
CHAPTER 37

INTRODUCTION TO ADVANCED BATTERIES FOR EMERGING APPLICATIONS

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The types and number of applications requiring improved or advanced rechargeable batteries are constantly expanding. The new and evolving applications include electric and electric hybrid vehicles, electric utility energy storage, portable electronics, and storage of electric energy produced by renewable energy resources such as solar or wind generators. In addition, the performance, life and cost requirements for the batteries used in both new and existing applications are becoming increasingly more rigorous. Commercially available batteries may not be able to meet these performance requirements. Thus, a need exists for both conventional battery technology with improved performance and advanced battery technologies with characteristics such as high energy and power densities, long life, low cost, little or no maintenance, and a high degree of safety.

37.1 PERFORMANCE REQUIREMENTS FOR ADVANCED RECHARGEABLE BATTERIES

Battery performance requirements are application dependent. For example, electric vehicle batteries need (1) high gravimetric and volumetric energy densities to provide adequate vehicle driving range, (2) high power density to provide acceleration, (3) long cycle life with no maintenance, and (4) low cost. On the other hand, batteries for electric hybrid vehicles require (1) very high gravimetric and volumetric power densities to provide acceleration, (2) capability of accepting high power repetitive charges from regenerative braking, (3) very long cycle life with no maintenance under shallow cycling conditions, and (4) modest cost. Batteries for electric-utility applications must have (1) low first cost, (2) high reliability when operated in megawatt-hour-size systems at 2000 V or more, and (3) high volumetric energy and power densities. Portable electronic devices require low-cost and readily available, lightweight batteries that have both high volumetric and gravimetric energy and power densities. Safe operation and minimal environmental impact during manufacturing, use and disposal are mandatory for all applications.

37.1.1 Batteries for Electric and Electric Hybrid Vehicles

The major advantages of the use of electric vehicles (EVs) and electric hybrid vehicles (EHVs) are reduced dependence on fossil fuels and environmental benefits. For electric vehicles, energy from electric utilities or renewable sources would be used for battery charging. These facilities can be operated more efficiently and with better control of effluents than automotive engines.

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Electric hybrid vehicles are expected to require less gasoline per mile of travel than current vehicles. This not only results in lower petroleum consumption, but also in lower emissions of undesirable pollutants.

Deteriorating air quality in a number of regions of the US in the mid- to late-1980s led to an increasing number of federal and state regulations designed to effect reductions of emissions from automobiles. The most important of the regulations from the perspective of the developers of EV batteries was the “EV Mandate” promulgated by the California Air Resources Board (CARB). In 1990, CARB issued a regulation requiring, among other things, that 2% of the passenger cars and light trucks offered for sale in 1998 would have to be battery-powered EVs. In order to be able to meet this regulation, the US auto companies, GM, Ford, and Chrysler, formed the United States Advanced Battery Consortium (USABC)^b, to expedite the development of EV batteries. In 1996, and again in 2000, the date for the first level (2%) of EV offerings and the other provision of the EV Mandate were delayed by three to four years, in part because it took longer than expected to develop EV batteries with the characteristics defined by the USABC. However, the delays were also necessitated by the poor sales of the EVs that were offered by both domestic and foreign auto makers. In fact, the most recent EV regulation from CARB appears to make the offering of EVs to be voluntary, rather than mandatory, apparently because EHV's are now regarded as a more viable competitor to gasoline-fueled autos with internal combustion engines than all-battery EVs.

During the 1990s, several battery development programs were conducted by the USABC. These programs were directed toward developing mid-term and long-term battery options for EVs. The batteries for the mid-term were originally intended to achieve commercialization in electric vehicles competitive with existing internal combustion vehicles by 1998. The long-term battery program was directed toward developing advanced batteries projected for commercialization starting in 2002. Both of these objectives were later relaxed due to continuing technical challenges, difficulties in meeting cost goals, and the changing political climate. The USABC criteria for performance of electric-vehicle batteries are shown in Table 37.1.¹

The severity of the performance requirements for EV batteries is typified by the dynamic stress test (DST) to which batteries developed with USABC funding were subjected. One cycle for the DST is shown in Fig. 37.1.² The DST simulates the pulsed power charge (negative percentage, required for regenerative braking) and discharge (positive percentage, for acceleration and cruising) environment of electric vehicle applications and is based on the Federal Urban Driving Schedule automotive test regime. The power levels are based on the maximum rated discharge power capability of the cell or battery under test. The vehicle range on a single discharge can be projected from the number of repetitions a battery can complete on the DST before reaching the discharge cutoff criteria. This test provides more accurate cell or battery performance and life data than constant-current testing because it more closely approximates the application requirements.

