94c

LBL-13199

# Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

## ENERGY & ENVIRONMENT DIVISION

Presented at the Royal Society of Chemistry, Annual Chemical Congress, Energy and Chemistry Symposium, University of Surrey, Guildford, Surrey, England, April 7-9, 1981

ELECTROCHEMICAL ENERGY STORAGE

Elton J. Cairns

April 1981

RECEIVED
LAWRENCE
BERKELEY LABORATORY

SEP 25 1981

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782

LBL-13199 c.2

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-13199

# ELECTROCHEMICAL ENERGY STORAGE

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

presented at

Royal Society of Chemistry
Annual Chemical Congress
Energy and Chemistry Symposium
University of Surrey
Guildford, Surrey
England

April 7-9, 1981

This work was supported by the U.S. Department of Energy
under Contract W-7405-ENG-48.

# Electrochemical Energy Storage

Elton J. Cairns

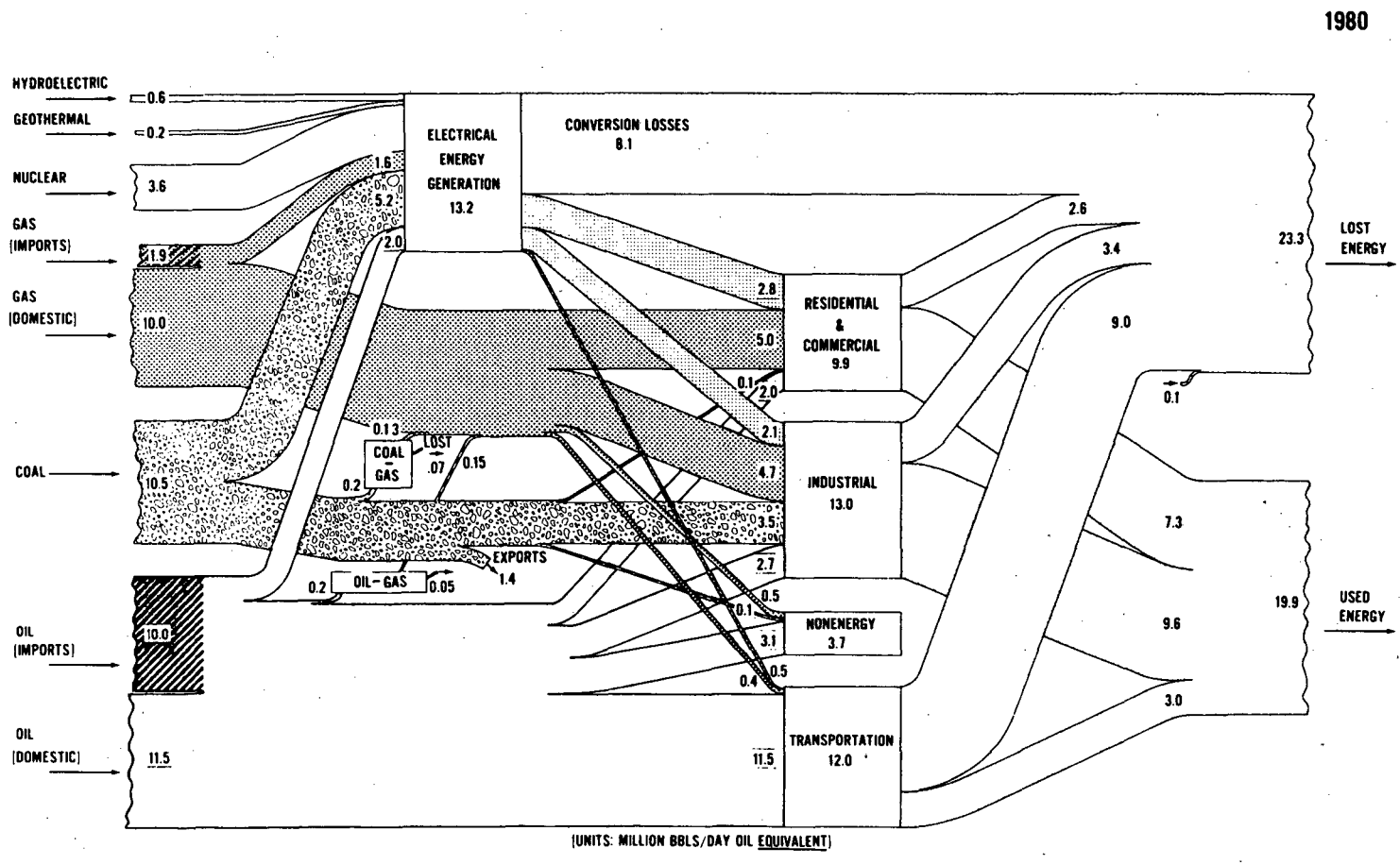
Lawrence Berkeley Laboratory, and
University of California
Berkeley, California 94720
U.S.A.

## I. Introduction

The energy economies of the world are rather heavily dependent upon petroleum, especially for the generation of electrical energy during peak demand periods, and for transportation. This is shown clearly in Figure 1, (1) which is an energy flow diagram for the U.S. energy economy of 1980, projected from several years earlier. It is evident from Figure 1, and the knowledge that much of the petroleum used by the electric utilities is for generation of power during the peak demand periods, that storage of energy in the utility system can reduce the demand for petroleum, and shift the demand toward other primary energy sources including coal and nuclear energy.

The storage of energy for electric utilities can be done in a number of ways. The most prominent is pumped hydroelectric storage. This requires large, elevated reservoirs, imposing rather severe geographic restrictions on its use. An alternative is to use storage (rechargeable) batteries, which can be installed in almost any location, and have few restrictions. Batteries can also be used to help match the energy supply to the energy demand in wind- or solar-powered electric energy generating systems.

The demand for petroleum used by electric utilities can also be reduced by providing electrical generating systems with the ability to effectively follow the peak load, while operating at




XBL 817-10590

Figure 1. Diagram of the energy economy of the U.S., projected to 1980. The units are expressed in millions of barrels of oil equivalent per day. (1 barrel of oil = $5.8 \times 10^6$ BTU)

high efficiency, and using non-petroleum fuels. This might be done by a fuel-cell power plant using gasified coal. The fuel cell is particularly appropriate because its part-load efficiency is even higher than its design-load efficiency, which can be above 50% (vs. 35-40% for present-day conventional plants).

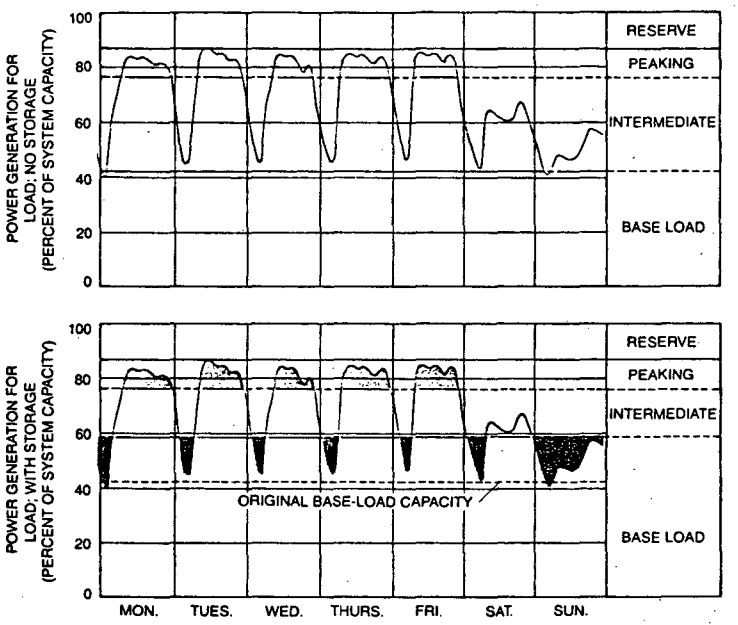
Another conclusion evident from Figure 1, is that the total petroleum demand could be reduced by shifting the transportation energy demand toward other primary energy sources. This can be done by the use of rechargeable batteries as the power source for electric vehicles. A number of electric vehicles are already in service, but their widespread use is limited by the relatively small amount of energy that can be stored per unit of battery weight. Clearly, higher-performance batteries are needed for vehicular applications. Fuel cells could also be used for electric vehicles, but they should rely on non-petroleum fuels such as methanol or ammonia.

