Advanced Storage Batteries: Progress, but Not Electrifying

Advanced secondary or storage batteries have the potential, as one jokester put it, to meet demands for electricity that fluctuate hourly and seasonly. Such batteries are also needed to power electric vehicles having a range and acceleration acceptable to the public. At present, advanced batteries that perform adequately and are cost-effective do not exist for these tasks. A symposium on advanced battery research held at the Argonne National Laboratory (ANL) near Chicago in March provided an opportunity to assess the effect of the recent infusion of R & D dollars (see box) as substantial, but widespread availability of such batteries is still many years away. And, while batteries that operate at high temperatures continue to receive the most attention, researchers are increasingly turning to less exotic solutions for near-term batteries.

Instead of relying on older, inefficient steam turbines for load leveling during daylight hours and on gas turbines that require a high-grade petroleum fuel for peak shaving at times of very high demand, utilities would like to make up the deficit between the power generated by base load plants that operate continuously and the instantaneous demand for power by storing electricity generated when not needed for later use. Load leveling usually refers to providing power ten or more hours a day, whereas peak shaving refers to satisfying short-term demands, such as those arising from the use of air conditioners on a summer day.

If the use of electric vehicles became widespread in the United States by the end of the century, estimated Albert Landgrebe of the Energy Research and Development Administration, a savings of up to 25 percent of imported oil could be effected. Electric vehicles would also play a load leveling role for utilities insofar as electricity for their use was generated at night. Acceptance of electric vehicles, however, requires the advent of energy storage devices that can propel a car at a cost and with a performance approximating that of the internal combustion engine.

Storage batteries, as an old and proved technology, have been the dominant avenue of investigation for energy storage for both utilities and vehicles. But the traditional lead-acid battery used for starting, lighting, and ignition of automobiles, trucks, and buses has not been up to the task of utility load leveling because it cannot sustain the deep discharge-charge cycles required, and heavy duty batteries that could function in this way have been too expensive. In vehicles, the large weight of lead-acid batteries prevents enough batteries being carried to provide a range greater than about 50 miles.

In recent years, researchers have looked to electrochemical cells that operate at temperatures well above ambient (principally lithium-sulfur and sodiumsulfur couples) to meet both cost and performance goals for utility load leveling (and more recently peak shaving) and electric vehicle propulsion. Although there are efforts in the United Kingdom and in the Soviet Union, research on lithium-sulfur cells has been centered in the United States. But major sodiumsulfur cell programs are under way in the United Kingdom, France, Germany, and Japan, as well as here in the United States. Moreover, there is relatively little interest anywhere in Europe in batteries for utility load leveling, apparently because there is an abundance of sites for pumped hydroelectric storage (Science, 17 May 1974, p. 785), and the Europeans feel that cost goals would be hard to meet.

A Goal of \$20 per Kilowatt-Hour

Researchers in the United States believe that storage batteries with a specific energy of 220 watt-hours per kilogram (1 watt-hour is equal to 3600 joules), a lifetime of 5 years (one charge-discharge cycle per day), and a cost of \$20 per kilowatt-hour could compete economically with gas turbines at recent oil prices or with pumped hydroelectric storage for load leveling and peak shaving.

In automobiles, achieving this goal for specific energy would enable a driving range comparable to that of gasolinepowered cars, and a specific power of 220 watts per kilogram would allow a comparable acceleration. To compete with internal combustion engines, batteries for vehicle propulsion could cost somewhat more than \$20 per kilowatthour and must have a lifetime of 3 years, according to Elton Cairns of the General Motors Research Laboratories.

The initial enthusiasm for the hightemperature batteries was based in part on a quantity called the theoretical specific energy, which is calculated from the free energy of the reaction between anode and cathode materials and the weight of the reactants. In practice, battery designers feel that, if the battery achieves 20 to 30 percent of the theoretical specific energy, they have done about as well as they can because all of the components of a battery other than the reactants in the electrodes add weight without contributing any energy.

For example, the electrodes are composite entities consisting of a reactant and a current collector. A metal or carbon current collector is needed to support the reactants which are often in the form of a liquid or other nonrigid body. The current collector also connects the electrodes to the terminals of the battery. In order to make the cell as compact as possible, the electrodes are placed quite close together, so that a separator material that allows ions in the electrolyte to pass through but prevents the electrodes from short circuiting is needed. If the cell is hermetically sealed, feedthroughs and seals are required, and if it operates at a high temperature, insulation is needed.