A multi-year program to develop EHV batteries was initiated by a government-industry cost-shared program in 1993. The EHV battery program is conducted by the Partnership for Next

^b The USABC is a partnership between General Motors Corporation, Ford Motor Company, and Daimler-Chrysler Corporation with participation by the Electric Power Research Institute and several utilities. It is funded jointly by the industrial companies and the U.S. Department of Energy.

Generation Vehicles (PNGV). The technical targets that were released by the PNGV for EHV batteries in 1999 are shown in Table 37.2.³ The requirements for EHV are even more stringent than indicated by the DST for EVs. The severity of these targets, particularly with regard to power capability, is more readily appreciated when it is realized that the power-assisted EHV targets translate to a specific power requirement of almost 750 W/kg. As described in the Table, two EHV operating modes are being considered: "power assist" and "dual mode". The power assist mode involves partial load leveling between the two power systems and includes recovery of braking energy. In this operating scenario, the battery power demands are very high in order to contribute to the acceleration demands of the vehicle. The dual mode option involves extensive load leveling by the two power systems and a second mode to operate the vehicle on battery power only. In this mode, the battery power demands are lower and the energy requirements more significant in order to provide an appreciable range for the vehicle when powered by the battery only.

37.1.2 Electric-Utility Applications

The use of battery energy storage in utility applications allows the efficient use of inexpensive base-load energy to meet peak shaving and other applications, which reduces utility costs and permits compliance with environmental regulations. Analyses have determined that battery energy storage can benefit all sectors of modern utilities: generation, transmission, distribution, and end use.⁴ The use of battery systems for generation load leveling alone cannot justify the cost of the system. However, when a single battery system is used for multiple, compatible applications, such as frequency regulation and spinning reserve, the system economics are predicted to be favorable in some cases.

The energy and power requirements of batteries for typical electric-utility applications are shown in Table 37.3. The concept of load leveling is illustrated in Fig. 37.2a, and a simplified test regime simulating a frequency regulation and spinning reserve application is illustrated in Fig. 37.2b. The frequency regulation and spinning reserve test profile simulates these two utility applications on a sub-scale battery in order to predict performance, life, and thermal effects. Charge (positive power) and discharge (negative power) vary according to a specified regime and provide a realistic environment for batteries used in these applications.

Commercially available lead-acid batteries can satisfy the requirements for certain utility energy storage applications and are being used in several demonstration projects worldwide. The use of advanced batteries offers still greater potential for reduced cost and could enable market opportunities to be enhanced. These opportunities result from the predicted advantages of advanced batteries for lower cost, smaller system footprint, no maintenance, and high reliability even when used with highly variable duty cycles.

37.1.3 Renewable Applications

Battery storage provides significant benefits in solar, wind, and other renewable generation systems where the energy source is intermittent. The battery is charged when the source is generating energy. This energy can then be discharged when the source is not available. Operating characteristics vary widely depending on application. For photovoltaic systems, typical applications include village power, telemetry, telecommunications, remote homes, and lighting. Operating characteristics for photovoltaic systems are shown in Table 37.4.⁵ Detailed

requirements are being developed, and considerations such as high energy efficiency, low self-discharge, low cost, long cycle and calendar life, and no maintenance are important.