In the sections below, the requirements of the above candidate applications for fuel cells and batteries will be shown, and the status and remaining research and development needs for these electrochemical systems will be discussed.

## II. Electrochemical Energy Generation and Storage for Electric Utilities

A weekly load curve for an electric utility is shown in Figure 2. (2) The part of the demand curve that falls in the zone labeled peaking could be met by either fuel cells or batteries, saving petroleum that is now used in gas turbines or diesel engines to meet peak loads. If batteries were to be used for energy storage, then base load plants could be used during the low-load periods of Figure 2 to charge the batteries. This would result in a reduced need for energy generation equipment during the peak demand period, and should result in a saving of capital. As can be seen from Figure 2, the time during which peaking power is required may be from 3 to about 10 hours per day, and the period available for recharging is about 5 hours on weekdays, and longer on weekends. These periods vary with the time of year.

Fuel cells for use in utilities have been under development in the U.S. for over fifteen years. (3) Significant advances have been made in all components of the system. The approach being developed as the first-generation utility fuel cell is shown in Figure 3. A carbonaceous fuel (coal or coal liquids) is steam-reformed to produce a hydrogen-rich fuel stream that is fed to a




XBL 818-10953

Figure 2. Example of a weekly load curve for an electric utility, showing energy available for storage during off-peak periods (dark shading), and energy that could be supplied by storage batteries.

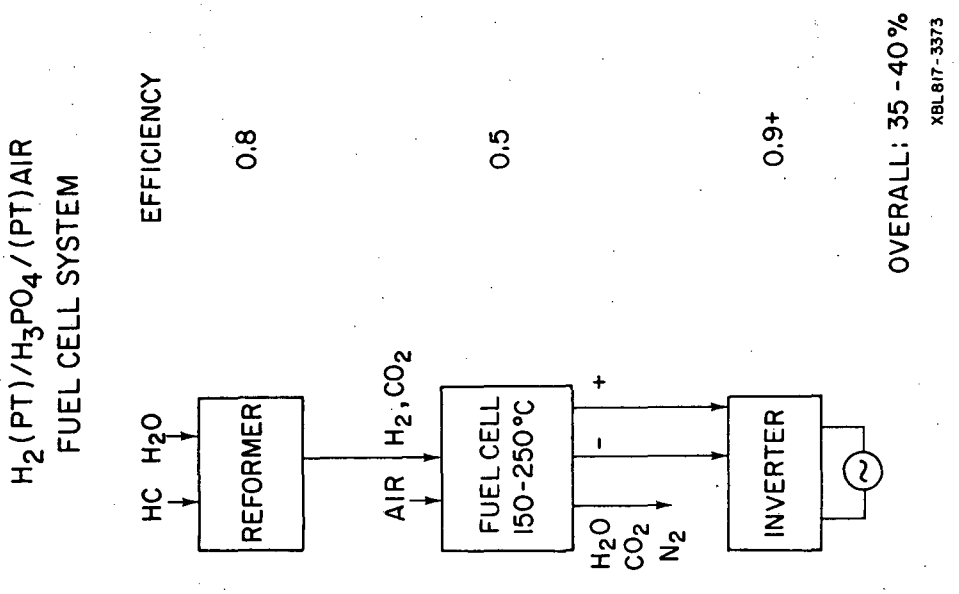



Figure 3. Schematic diagram of a fuel-cell system.

phosphoric-acid fuel cell operating at about 200° C and about 3.5 atm pressure (using turbocompressors). (4) The direct current from the fuel cell is passed through a solid-state inverter, which produces regulated alternating current for the utility grid, or for direct application to the load. The overall efficiency of this system is 35 to 40 percent, resulting from the component efficiencies given in Figure 3.

Overall, the fuel cell system has the advantage that it is not a heat engine, and therefore its efficiency is not limited by the Carnot efficiency. (5) A large fraction of the efficiency loss in the fuel cell system is attributable to the overvoltage of the air electrode. Thus, as the system operates at part load, its efficiency increases (above that for design load), a unique and advantageous characteristic as compared to heat-engine systems. The fuel cell system operates at lower temperatures than combustion systems, hence pollutants such as $NO_x$ are essentially absent.

A number of multi-kilowatt fuel cell systems have been tested, and lifetimes with maintenance and cell stack exchange has exceeded 10,000 hr. Scale-up of cells and components has taken place, and stacks of 20-24 cells sized for use in 4.8 MW systems have demonstrated lifetimes up to 14,000 hr. A short test of a 1 MW system has taken place, and two 4.8 MW systems are now under construction for testing in the U.S. and Japan. (4)

Although the advantages of fuel cell systems are very attractive, a number of problems remain to be solved before they can be commercially successful. Acceptable cost and lifetime are the key issues. The cost is related to the precious metals (platinoid elements as electrocatalysts) content, and the life is related in a complex way to the changes that occur in electrocatalysts with continued use (crystallite growth, corrosion of the graphite substrate). The status of the phosphoric acid fuel cell system is shown in Table 1.

Advanced work on higher-efficiency, lower-cost fuel cell systems centers around the molten carbonate fuel cell, which uses nickel electrodes and a mixed alkali carbonate electrolyte, and operates near 700° C. Work on this system is at a much earlier stage than that for the phosphoric acid system. Single molten carbonate cells have operated for about 2 years and some stacks of 900 $cm^2$ cells have been tested. (4)

Batteries for use in utility networks could be arranged as shown schematically in Figure 4. (2) As indicated above, the times available for charging and discharging are in the range of 3-8

Table 1

$H_2(Pt)/H_3PO_4/(Pt)$Air Fuel Cell System

Advantages

- Good efficiency for small systems (35-40%)
- Efficiency increases for lower loads
- Low pollution from reformer and cell

Status

- Multi-kW systems tested - over 10,000 hr. with maintenance and stack exchange
- Short tests of 1-MW system completed
- 4.8 MW systems under construction

Problems

- Performance decay-catalyst sintering
- High cost
- Short life
- Efficiency too low for base load systems

Recent Work

- Pressurized operation for higher performance
- Continued catalyst development
- Lower-cost cell parts
- Large cells (0.35 $M^2$) and systems (1 MW)

hours. In order to be competitive with pumped hydroelectric energy storage, which has an efficiency of 65-70%, the battery system should be at least 70% efficient. The battery system would require a building, and the tolerable cost of the building is such that the battery should store at least 80 kWh of energy per square meter of floor area (with a height of less than 6.1 meters (this corresponds to 30 Wh/ℓ). For a significant-sized energy-storage substation, the battery should store 100-200 MWh of energy. If the battery were to cost $30/kWh and last for 2000 deep cycles, (perhaps 200 cycles/yr. for 10 years) then this would amount to 1.5¢/kWh of energy stored. In some areas significantly higher costs can be tolerated. These requirements are summarized in Table 2.

If the requirements of Table 2 are met, then batteries would have an economic advantage over almost any other means of energy storage for discharge times of up to about 10 hours per day. At higher costs (up to about $100/kWh), batteries would still have an advantage for shorter discharge times. A detailed discussion of the various economic and other trade-off considerations for

Table 2

Requirements for Off-Peak Energy Storage Batteries

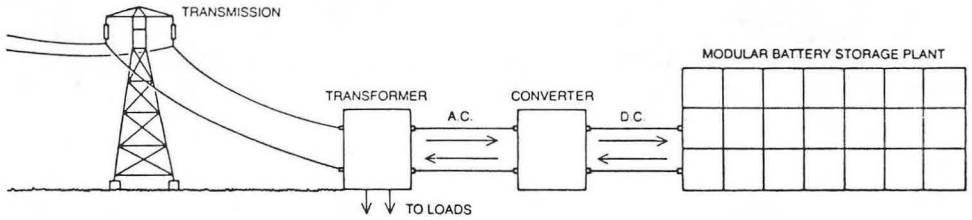
| | |
|---|---|
| Discharge time | 3-8 hours |
| Charge time | 5-7 hours |
| Overall efficiency | >70% |
| Energy/floor area (6.1 m max. height) | 80 kWh/$m^2$ |
| Typical size | 100-200 MWh |
| Cycle life | 2000 |
| Lifetime | 10 years |
| Cost | $30/kWh |

batteries versus other energy storage and generation technologies is presented in Reference 6.