For electrochemical cells with a lithium anode and a sulfur cathode, the theoretical specific energy is 2600 watt-hours per kilogram. Even 10 percent of this would exceed the required performance, whereas the entire 200 watt-hours per kilogram theoretically extractable from lead-acid cells would still fall short.

Lithium-sulfur cells operate at temperatures between 400° and 450°C so that the electrolyte, a eutectic mixture of lithium chloride and potassium chloride, is molten and hence has a high ionic conductivity. Researchers soon discovered that the liquid sulfur from the cathode was dissolving in the electrolyte, but it was some time before they overcame this instability by using a solid iron sulfide compound (either FeS₂ or FeS) as the cathode. Now generally known as a lithium-metal sulfide cell, these cells suffer from theoretical specific energies reduced by factors of 2 and 3, respectively.

Liquid lithium anodes have likewise been subject to degradation due to loss of lithium, a problem which scientists solved by using solid lithium-aluminum alloys for the negative electrode, but at the cost of another factor of 2 in the specific energy.

William Walsh of ANL, which has the largest lithium-metal sulfide program in the United States, summarized the current status of these cells as produced in that laboratory. Up from about 30 watthours per kilogram 3 years ago, engineering scale cells with a capacity of 130 ampere-hours and 200 watt-hours which have specific energies up to 155 watthours per kilogram are now being tested by ANL scientists. Similarly, researchers there have achieved an enhancement of a factor of 10 over the 1974 lifetime in cells with lower specific energies that have run for 5000 hours and are still going. Unfortunately, specific energy and lifetime tend to be inversely related.

According to Paul Nelson and Richard Ivins of ANL, much of the present effort

New Funding Sparks Battery Research

If there is any correlation between the level of support for research and development and the emergence of a viable product, advanced storage batteries for utilities and electric vehicles may come into existence in the decade beginning about 5 years from now.

Two years ago, before the establishment of the Energy Research and Development Administration (ERDA) and when the Electric Power Research Institute (EPRI), Palo Alto, California, was newly born, estimates of funding for advanced batteries totaled something less than \$2 million. This year, ERDA has allotted \$8.4 million, and EPRI is spending \$3.3 million (of which about two-thirds is matched by cost-sharing by the contractors). Additional support comes from the National Science Foundation's RANN program and from independent industrial research.

In addition, a battery energy storage test (BEST) facility costing \$6.5 million will soon be under construction. Supported equally by ERDA and EPRI with an additional \$1 million contribution from the Public Service Electric and Gas Company of New Jersey, BEST will begin operation in 1979 as a part of the New Jersey electric power grid. The facility will have three bays, each servicing a 1-megawatt battery system with a storage capacity of 10 megawatt-hours. Advanced lead-acid batteries will be evaluated first, but the high-temperature batteries that many see as the eventual solution to energy storage problems (see story) probably will not be tested before 1981, and will not appear in commercial quantities before 1985.

Testing and demonstration of new batteries to power electric vehicles face a less certain future. A year ago, Representative Mike McCormack (D-Wash.) introduced a bill designed to stimulate interest in electric vehicles. After substantial revisions in committee, the McCormack Bill (H.R. 8800) passed the House last September. Since then, however, it has languished in the Senate Commerce Committee, reputedly as a political hostage for a Senate bill that the House committee is sitting on. A source on the Commerce Committee says he expects action to perk up later this spring.

As passed in the House, H.R. 8800 provides for \$160 million to be spent on electric vehicle research, development, and demonstration over 5 years. Another \$60 million would go toward loan guarantees for manufacturers undertaking production of such vehicles. In the demonstration phase, the bill provides that within 12 months after enactment, a selection of currently available electric or hybrid vehicles of various types be procured; that within 15 months, procurement begin on 2500 vehicles designed with the best current technology; and that within 42 months, procurement begin on an additional 5000 or more vehicles designed with advanced technology. These vehicles are to be distributed throughout government agencies and perhaps to individuals as well for testing and evaluation.

Battery researchers predictably say that these large-scale purchases come too soon and that no advanced batteries could be ready in time to be tested under the provisions of H.R. 8800. Some worry that, if no vehicles with acceptable performance can be engineered in this short time, electric vehicles and batteries may get an undeservedly bad name.