37.1.4 Portable Electronics

The demand for batteries used in portable electronics, such as communication, photographic and video equipment, computers, and many other consumer, industrial, and military devices, has been increasing dramatically since the mid-1980s and is now a substantial market for advanced rechargeable batteries. Progress in the miniaturization of electronics resulted in a demand for batteries that were smaller, weighed less, and offered longer service. Also important are power output, storage life, reliability, safety, and cost. Currently available conventional primary and secondary batteries did not meet all of these needs, and new battery systems with advanced performance characteristics were required. Valve-Regulated lead-acid (VRLA) batteries (primarily in Europe) and nickel/cadmium batteries (more popular in North America) are still used extensively for less demanding applications such as power tools and electric toothbrushes. During the 1990s, nickel/metal hydride batteries became the system of choice for applications requiring higher performance (cell phones, laptop computers), but by the early 2000s, sales of lithium-ion batteries became comparable with those for nickel/metal hydride batteries. Portable fuel cells, larger versions of which are being developed for advanced EHV and stationary (distributed electricity generation) applications, may become a factor for powering portable electronic equipment in the future. Chapter 42 provides a discussion of portable fuel cells.

37.2 CHARACTERISTICS AND DEVELOPMENT OF ADVANCED RECHARGEABLE BATTERIES

A number of battery chemistries and technologies are being explored and developed in order to meet the requirements described in the previous section. These activities can be categorized as follows:

- 1.** Near-term activities to improve the performance of existing conventional technologies for use within the next few years.
- 2.** Midterm activities to complete the development of those advanced battery technologies that are not commercialized but, with necessary progress, can be introduced to the market within 5-10 years.
- 3.** Long-term activities to develop new electrochemical technologies such as refuelable batteries and fuel cells which offer the potential of higher energy and power, but which require significant development before commercialization.

In the United States, the development of batteries for EVs and EHV has been mostly carried out under the auspices of the USABC since the early 1990s, see above. In addition to the USABC, the Advanced Lead-Acid Battery Consortium (ALABC) was formed by the International Lead Zinc Research Organization and the lead-acid battery industry to develop that technology for EV applications.

Significant effort has gone into the development of many advanced batteries for these applications. In recent years, decisions were made to focus on lead-acid, nickel-metal hydride, and lithium-ion. These technologies have become the most likely to be used in either EVs or

EHV's due to a combination of performance capability, safety, life, and cost. Earlier development of high temperature and flowing electrolyte technologies for EVs or EHV's has been mostly redirected or discontinued due to these decisions.

In a recent survey⁶ of alternative propulsion vehicles, of 68 vehicle models, about 2/3 were hybrid or all-electric. Only 26 of the 68 are currently available; the rest are being planned. Of those planned, about 35% are EVs and the rest are either gasoline/hybrid or diesel hybrid. Three battery types were identified as being used in these vehicles. About half use lead-acid batteries, about 40% use nickel/metal hydride, and the rest use lithium-ion. Of the vehicles available at this time, over 60% use lead-acid, 30% use nickel-metal hydride, and the rest lithium-ion. Some of the vehicles in the planning stage may use fuel cells as part of the power system.

A recent study⁷ has evaluated the possible advances in vehicle technologies by the year 2020 with respect to alternative propulsion systems, and characterized their potential for efficiency improvements, carbon emissions reductions, and cost changes. While the uncertainty in the estimates is significant (as high as plus or minus 30%), the hybrid electric system is predicted to have about a 33% lower life-cycle energy use and about 20% lower life-cycle carbon emissions compared to a pure electric. The predicted cost per km driven of the pure electric is about 15% higher than the hybrid. These results agree in principle with cost and lifetime experiences with battery-powered electric vehicles. Further, due to the inherently limited range of pure electrics and uncertainty regarding possible battery breakthroughs in the foreseeable future, the emphasis in alternative propulsion technologies has changed to focus on EHV concepts.

In stationary applications, there has been significant support for developing batteries for electric utility energy storage from the U.S. DOE through Sandia National Laboratories since the 1980s, and from EPRI (formerly the Electric Power Research Institute) in the 1980s and early 1990s. In 1991, the DOE/Sandia and EPRI cooperatively worked with the utility industry to form the Utility Battery Group that promoted the exchange of information and data on technologies for these applications. Now named the Energy Storage Association, this group includes electricity providers, technology developers, and international participants carrying out the promotional objectives for a wide range of energy storage technologies.