The electric utilities in the U.S. are seriously evaluating the viability of energy storage in batteries. A Battery Energy Storage Test facility (BEST facility) has been constructed in Somerset County, New Jersey for the testing of battery modules, up to 5 MWh each, in regular utility service. A photograph of a model of this facility is shown in Figure 5. (7) The first battery to be used in evaluating the operation of the facility is a $Pb/H_2SO_4/PbO_2$ battery; the second one will probably be $Zn/ZnC\ell_2/C\ell_2 \cdot 8H_2O$. These tests will be taking place in 1981 and following years.

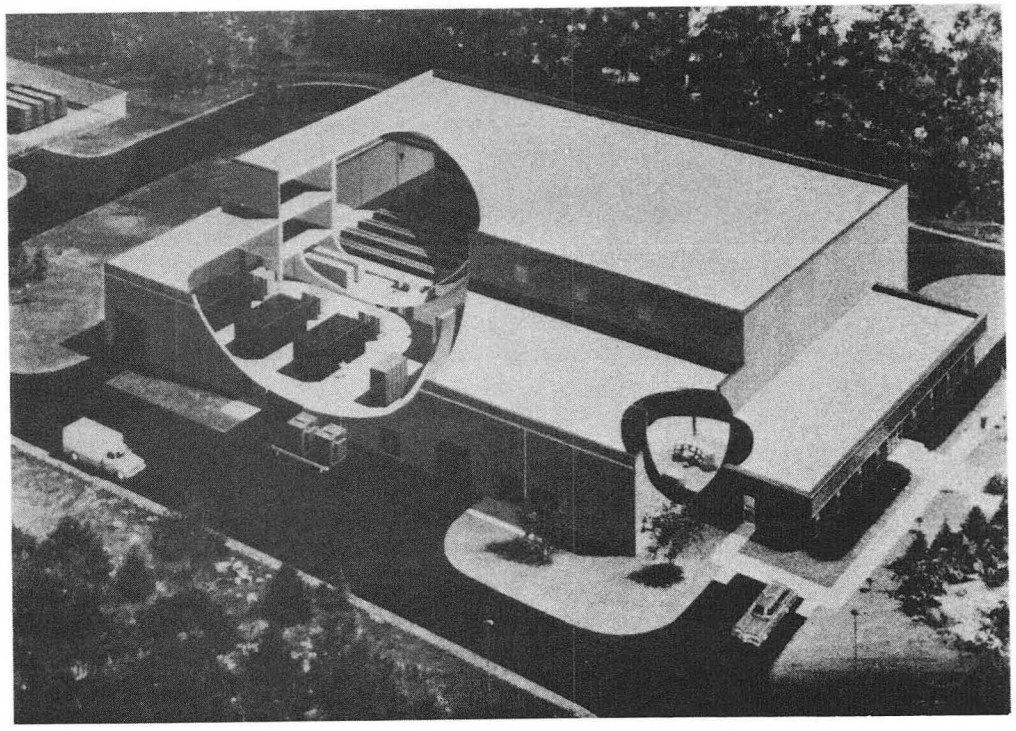
In order to gain perspective with regard to the present status of and future prospects for batteries in electric utility systems, it is useful to review some of the individual candidate batteries for this application. As a baseline for comparison, the $Pb/H_2SO_4/PbO_2$ system is most appropriate, since it is the only commercially-available battery that approaches most of the performance, life, and cost requirements.

The status of the $Pb/PbO_2$ cell is shown in Table 3. For utility applications, requiring long cycle life, it is possible to obtain 1500-2000 cycles, but at a low specific energy of about 20 Wh/kg. The cost of these long-lived batteries is greater than that shown in Table 3 (for vehicle batteries) and may be about $125-150/kWh. Recently, maintenance-free cells have been developed in automotive sizes, and it is expected that this feature will be employed in larger cells. If large $Pb/PbO_2$ battery systems are to be used, it probably will be a great benefit to develop sealed cells, with internal recombination of the gases. This has already been done in very small sizes (several Ah).




XBL 818-10952

Figure 4. Schematic diagram of how batteries might be used for energy storage in a utility network.



XBB 803-2608

Figure 5. Battery Energy Storage Test Facility, Sommerset County, New Jersey.

Table 3

$Pb/H_2SO_4/PbO_2$

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

E = 2.095 V; 175 W·h/kg Theoretical

Status

| | |
|---|---|
| Specific Energy | 22-40 W·h/kg @ 10 W/kg |
| Specific Power | 50-100 W/kg @ 10 W·h/kg |
| Cycle Life | 300+ @ 10 W/kg, 60% DOD |
| Cost | $50/kW·h |

Recent Work

- Replace Sb with Ca in positive current collector
- Maintenance-free cells
- Use $4PbO \cdot PbSO_4$ instead of $PbO + Pb_3O_4$ in positives
- New, low-resistance current collectors

Problems

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

Advances have also been made in the design of current collectors for minimum cell resistance, using computer-aided design techniques. The cost and lifetime projections for $Pb/PbO_2$ cells are such that it does not appear likely that this battery will be widely used for off-peak energy storage.

A system which may prove to be economically acceptable for off-peak energy storage is zinc/chlorine. A schematic diagram of this system is shown in Figure 6. This is a flow system, with the chlorine stored as $C\ell_2 \cdot 8H_2O$, an ice-like solid, in a separate compartment. During the charging process, zinc is deposited on the dense graphite negative electrodes, while chlorine is evolved from porous graphite positive electrodes. The chlorine-saturated aqueous $ZnC\ell_2$ electrolyte is circulated through a chiller, bringing its temperature below 9°C, where the $C\ell_2 \cdot 8H_2O$ forms. The solid $C\ell_2 \cdot 8H_2O$ is filtered out in the storage area, and the $ZnC\ell_2$ electrolyte is recirculated to the cell stacks. The reverse of these processes takes place during discharge.

The status of the $Zn/ZnC\ell_2/C\ell_2 \cdot 8H_2O$ system is shown in Table 4. (8) With a theoretical specific energy of 405 Wh/kg, it is possible that a practical specific energy of 80-90 Wh/kg might be achieved (66 Wh/kg has already been demonstrated). In a small

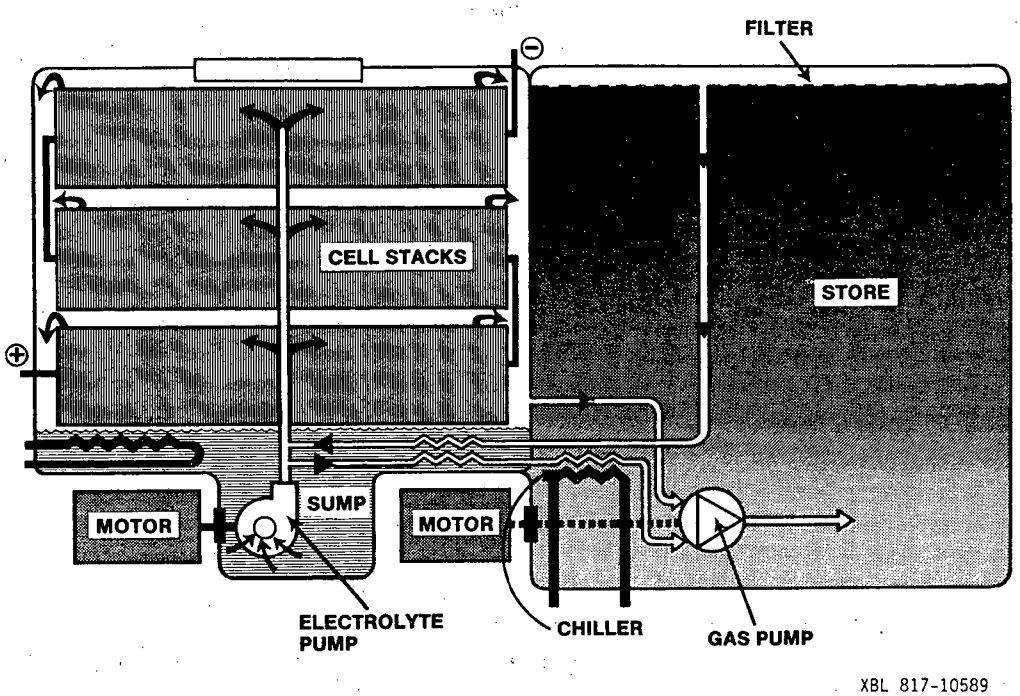



Figure 6. Diagram of the zinc/chlorine system. (Courtesy of Energy Development Associates)

system, a cycle life of 1400 cycles, with electrolyte maintenance (for purity) has been achieved. Systems as large as 50 kWh have been built, and will probably serve as modules for the BEST facility battery to be tested in 1981 or 1982.