Nonetheless, ERDA has already issued requests for proposals for several near-term batteries, including advanced lead-acid batteries and alkaline electrolyte batteries with nickel cathodes and either iron or nickel anodes. These are expected to be ready for demonstration in commercial quantities in from 2 to 5 years, and preparations for a national battery test facility at the Argonne National Laboratory near Chicago to evaluate them prior to large-scale production have begun.—A.L.R.

there is in cooperating with commercial battery manufacturers to develop engineering prototype cells, which researchers hope will be ready to test on vehicles in about 2 years. (Full-size batteries may be available for testing by 1981.)

A number of substantial problems remain to be solved, however, which involve finding inexpensive, readily available materials that can function in the highly corrosive environment found in high-temperature lithium-metal sulfide cells. For example, the favored separator material is boron nitride in the form of a thin cloth that costs in the neighborhood of \$500 per kilogram to make.

As a result, it now costs about \$2000 per kilowatt-hour to make experimental lithium-metal sulfide cells of the new design. High-volume production could drop the cost to \$30 per kilowatt-hour, according to Walsh.

While large-scale production will have the largest effect on the final cost, technical innovations could also be important. Researchers at Atomics International division of Rockwell International, Canoga Park, California, are enthusiastic about the use of lithium-silicon (Li₄Si) anodes, which could raise the specific energy by 50 percent.

Research in the United States on sodium-sulfur cells is at a slightly lower funding level than that on lithium-metal sulfide. But, internationally, research on the sodium-sulfur system receives about twice as much financial support as research on lithium-metal sulfide.

At 750 watt-hours per kilogram, the theoretical specific energy for sodiumsulfur is comparable to that of lithiummetal sulfide. In most sodium-sulfur cells, a solid electrolyte made from a ceramic called beta-alumina (Na₂O- $11Al_2O_3$) is used. The ceramic requires an operating temperature between 300° and 400°C in order to increase the sodium ion conductivity of the electrolyte to a useful level.

Sodium-sulfur systems have at least two advantages over lithium-metal sulfide. First, there is no question as to the availability of materials, whereas the availability of lithium has recently been questioned. Second, the solid electrolyte permits a simpler cell design because it also serves as a separator and as a container for one of the liquid electrodes (usually the sodium) and because it prevents self-discharge of the cell.

Cracking of the alumina during recharging, however, has been a major factor limiting cell lifetime, and the cost of the material is high. Steven Weiner of the Ford Motor Company, which has the largest sodium-sulfur program in the United States, reported that, at current prices, materials for a laboratory cell would cost \$62 per kilowatt-hour, of which more than \$50 is for the beta-alumina.

On the whole, the development status of the sodium-sulfur cell is probably comparable to that of the lithium-metal sulfide cell. Laboratory cells with a specific energy of 80 watt-hours per kilogram, cells with a specific power of 140 watts per kilogram, and cells with a lifetime of more than 10.000 hours have been made at Ford. These cells, however, were in glass containers, rather than metal, and were operated in a partially discharged mode that probably will be impractical for actual batteries. The restricted operation results from the existence of two immiscible phases in the molten sulfur as sodium accumulates there during discharge. When the cell is being recharged, one phase coats the current collector at the sulfur electrode and prevents completion of the recharging reaction. Special geometries for the current collector may overcome this problem.

In other respects, materials problems are similar to those of lithium-metal sulfide. In neither case do observers expect to see batteries available in large numbers in the United States before about 1985. For one thing, little testing of multiple cells has been done, and batteries, of course, are multiple cells connected in series or parallel. A major problem in batteries is cell reversal, which occurs when one cell dies but continues to be driven (overdischarged) by the other cells. Not only is the battery performance lowered, but damage to the other parts of the battery can occur.

The sodium-sulfur research and development program in the United Kingdom is comparable in size to that in the United States, but the British effort has been a large one for a longer time. For this reason and because of the somewhat different goals (and thus different emphases) of researchers in the United Kingdom, sodium-sulfur batteries may appear there before they do in the United States.

For example, the British program has emphasized engineering along with basic battery research and thus has been addressing engineering and economic problems not yet dealt with by the Americans.