The DOE has continued to provide research and development support for batteries, and recently, other energy storage technologies, for utility energy storage applications⁸. In the mid-1990s, the DOE program broadened its scope and became the Energy Storage Systems Program. Working through Sandia, the Program has collaborated with industry to develop battery technologies, power electronics, and controls, and is now evaluating flywheels and superconducting magnetic energy storage concepts. Battery technologies such as lead-acid, zinc/bromine, and sodium/sulfur have been intensively developed and placed in complete systems for operation in utility and off-grid systems. Applications of interest include power quality, peak shaving, back-up power, and a number of other utility-related uses. In partnership with industry, systems ranging in capacity from hundreds of kW/kWh to tens of MW/MWh have been successfully built, tested, and characterized and some are now being commercialized by industry. The DOE Program continues to work closely with industry and the Energy Storage Association to develop and test promising technologies and systems for many increasingly important utility energy storage uses.

In Japan, the development of advanced secondary battery systems for electric-utility applications was carried out from 1981-91 as a part of the 'Moonlight Project'⁹. Development on four systems proceeded through 60-kW class modules, and 1-MW pilot plants were built for two systems: sodium/sulfur and zinc/bromine. Testing was satisfactorily concluded in March 1992 with 76% energy efficiency (211 cycles) for sodium/sulfur and 66% energy efficiency (158 cycles) for zinc/bromine. Areas for further research were identified, and improvements in reliability, maintainability, compactness, and cost reduction are expected to yield systems that are practical for utility applications. Following completion of the Moonlight Project, work in Japan focused on sodium/sulfur batteries with funding from the Tokyo Electric Power Company and, to a much smaller extent, on redox batteries with funding from the Kansai Electric Power Company. There were, as far as is known, no other national efforts on batteries for the advanced applications, although there were privately-funded efforts on redox batteries for utility applications in the United Kingdom and Australia during the 1990s. The results of these efforts and others are discussed in this section of the Handbook.

Several test facilities are in existence in the U.S.A. for the evaluation of improved and advanced battery systems. Batteries of all types are tested at Argonne National Laboratory, Idaho National Engineering Laboratory, Lawrence Berkeley National Laboratory, and Sandia National Laboratories. Certain tests for satellite and military applications are conducted at the Naval Weapons Support Center in Crane, Ind. There are also specialized testing facilities that are set up by companies in the private sector. There are also test facilities in some other countries.

The major battery technologies that have been considered from time to time for electric-vehicle, utility energy storage, and renewable energy storage applications are listed in Table 37.5, together with the chapter numbers in the Handbook in which each is discussed. The companies that are most active in the development of improved and/or advanced batteries for these applications are listed in Table 37.6. U.S. National Laboratories and similar organizations that are involved in advanced battery R&D are also shown in Table 37.6.

Comparative background data for rechargeable battery technologies are listed in Table 37.7¹⁰. The performance of these battery systems is compared in a plot of specific power vs. specific energy in Fig. 37.3. More information on each technology is contained in Table 37.8 with data for technologies for current and emerging applications, and Table 37.9, which describes other technologies of interest.

37.3 NEAR-TERM RECHARGEABLE BATTERIES

The major candidates for near-term applications are those rechargeable battery technologies that are now available commercially. Most of these require some improvement or adaptation to be used in the emerging applications.

Of the currently commercialized battery chemistries, the lead-acid battery is the most widely used and economical and has an established manufacturing base. It is being used in both mobile and stationary applications. Its main disadvantage is low specific energy. Lead-acid batteries with improved performance are being developed for EVs and EHV. High surface area electrodes with thin active material layers are being investigated using materials and designs such as lightweight fiber-glass reinforced lead wire grids, thin metal foils, bipolar plates, forced-flow electrolyte systems and unique cell assemblies. Methods for fast-charging lead-acid batteries are

being developed because the ability to rapidly recharge batteries in as little as an hour is considered an important factor for the acceptance of electric vehicles.