Some of the remaining problems of the $Zn/C\ell_2 \cdot 8H_2O$ system to be addressed include the necessity of periodically discharging all of the zinc in order to avoid severe dendrite formation, shorting the cells. Additives are used in the electrolyte to help control the morphology of the zinc deposit, and minimizing the frequency of complete discharge. It has been found that low concentrations of iron (in the ppm range) and some other metals in the electrolyte result in excessive hydrogen evolution from the zinc electrode, so maintenance of a high purity electrolyte (with regard to low $H_2$ overvoltage metals) is important. Recombination of the $H_2$ with $C\ell_2$ is promoted by an ultraviolet light source in the gas space above the cells. Because this system does not use separators, the dissolved $C\ell_2$ remaining in the electrolyte after it passes through the porous graphite positive electrode may combine directly with the zinc on the negative electrode, resulting in an efficiency loss. Consequently, the $Zn/C\ell_2 \cdot 8H_2O$ system operates at

Table 4

$Zn/ZnC\ell_2/C\ell_2 \cdot 8H_2O$

$Zn + C\ell_2 \cdot 8H_2O \rightarrow ZnC\ell_2 + 8H_2O$

E = 2.12 V; 405 W·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 $C\ell_2$
- 35-50 kWh systems
- Systems components

Problems

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

*1 kWh system only, with electrolyte maintenance

about 60-70% efficiency, which could be a problem. Work continues on the improvement of the system as 50 kWh units are prepared for test. Cost projections fall below $100/kWh, and make this system potentially attractive for stationary energy storage.

A high-temperature cell which has been under development for about fifteen years, and is a candidate for utility energy storage is the sodium/sulfur cell, which uses a $Na_2O \cdot 9A\ell_2O_3$ (beta alumina) ceramic electrolyte, and operates at 350°C. The ceramic electrolyte is used in the form of a closed-end tube, and has one reactant inside, the other outside, as shown in Figure 7. (9) The sulfur is held in the pores of a graphite felt current collector, and the cell must be sealed in order to avoid reaction with air and moisture. A number of batteries (about 10 kWh) have been built for demonstration purposes, but none of these have shown a significant life.

Some discharge and charge curves for a parallel-connected Na/S battery of about 25 cells (∿120 Ah each) are shown in Figure 8. (10) The lifetimes of individual cells in the

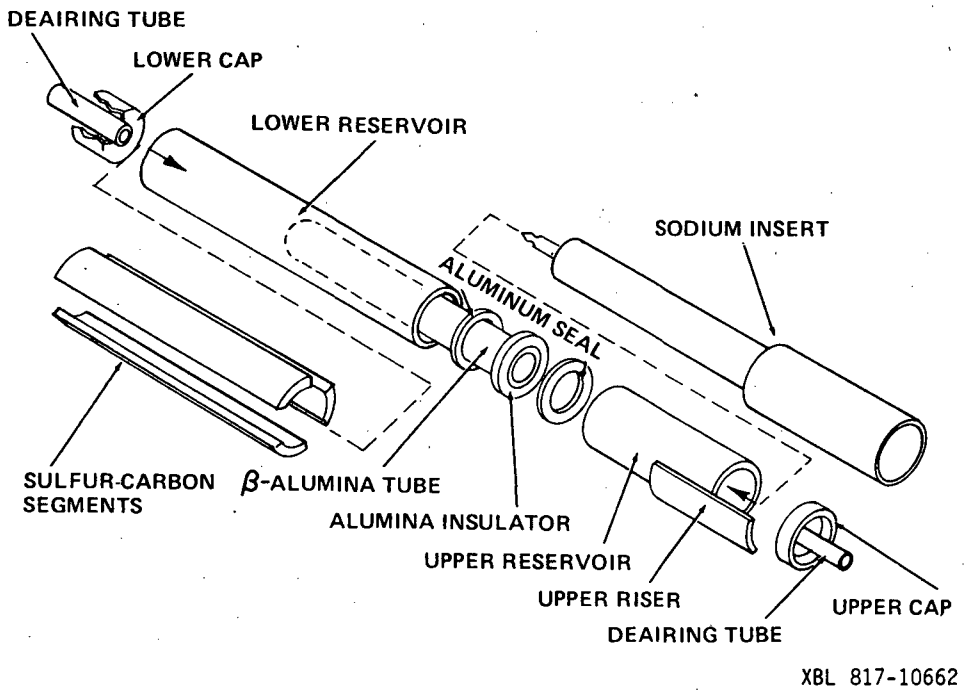



Figure 7. Exploded view of a Na/S cell.

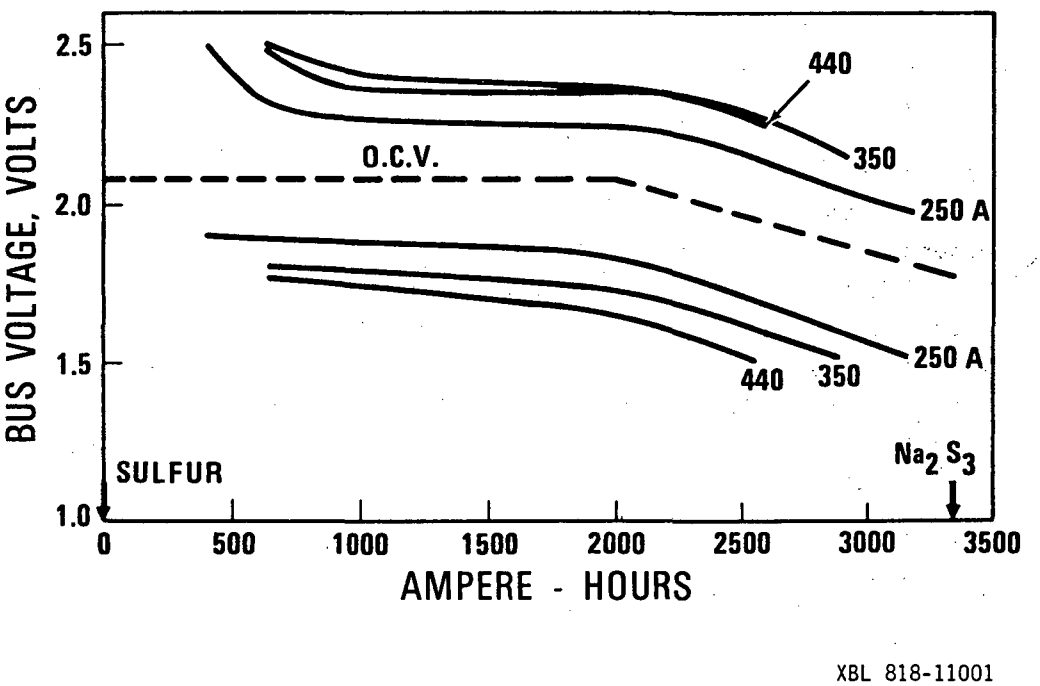



Figure 8. Charge and discharge curves for a 25-cell parallel-connected Na/S battery. (10)

100-200 Ah size range has been highly variable (between 200 and 1500 cycles). The results of one life test are given in Figure 9, (10) where it can be seen that capacity maintenance was good for over 700 cycles, before a sudden failure occurred.

