and the reactants are both very inexpensive. These cells are not yet commercially available.

The Lithium/Titanium Disulfide Cell.

Cells using alkali metals such as lithium or sodium as the negative electrode require the absence of air and water. Therefore, non-aqueous electrolytes and hermetic seals are required. These inconveniences are accepted because alkali metal electrodes permit high specific energies to be achieved (100-200 Wh/kg). The Li/TiS$_2$ cell with an electrolyte of LiClO$_4$ in dioxolane is an example of one system among several that are being investigated as rechargeable, ambient-temperature non-aqueous cells. The advantages and problems with this system are typical of many non-aqueous, ambient-temperature cells.

Table 11 shows that specific energies above 100 Wh/kg are probably feasible. There are several significant problems with this class of cells.

Lithium is not thermodynamically stable in contact with any organic solvent, so there is always a question about safety. Small concentrations of water or oxygen as impurities can cause the formation of a passivating film on the surface of the lithium. Films also form as a result of reaction between lithium and the solvent. As the lithium electrode is charged and discharged, parts of the lithium are isolated by the films, and are rendered inactive, leading to failure of the electrode.

Reactants for the positive electrode also present problems: they should have a low equivalent weight, and take part in reversible reactions with lithium. Titanium disulfide is interesting because its layered structure permits lithium to move easily into the spaces between the layers, forming an intercalation compound, LiTiS$_2$. Other candidate reactants for the positive electrode include V$_2$O$_5$, V$_6$O$_{13}$, WO$_2$, WO$_3$, and TiO$_2$.

Rechargeable, ambient-temperature lithium cells is an active area of

Table 11. Summary of Li/LiClO$_4$ in Dioxolane/TiS$_2$ Cell

$$Li + TiS_2 \rightarrow LiTiS_2$$

$$\bar{E} = 2.15 \text{ V}; \quad 480 \text{ W·h/kg Theoretical}$$

Status

Specific Energy	45 W·h/kg @ 15 W/kg
	(Est.) 125 W·h/kg @ 25 W/kg
Specific Power	45 W/kg
	(Est.) 110 W/kg (peak)
Cycle Life	250+ @ 60% DOD, 3-h rate
Cost	>$100/kW·h

Recent Work

    Safer solvents and electrolytes
    Sealed cells and small batteries (20 A·h)

Problems

    Sealing of cells
    High internal resistance
    Low current densities (<10 mA/cm^2)
    Slow recharge
    Safety
    Scale-up of cells and batteries
    Economics
    Overcharge and overdischarge gas evolution

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current research. Progress is being made slowly in this difficult area. There are no cells of this type commercially available, although lithium non-rechargeable cells are available. Additional information about the Li/TiS$_2$ cell is given in Table 11.[16]

The Lithium/Iron Sulfide Cells.

Because of the difficulties of developing high-performance, high specific energy cells that operate at room temperature, there is an interest in high-specific-energy cells that operate at elevated temperatures, thereby avoiding some of the problems encountered at ambient temperature. The reactions and transport processes take place at much higher rates at elevated temperatures. Also, molten salts can be used as electrolytes. The alkali halides, which are stable in contact with lithium and iron-sulfide, are very attractive electrolytes with high ionic conductivity.

During the last several years, two types of lithium/iron sulfide cells have been under development: LiAl/LiCl-KCl/FeS, and Li$_x$Si/LiCl-KCl/FeS$_2$. Both operate at 450°C, and are capable of specific powers of at least 100 W/kg, and several hundred cycles. The LiAl/FeS cell has a specific energy of 100 Wh/kg; the Li$_x$Si/FeS$_2$ cell stores 180 Wh/kg, in cells as small as 70 Ah. These cells are probably not appropriate for use in batteries smaller than 1 kWh, because of the need for a high-quality thermal insulation and control system.

Possible applications include power for electronics in spacecraft, power in high-temperature environments, and power where high specific energy is essential. These systems are not yet commercially available, but are under development for special applications including space power, electric vehicles, and off-peak energy storage for electric utilities. A number of problems remain to be solved before commercial success is possible. These are summarized in Tables 12[17] and 13.[18]

The Sodium/Sulfur Cell.

This cell is of interest for the same reasons that the lithium/iron sulfide cells are. It offers high performance, but a temperature of 350°C is necessary to achieve this. The sodium/sulfur cell is unique in that it makes use of liquid electrodes and a solid electrolyte. The electrolyte is a tube of beta alumina ceramic (Na$_2$O·11Al$_2$O$_3$), which conducts sodium ions. Usually, sodium is placed inside the beta alumina tube, and sulfur is held around the outside in a graphite felt current collector. Of course, the cell must be sealed to protect the sodium from the atmosphere. The Na/S cell has been under development for about 15 years, and batteries up to 100 kWh in size have been tested with varying degrees of success.

Table 14 contains a summary of the work on Na/S cells.[19,20] Note that the performance and lifetime are similar to those for the lithium/iron sulfide cells. The applications for these high-temperature, high-performance cells are likely to be similar. The main applications will probably involve batteries of 1 kWh and larger. A number of problems remain to be solved, including the development of a low-cost electrolyte, corrosion-resistant cell parts for use in contact with sulfur, and cell designs which permit repeated freeze-thaw thermal cycling without damage or loss of performance. With continued success in the development and demonstration of Na/S cells, it is conceivable that, some batteries will be sold commercially in the 1980's.