In addition, the United Kingdom is unique among the industrialized nations in having a large fleet of battery-powered trucks (60,000 grocery and milk delivery vans), all of them driven by lead-acid batteries. In this tradition, the British are orienting their sodium-sulfur battery program toward large vehicles, such as trucks, buses, and trains, and this orientation reduces their performance and cost goals. Because large vehicles can carry proportionately more weight in batteries than small ones, a somewhat reduced specific energy can be tolerated. And, because of the higher price of gasoline in Britain (\$1.55 per U.S. gallon in June 1975), costs of \$50 to \$70 per kilowatt-hour are acceptable for large vehicles.

According to A. R. Tilley of the British Railways Board, Derby, his organization, Chloride Silent Power Ltd., Runcorn, and the U.K. Atomic Energy Authority, Harwell, are participating in an integrated research effort. Engineers have settled on a fixed cell design, and this has permitted them to begin building large numbers of cells in a partially automated production facility. These cells are suitable only for vehicles, however. Also completed are two 10-kilowatt batteries, with 50-kilowatt batteries to be built next year and tested in a van, beginning 2 years from now. Testing of an electric-powered train in a laboratory mock-up is to begin then as well.

British Lead in Sodium-Sulfur

This timetable seems to suggest that the British are 3 to 4 years ahead of their American counterparts in sodium-sulfur development. Some skeptical observers caution, however, that the U.K. scientists may have to go back to the laboratory later on to work on the technical details that U.S. researchers are concentrating on now.

There are high-temperature batteries other than lithium-metal sulfide and sodium-sulfur. For example, John Werth of ESB Incorporated, Yardley, Pennsylvania, reported on a cell that operates at 200°C with a sodium anode, a beta-alumina electrolyte, and a mixture of antimony trichloride, aluminum trichloride, and sodium chloride at the cathode. The relatively low operating temperature could simplify cell construction considerably. For example, polymer seals rather than ceramic seals could be used.

Although the ANL symposium was heavily dominated by high-temperature batteries, in the last 2 years, there has been a resurgence of interest in ambient temperature batteries on the part of those not willing to wait 10 years for an advanced battery. The largest Electric Power Research Institute program, for example, is for the development by Energy Development Associates, Madison Heights, Michigan, of a battery with a zinc anode, a gaseous chlorine cathode, and an aqueous zinc chloride solution as the electrolyte.

But improved lead-acid batteries may yet be the primary hope for near-term advanced batteries. A. C. Simon of the Naval Research Laboratory, Washington, D.C., pointed out that, over the years, the improvements in lead-acid batteries have been mainly in engineering and design. Little basic research on how lead-acid batteries work has been done. Thus, the possibility of substantial improvements ought not to be discounted prematurely. In Europe, the British, French, and German battery companies have been doing the kind of engineering refinements Simon referred to and have made lead-acid batteries with specific energies near 40 watt-hours per kilogram and lifetimes of more than 1500 cycles that are being tested in trucks and buses.

Meanwhile, the Japanese have had a large government-sponsored electric vehicle development program under way since 1971. To be concluded in 1977, this program was undertaken primarily to reduce pollution and noise in the cities. The Japanese are also said to be readying themselves for an early start in what they see as a potentially large worldwide electric vehicle industry.

As phase one of their project, in 1974, researchers in Japan demonstrated personal cars, trucks, and buses powered by lead-acid batteries. The batteries were reported to have specific energies near 60 watt-hours per kilogram, some 50 percent higher than the best European batteries. Some skeptics point out, however, that the cycle lifetime of these batteries was not reported and might be poor. Researchers have long known that impressive specific energies could be achieved at the sacrifice of a respectable lifetime.

Nobody knows when an advanced battery will be ready nor what it will be. There are many candidates that have not been mentioned here. For example, A. J. Appleby of the French Compagnie Générale d'Electricité, Marcoussis, described a vehicle battery consisting of a zinc anode and an air cathode. A slurry mixture of the zinc and a potassium hydroxide electrolyte from a reservoir circulates rapidly over a tubular metal current collector, which is the innermost of several concentric layers, inside a connected series of 2-centimeter diameter metal tubes-in effect, a rechargeable fuel cell. Appleby cited a specific energy of about 110 watt-hours per kilogram and a cost of \$40 per kilowatt-hour. Several observers were excited about the way in which the French researchers have overcome several long-standing problems of the zinc-air system.

-Arthur L. Robinson