The status of the world-wide development efforts on the Na/S cell with beta alumina electrolyte is indicated in Table 5. Notice that the theoretical specific energy is 758 Wh/kg. Applying the rule of thumb multiplier of 0.23, the specific energy that may be achieved with good cell design is about 175 Wh/kg. As shown in the table, values up to 140 Wh/kg have already been reported. The ultimate cost that could be reached by these cells might be well below $100/kWh, if inexpensive manufacturing methods can be developed, especially for the electrolyte. Innovative approaches have been used to improve the utilization of the sulfur electrode, including specially shaped and layered current collectors, and current collectors of graded resistivity. Much work has been done to identify electronically-conductive materials which are resistant to sulfur attack, including doped $TiO_2$. New electrolytes having higher conductivity at lower temperatures have been sought, including Nasicon ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$), but beta" alumina remains best (with 1% $Li_2O$ and ~2% MgO as stabilizers). Thermal cycling has been a major problem. Usually one freeze-thaw cycle causes failure, but progress has been made in England on this problem. (11)

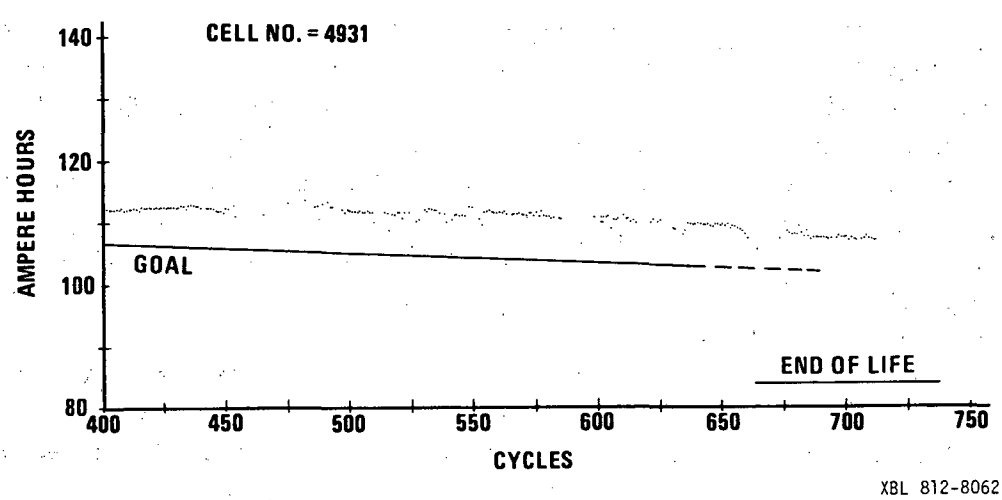



Figure 9. Capacity vs. cycle number for a full-sized Na/S cell. (10)

Table 5

Na/Na+ Solid/S

$2Na + 3S \rightarrow Na_2S_3$

$\bar{E}$ = 2.0 V; 758 Wh/kg Theoretical

Status

| | |
|---|---|
| Specific Energy | 85-140 Wh/kg @ 30 W/kg |
| Specific Power | 60-130 W/kg peak |
| Cycle Life | 200-1500 |
| Lifetime | 3000-15,000 h |
| Cost | >$100/kWh |

Recent Work

- Batteries, ∿10 kWh
- $C_6N_4$ additive to S
- Ceramic ($TiO_2$) electronic conductors
- Shaped current collectors
- Tailored resistance current collectors
- Sulfur-core cells
- $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$
- Thermocompression bonded seals

Problems

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

Another high-temperature cell under consideration for energy storage in electric utilities is the LiAℓ/FeS cell, which uses a molten-salt electrolyte of LiCℓ-KCℓ, and operates at 450°C. A cutaway view of this type of cell is shown in Figure 10. (12) The electrodes are prepared from mixtures of powdered salt electrolyte and powdered reactant (LiAℓ, FeS) pressed into a plaque, and assembled with current collectors, particle retainers, and BN felt separators as shown in Figure 10. The cell is sealed to prevent reaction with air and moisture.

Typical discharge curves for a LiAℓ/LiCℓ-KCℓ/FeS cell are shown in Figure 11. (13) This cell had a capacity of 80-90 Ah, but cells currently under test have capacities of about 350 Ah because they contain a number of electrodes internally connected in parallel. The cycle life of such cells is about 350 cycles; the specific energy of the most recent cells of this general type has been about 100 Wh/kg.

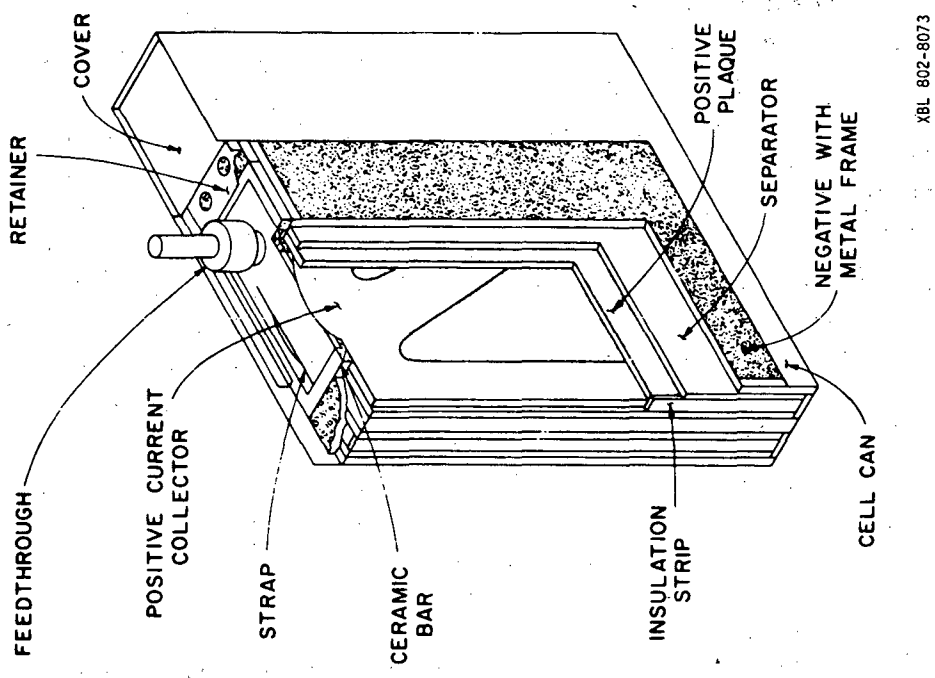



Figure 10. Cutaway drawing of a LiAℓ/FeS cell.

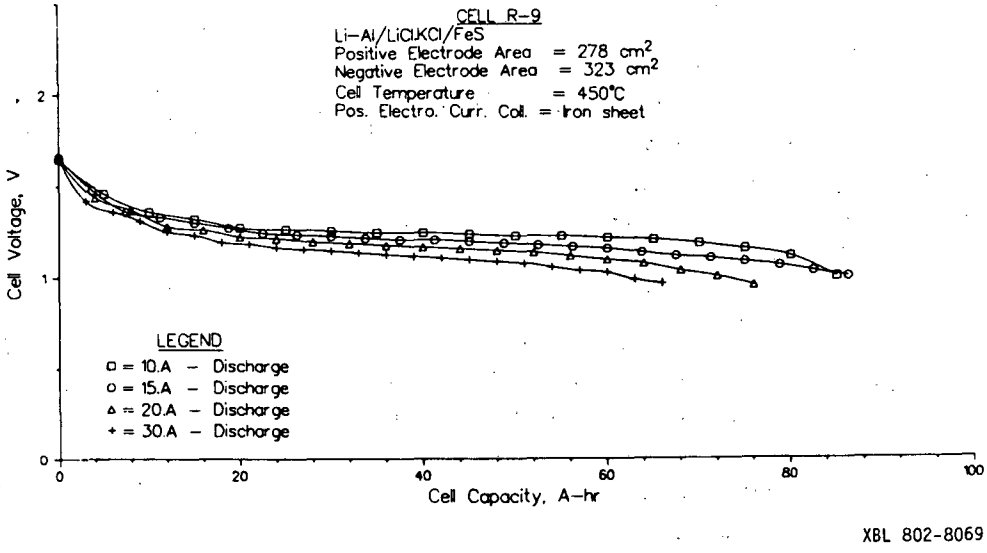



Figure 11. Discharge curves for a LiAℓ/FeS cell operated at various constant currents, as labeled.