SUMMARY AND FUTURE DIRECTIONS

The field of advanced rechargeable batteries is very active, as can be deduced from the material presented above. A wide variety of electrochemical cells, old and new, are being developed for many applications. Recent emphasis has been in the areas of high specific energy, low cost and long life. These are conflicting requirements, and result in the need for highly innovative research and development, involving new, light-weight materials, sophisticated design methods, and greatly enhanced understanding of the details of the physical, chemical, and electrochemical processes occurring in the cells.

Table 15 is a summary of the characteristics of all of the cells discussed in this paper. It can be seen that the specific energy of the Pb/PbO$_2$ and Cd/NiOOH cells have been surpassed by wide margins in some of the advanced cells still being developed, without sacrifice of cycle life. The costs of

Table 12.   Summary of LiAℓ/LiCℓ-KCℓ/FeS Cell

$$2LiA\ell + FeS \rightarrow Li_2S + Fe + 2A\ell$$
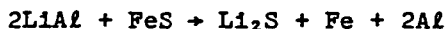
$$E = 1.33 \text{ V}; \ 458 \text{ Wh/kg Theoretical}$$

$$T = 450°C$$

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

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the new systems are likely to lie between those for Cd/NiOOH and those for Pb/PbO$_2$.

In the future, there is likely to be more emphasis on advanced materials for new rechargeable cells. This includes active materials (electrode reactants, electrolytes) and inactive materials (current collectors, cell cases, seals). As the new cells move into battery applications, the science of battery reliability and cell interconnections will receive more attention, along with the thermal management of batteries. Advanced methods of cell design and modeling will be critical tools in achieving high performance without sacrifice of cycle life. The future of rechargeable cell research will be a rich, active and productive one that will provide new batteries for advanced applications.

Table 13. Summary of Li$_4$Si/LiCl-KCl/FeS$_2$ Cell

Li$_4$Si + FeS$_2$ → 2Li$_2$S + Fe + Si
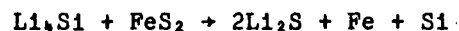
E = 1.8, 1.3 V; 944 Wh/kg Theoretical

T = 450°C

Status

|	
Specific Energy	120 Wh/kg @ 30 W/kg
	180 Wh/kg @ 7.5 W/kg
Specific Power	100 W/kg, peak
Cycle Life	700 @ 100% DOD
Lifetime	∿15,000 h
Cost	>$100/kWh

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 14. Summary of Na/Na+ Solid/S Cell

2Na + 3S → Na$_2$S$_3$
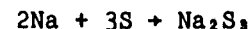
E = 2.0 V; 758 Wh/kg Theoretical

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
C$_6$N$_4$ 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$_x$P$_{3-x}$O$_{12}$
Thermocompression bonded seals

Problems

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

Table 15. Summary of Battery Characteristics

Cell	Volts	Theor. Wh/kg	Cell Size Ah	Wh/kg	Peak W/kg	Cycle Life	Battery Comments	Problems
$Pb/H_2SO_4/PbO_2$	2.1	175	1-150	30-40	50-100	400+	10-15 kWh	Low Wh/kg
Cd/KOH/NiOOH	1.3	210	<1-200	25-40	100+	500-5000	up to 10 kWh	High cost
H_2/KOH/NiOOH	1.3	380	<1-50	45-60	60	1000-2000	up to 1 kWh	High cost
Fe/KOH/NiOOH	1.4	267	300	40-50	50-100	300-600	up to 15 kWh	Low efficiency, H_2
Zn/KOH/NiOOH	1.7	326	1-400	60-75	100-150	100-300	up to 20 kWh	Short cycle life-Zn
Zn/KOH/AgO	1.86-1.6	434	1-300	80-100	100+	50-150	up to 20 kWh	Costly, short life
$Zn/ZnCl_2/Cl_2 \cdot 8H_2O$	2.1	405	300	66	70	1400[a]	35-50 kWh	Impurities, bulky
$Zn/ZnBr_2/Br_2$	1.8	430[b]	40+	40-60	30-70	700	2-20 kWh	Bulky
$Li/LiClO_4$ in Dioxolane/TiS_2	2.15	480	20	125[c]	110[c]	250	---	Safety, life
LiAl/LiCl-KCl/FeS, 450°C	1.33	458	100-350	60-100	60-100	300-1000	4 kWh	Low Wh/kg for high T
Li_4Si/LiCl-KCl/FeS_2, 450°C	1.8-1.3	944	70	120-180	100	300-700	---	Corrosion
$Na/Na_2O \cdot 11Al_2O_3/S$, 350°C	2.0	758	15-150	90-180	60-180	300-1500	up to 100 kWh	Corrosion, cost

[a] With maintenance and electrolyte renewal; 1 kWh system only.

[b] Not including Br_2 complexing agent.

[c] Estimated.

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