Nickel/cadmium batteries are being considered for use in large EHV's such as city buses¹¹ and for electric utility storage applications.¹² They offer good power density, maintenance-free operation over a wide temperature range, long cycle life, and a relatively acceptable self-discharge rate. Another advantage is their capability for rapid recharge. The specific energy of the nickel/cadmium battery is higher than that of the lead-acid battery but, as with most nickel batteries, their initial cost is much higher. Their longer cycle life may offset some of this cost on a life cycle basis. New electrode developments such as plastic-bonded and nickel foam electrodes promise to improve performance and reduce costs. The use of cadmium presents environmental challenges that will have to be resolved.¹³

Nickel/hydrogen batteries have been used primarily in satellite applications. They are highly reliable, have a long cycle life, and are able to tolerate deep discharges. They have a high initial cost due to expensive catalysts used in the hydrogen electrode and the nickel positive electrode. Their low volumetric energy density and high self-discharge rate as well as the need to store hydrogen in the interior of the cell are barriers to the wider deployment of this system.

Some of these limitations are overcome by the nickel/metal hydride battery. This battery has characteristics similar to the nickel/cadmium battery, but it is cadmium-free and has a higher specific energy. It does not match the nickel/cadmium battery in power density and requires more careful charge control to prevent overcharge and overheating. Costs should be similar to those of other nickel batteries.

37.4 ADVANCED RECHARGEABLE BATTERIES- GENERAL CHARACTERISTICS

Advanced rechargeable batteries can be classified into three main types – advanced aqueous electrolyte systems, or as they are more-commonly known, flow batteries, high-temperature systems, and ambient-temperature lithium batteries.

37.4.1 Flow Batteries

These advanced aqueous-electrolyte battery systems have the advantage of operating close to ambient temperature. Nevertheless, complex system design and circulation of electrolyte are needed to meet performance objectives. Work on developing flow batteries started with the invention of the zinc/chlorine hydrate battery in 1968.¹⁴ This system was the subject of development for EV and electric utility storage applications¹⁵ from the early-1970s to the late-1980s in the United States, and from 1980 to 1992 in Japan¹⁶, but has now been abandoned in favor of other flow battery chemistries that appear more attractive. Three main types of flow batteries continue to be developed: zinc/bromine, vanadium-redox, and Regenesys.

The zinc/bromine battery technology is currently being developed primarily for stationary energy storage applications. (See Chapter 39.) The system offers good specific energy and design flexibility, and battery stacks can be made from low-cost and readily available materials using conventional manufacturing processes. Bromine is stored remotely as a second-phase polybromide complex that is circulated during discharge. Remote storage limits self-discharge

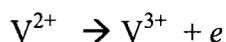
during standby periods. An added safety benefit of the complexed polybromide is greatly reduced bromine vapor pressure compared to that of pure bromine.

Another type of aqueous flowing electrolyte systems is the redox flow technology. There are several systems of this type, only one of which, the Vanadium Redox Battery or VRB as it is known, has any significant development continuing as of 2001. Work on this category of flow battery started with a development program at NASA¹⁷ on a system using FeCl₃, as the oxidizing agent (positive) and CrCl₂, as the reducing agent (negative). The aim of this work was to develop the redox flow batteries for stationary energy storage applications. The term "redox" is obtained from a contraction of the words "reduction" and "oxidation." Although reduction and oxidation occur in all battery systems, the term "redox battery" is used for those electrochemical systems where the oxidation and reduction involves only ionic species in solution and the reactions take place on inert electrodes. This means that the active materials must be mostly stored externally from the cells of the battery. Although redox systems are capable of long life, their energy density is low because of the limited solubility of the active materials typically involved¹⁸.

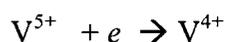
In Japan, development of iron/chromium redox flow battery technology was included as part of the Moonlight Project⁹ in the 1980s. The goal of this work was electric utility energy storage. Improvements made in the course of the Moonlight Project included new electrode materials and a reduction in the requirement for pumping power.¹⁹ A 60kW battery was tested²⁰ and 1-MW system was designed²¹, but the redox flow technology was not chosen to advance to the 1-MW pilot plant stage.²²

Other redox systems were also proposed in the past, such as the zinc/alkaline sodium ferricyanide [Na₃Fe(CN)₆·H₂O] couple, and initial development work was performed.²³ However, none of these efforts proved successful, mainly because of difficulties resulting from the efficacy and resistance of the ionic exchange membranes, until the development of the vanadium redox battery, or VRB, by the University of New South Wales, Australia, in the late 1980s. Almost concurrently with this, development work started on VRBs at Sumitomo Electric Industries (SEI) of Osaka, Japan²⁴. Starting in the mid-1990s, VRB development has also been conducted at Mitsubishi Chemical's Kashima-Kita facility, although at a lower level of effort than at SEI.