Recent work on LiAℓ/FeS cells has included improvements in the wetting of the BN separator by the electrolyte, improved current collectors for lower internal resistance and higher specific power, and cost reduction measures for the BN separator. Electrical shorting of the cells, due to extrusion of the positive electrode active material and protrusions of the negative electrode active material, remains the main failure mode. Recent progress has been made on tolerance to thermal cycling. Up to 30 freeze-thaw cycles can be experienced by these cells without capacity loss. The status of the LiAℓ/FeS cell is summarized in Table 6.

Table 6

LiAℓ/LiCℓ-KCℓ/FeS

$2LiA\ell + FeS \rightarrow Li_2S + Fe + 2A\ell$

E = 1.33 V; 458 Wh/kg Theoretical

T = 450°C

<u>Status</u>

| | |
|---|---|
| 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 |

<u>Recent Work</u>

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

<u>Problems</u>

- 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

Some conceptual design work has been performed on utility energy storage modules. Figure 12 shows a drawing of a truckable utility module, which would have an energy storage capability of about 5.6 MWh, and would contain its own thermal control system and electronics. (14)

It is clear from the discussion above that there are several battery systems under development that may provide for storage of a significant amount of energy for utility systems. Evaluations in the BEST facility during the next few years should provide guidance to the selection of the most appropriate batteries for this application.

## III. Energy Storage for Solar- and Wind-Powered Systems

During the last several years, the idea of solar- and wind-powered electrical systems has gained in popularity because of the desire to decrease dependence on petroleum and other polluting energy sources. Unfortunately, solar and wind energy are not necessarily available when energy is needed. This introduces the need for an energy storage system which may be required to provide

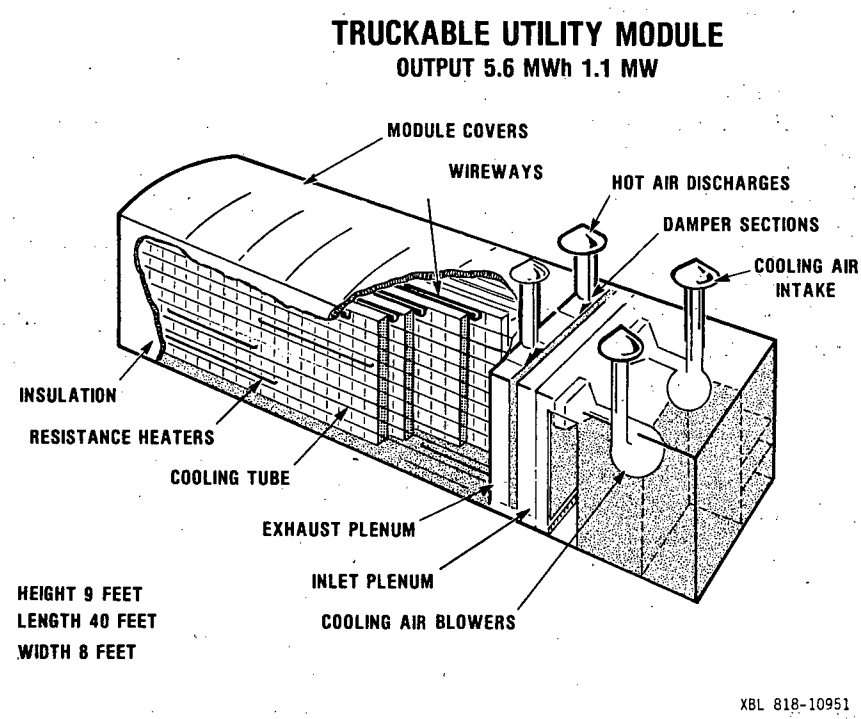



Figure 12. Schematic cutaway drawing of a LiAℓ/FeS truckable battery module for possible use in electric utility networks. (14)

energy for periods of 12 hours to a few days. Because of this extended energy delivery period, flow batteries with storage of reactants in tanks are the most popular concept for this application. In this way, the energy storage part of the system can be at least partially decoupled from the energy conversion part of the system.

The $Zn/ZnC\ell_2/C\ell_2 \cdot 8H_2O$ system has been proposed for the solar and wind energy storage application. The status of this system was discussed above. A related system is $Zn/ZnBr_2/Br_2$, in which the bromine is stored as a chemical complex in a separate tank. A few, relatively small multi-kWh systems have been built and tested. These systems have efficiencies in the 60-70% range. The cells make use of an ion-exchange membrane to prevent direct reaction between $Br_2$ and Zn. (15) Another system making use of the Zn electrode is the $Zn/Fe(CN)_6^{-3}$ cell, which also contains an ion exchange membrane, and uses external storage of the ferricyanide solution. Finally, there is under investigation a system in which both reactants (a $Cr^{+2}$ solution, and a $Fe^{+3}$ solution) are stored in tanks. All of these systems are less well developed than those discussed in the previous section of this paper, and it is probably premature for a detailed report.

## IV. Energy Storage for Electric Vehicles

The specific power and specific energy requirements for electric vehicle applications can be assessed by applying the equations of motion for vehicles to typical driving profiles. This has been done as discussed in References 16 and 17. The results of those calculations can be summarized conveniently in the form of Table 7. A useful value for urban vehicle battery energy calculations is 0.15 kWh/T-km. The range that can be expected from an electric vehicle operating on an urban driving profile is:

$$R(km) = \frac{SpE(Wh/kg)}{0.150(Wh/kg\text{-}km)} \times \frac{Mb(kg)}{Mv(kg)} \qquad (1)$$

where SpE is the specific energy of the battery

Mb is the mass of the battery

Mv is the test mass of the vehicle.

It can be seen from Equation 1 that for a range of 150 km, and Mb/Mv = 0.3 (the maximum for good automotive design), the specific energy must be at least 75 Wh/kg. Because of the fact that there are no batteries available with a specific energy of 75 Wh/kg, a reasonable cycle life (>300 cycles) and an acceptable cost

Table 7

Energy and Power Requirements for Urban Electric Vehicles

| | |
|---|---|
| Energy Consumption | |
| At axle: | 0.10-0.12 kW·h/T·km |
| From battery: | 0.14-0.17 kW·h/T·km |
| From plug: | 0.18-0.23 kW·h/T·km |
| Peak Power Required (0-50 km/h, ≤10 s) | |
| At axle: | 25 kW/T (Test wt.) |
| From battery: | 35 kW/T (Test wt.) |
| Average Power Required at Axle | |
| Fed. Register | ∿5 kW/T (Test wt.) |
| 50 km/h cruise | ∿3 kW/T (Test wt.) |
| Peak for 0-50 km/h, ≤10 s | ∿25 kW/T (Test wt.) |

<$100/kWh, there has been a significant effort to develop advanced batteries for electric vehicles.

The battery that is closest to meeting the performance, cycle life and cost goals for electric automobiles is zinc/nickel oxide. The electrolyte is aqueous potassium hydroxide (∿33 w/o). This cell has a theoretical specific energy of 326 Wh/kg, and should therefore be capable of providing 75 Wh/kg in a practical configuration. Values of 60-80 Wh/kg have already been demonstrated in batteries up to full electric vehicle size, such as the one shown in Figure 13.

The zinc/nickel oxide batteries that have been tested in electric vehicles have demonstrated the expected high performance and improved range (over $Pb/PbO_2$). Unfortunately Zn/NiOOH cells have not delivered acceptable cycle lives, typical values being only 100 to 200 deep cycles. The main cause of short cycle life has been failure of the zinc electrode and/or the separator. Significant efforts have been devoted to improvements in the zinc electrode, but only gradual gains have been realized. Efforts continue on the zinc electrode, and the separator, as well as on cost reduction, especially for the NiOOH electrode. Because of the fact that Zn/NiOOH cells can be operated in the sealed state, they show promise of being developed as totally maintenance-free devices, with internal provision for gas recombination. The status of this cell is summarized in Table 8.

Table 8

Zn/KOH/NiOOH

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

E = 1.735 V; 326 W·h/kg Theoretical

Status

| | |
|---|---|
| Specific Energy | 60-75 W·h/kg @ 30 W/kg |
| Specific Power | 200-300 W/kg @ 35 W·h/kg |
| Cycle Life | 100-200 @ 25-50 W/kg, 60% DOD |
| Cost | >$100/kW·h |

Recent Work

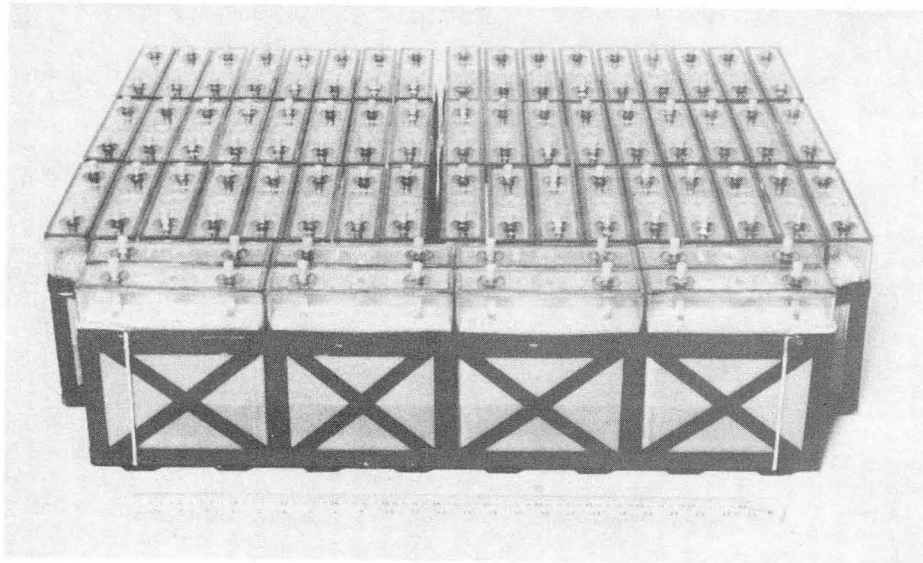
- Inorganic separators (e.g., $ZrO_2$, $Ni(OH)_2$, $Ce(OH)_3$, others)
- Sealed cells
- Nonsintered electrodes

Problems

- Sealing of cells - $O_2$ evolution and recombination
- Zn redistribution
- Separators

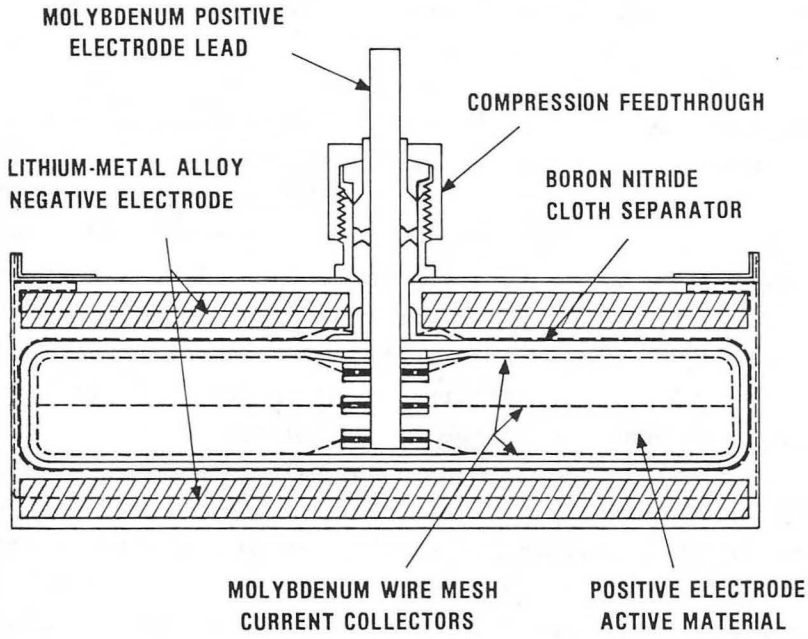
A high-temperature cell that could be developed as a power source for electric vehicles is the $Li_4Si/FeS_2$ cell, which uses LiCℓ-KCℓ molten salt electrolyte, and operates at 450°C. Because it has a theoretical specific energy of 944 Wh/kg, there is the expectation that cells capable of 200 Wh/kg can be developed. A schematic cross section of a laboratory $Li_4Si/FeS_2$ cell is shown in Figure 14. It can be seen that the structure of this cell is similar to that of the LiAℓ/FeS cell, discussed above. Cells like that of Figure 14, in 70-80 Ah sizes have yielded the performance data shown in Figure 15. (18) Note that a specific energy of over 180 Wh/kg was realized.

The status of the $Li_4Si/LiC\ell-KC\ell/FeS_2$ cell is given in Table 9. Cell lives of about 2 years have been achieved, and specific energies of 120 Wh/kg have been maintained at a specific power of 30 W/kg (typical average specific power for urban driving). These cells must be scaled up to larger sizes and incorporated into thermally self-sustaining batteries before they can be tested in vehicles. Some of the problems that remain to be solved include: inexpensive, corrosion-resistant materials for the current collector in the $FeS_2$ electrode (Mo and graphite are used now), lower-cost separators (BN felt is used now), and low-cost leak-free feedthroughs.



CBB 817-6187

Figure 13. Photo of a zinc/nickel oxide battery for an electric automobile.




XBL 818-10950

Figure 14. Schematic cross-section of a $Li_4Si/FeS_2$ cell.

Table 9

$Li_4Si/LiC\ell-KC\ell/FeS_2$

$Li_4Si + FeS_2 \rightarrow 2Li_2S + Fe + Si$

E = 1.8, 1.3 V; 944 Wh/kg Theoretical

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 |

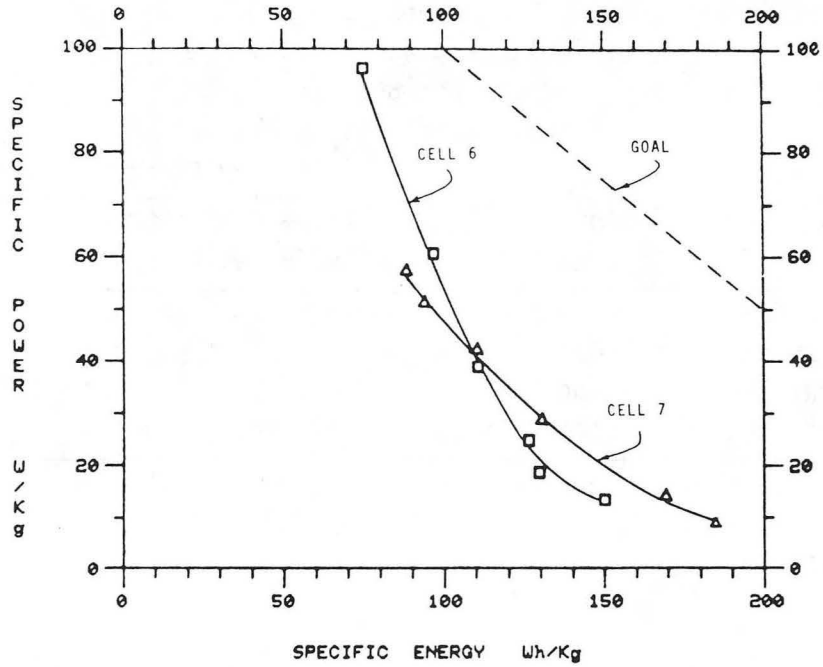
Recent Work

- 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

In order to bring some perspective to the assessment of candidate batteries for electric vehicles, some design calculations were performed, based on a 1000-kg urban vehicle, of the type shown in Figure 16. Allowance was made for the added battery mass, when making energy consumption comparisons to the gasoline reference vehicle. The vehicles were designed for a 160 km range, except for the $Pb/PbO_2$ version, which had a design range of 75 km. For each vehicle, the primary energy consumption was calculated, referring to resource in the ground, using efficiency values given in Reference 17. As can be seen from the results in Table 10, the higher specific energy batteries offer the opportunity to conserve energy, as well as to shift energy demand away from petroleum. There is thus a strong incentive to develop high specific energy batteries for widespread use in urban automobiles. In addition to high specific energy, it is necessary that electric vehicle batteries have acceptable durability and cost. Recent goals for performance, durability, and cost for electric vehicle batteries are given in Table 11. Finally, Figure 17 presents a comparison of the specific power vs. specific energy plots for a number of




XBL 802-8065

Figure 15. Specific power vs. specific energy for two $Li_4Si/FeS_2$ cells. (18)

CBB 817-6183

Figure 16. Photo of General Motors Electrovette, an urban electric automobile. (Courtesy of General Motors)

Table 10

Effectiveness and Primary Energy Consumption Comparison

Urban Autos, 135 kg Payload

| | GVM kg | kW·h† / km | Primary Energy Consumption: Petroleum kW·h/km | Coal kW·h/km | Nuclear kW·h/km |
|---|---|---|---|---|---|
| Gasoline | 1050 | 0.86 | 0.92 | 1.34 | 3.04 |
| $Pb/PbO_2$* | 1620 | 0.38 | 1.32 | 1.21 | 1.32 |
| Zn/NiOOH** | 1400 | 0.32 | 1.14 | 1.05 | 1.14 |
| $Li\text{-}Si/FeS_2$** | 1100 | 0.25 | 0.90 | 0.82 | 0.89 |

†Energy input to vehicle

*75 km range

**160 km range

Table 11

Battery Goals

| BATTERY | | PERFORMANCE* | | | DURABILITY | | | COST† | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Type | Mass (kg) | Specific Energy (W·h kg) | Energy Stored (kW·h) | Urban Range (km) | Cycles 100% DOD | Years | km | $/kW·h | $/Battery | $/km |
| Lead-Acid (Advanced) | 300 | 30 | 9 | 60 | 400 | 3 | 24,000 | 50 | 450 | 0.019 |
| Zinc/Nickel Oxide (3-5 Years) | 250 | 75 | 18.75 | 125 | 300 | 3 | 37,500 | 70 | 1300 | 0.035 |
| Lithium/Iron Sulfide (10+ Years) | 150 | 200 | 30 | 200 | 1000 | 3-5 | 200,000 | 40 | 1200 | 0.006 |

*Basis 1000 kg vehicle, 0.15 kW·h/T·km

†Battery amortization cost only;

Electricity Cost 0.25 kW·h/km x $0.04/kW·h = $0.01/km

battery systems. The high-temperature batteries offer the highest performance, but they still fall short of the spark ignition engine plus fuel tank: an incentive for future work!

## V. Conclusions

The discussion above, and the data presented allow the following conclusions to be drawn.

1. Electrochemical energy conversion systems offer opportunities to decrease our dependence upon petroleum through more efficient energy conversion, and through energy storage in electric utility networks.

2. Batteries of higher specific energy (>70 Wh/kg) may provide useful electric automobiles, decreasing our dependence on petroleum for transportation.

3. The usefulness of solar- and wind-powered systems is increased by the storage of energy in batteries.

4. Battery lifetime and cost require improvement to meet the needs of the above applications.

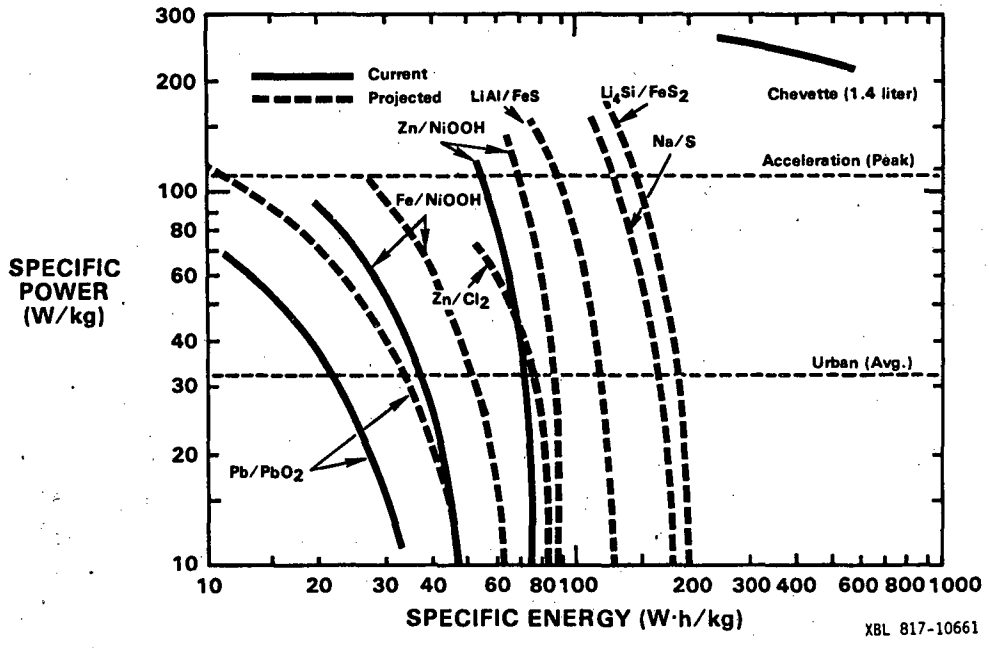



Figure 17. Specific power vs. specific energy plot for various batteries.

REFERENCES


1. A.L. Austin, B. Rubin, and G.C. Werth, Lawrence Livermore Laboratory Report UCRL 51221, May 30, 1972.
2. F.R. Kalhammer, Scientific American, 241, 56, December 1979.
3. S. Orlofsky, in Preprints of Papers Presented at the ACS Division of Fuel Chemistry Biennial Fuel Cell Symposium, Chicago, IL, 1967, p. 309.
4. United Technologies Corporation, Advanced Technology Fuel Cell Program, EPRI Report - EPRI EM-1730-SY, March 1981.
5. H.A. Liebhafsky and E.J. Cairns, Fuel Cells and Fuel Batteries, John Wiley & Sons, Inc., New York, 1968, Chapter 3.
6. M.L. Kyle, E.J. Cairns, and D.S. Webster, Argonne National Laboratory Report ANL-7958, March 1973.
7. E.J. Cairns and R.R. Witherspoon, Batteries, Primary--Fuel Cells, in Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., New York, 1978.
8. C.H. Chi, P. Carr and P.C. Symons, in Proceedings of the 14th IECEC, Volume 1, American Chemical Society, Washington, D.C., 1979, p. 692.
9. General Electric Review of the Advanced Battery Development Program for Electric Utility Application, May 1979.
10. Ford Aerospace & Communications Corporation, Annual DOE Review of the Sodium-Sulfur Battery Program, April 1980.
11. J.L. Sudworth, private communication to E.J. Cairns, April 1981.
12. P.A. Nelson et al, Progress Report for the Period October 1977 - September 1978, Argonne National Laboratory Report ANL 78-94, November 1978.
13. H. Shimotake et al, in Proceedings of the 11th IECEC, Volume 1, American Institute of Chemical Engineers, New York, 1976, p. 473.
14. S.M. Zivi, in Annual DOE Review of the Lithium/Metal Sulfide Battery Program, June 1979.
15. R. Bellows et al, in Extended Abstracts of the Electrochemical Society Meeting, Los Angeles, October 1979, 79-2, Abstract 112.
16. E.J. Cairns and E.H. Hietbrink, Electrochemical Power for Transportation, in Comprehensive Treatise of Electrochemistry, Volume 3, J. O'M Bockris, B.E. Conway, E. Yeager, and R.E. White, eds., Plenum Publishing Corporation, 1981, p. 421.

17. E.J. Cairns, in Materials for Advanced Batteries, D.W. Murphy, J. Broadhead, and B.C.H. Steele, eds., Plenum Publishing Corporation, New York, 1981.
18. E.J. Zeitner and J.S. Dunning, in Proceedings of the 13th IECEC, Society of Automotive Engineers, Warrendale, PA, 1978, p. 697.

This work was supported by the U.S. Department of Energy under Contract W-7405-ENG-48.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*TECHNICAL INFORMATION DEPARTMENT*
*LAWRENCE BERKELEY LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*