The electrolytes in the positive and negative electrode compartments of VRBs are different valence states of vanadium sulfate. Both solutions are 2M in concentration and contain sulfuric acid as a supporting electrolyte. The electrode reactions occur in solution, with the reaction at the negative electrode in discharge being:



and at the positive electrode:



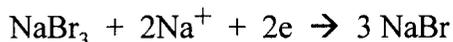
Both reactions are reversible on the carbon felt electrodes that are used. An ion-selective membrane is used to separate the electrolytes in the positive and negative compartments of the cells. Cross-mixing of the reactants would result in a permanent loss in energy storage capacity for the system because of the resulting dilution of the active materials. Migration of other ions

(mainly H^+) to maintain electroneutrality, however, must be permitted. Thus, ion-selective membranes are required.

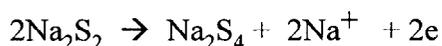
A schematic of a VRB system is shown in Fig. 37.4²⁴. The construction of the cell stacks is bipolar. The electrolyte solutions are stored remotely in tanks and are pumped through the cells when needed. The capacity of the redox flow system depends on the size of the storage tanks. The volume of electrolyte needed is large and results in a low energy density for this technology.

Several multi-kW systems have been built and tested by SEI and Mitsubishi Chemical. A photograph of an SEI 100kW-8hr VRB system is shown in Figure 37.5. The tanks for the two electrolytes are not in view in the photograph, since they are installed in a sub-basement below the level of the battery stacks and the AC-DC-AC converter that are shown.

The third type of flow battery that it is being actively developed is the polysulfide-bromine or Regenesys system of Innogy (formerly National Power) of the United Kingdom. Innogy has been involved in the development of this redox-like system, in which both reactants and products of the electrode reactions remain in solution, since the early 1990s. Regenesys is not truly a redox system since both the positive and negative reactions involve neutral species, unlike a true redox system that involves only dissolved ionic species. The discharge reaction at the positive electrode is:



and that at the negative is:



Sodium ions pass through the cation exchange membranes in the cells to provide electrolytic current flow and to maintain electroneutrality. The sulfur that would otherwise be produced in discharge dissolves in excess sodium sulfide that is present to form sodium polysulfide. The bromine produced at the positives in charge dissolves in excess sodium bromide to form sodium tribromide. A block diagram of a Regenesys energy storage plant is shown in Figure 37.6.

Innogy built many multi-kW batteries in their development program in the 1990s, with this part of the effort culminating in construction of 100kW cell stacks (modules) with electrodes of up to one square meter in area²⁵. See Figure 37.7. Innogy has announced that by the end of 2002 they should have completed construction and acceptance testing of a 15MW, 120MWh Regenesys energy storage plant at the Little Barford power station in the United Kingdom.

37.4.2 High-Temperature Systems

High-temperature systems operate in the range of 160-500°C and have high-energy density and high specific power compared to most conventional ambient-temperature systems. The negative electrode material is an alkali metal, such as lithium or sodium, which has a high voltage and electrochemical equivalence. Aqueous electrolytes cannot be used because of the chemical reactivity of water with alkali metals. Molten salt or solid electrolytes that require high temperatures are used instead. Benefits are high ionic conductivity, which is needed for high power density, and insensitivity to ambient temperature conditions. However, high operating temperatures also increase the corrosiveness of the active materials and cell components and thereby shorten the life of the battery. Also, thermal insulation is needed to maintain operating

temperatures during standby periods. The main high-temperature battery systems are the sodium/beta and lithium/iron sulfide systems.

The sodium/beta battery system includes designs based on either the sodium/sulfur or the sodium/metal chloride chemistries. The sodium/sulfur technology has been in development for over 25 years and multi-kW batteries are now being produced on a pilot plant scale for stationary energy storage applications.²⁶ At least two 8MW/40MWh sodium/sulfur batteries have been put into service for utility load leveling by TEPCO in Japan.

Sodium/sulfur technology is also considered a possible successor to nickel/hydrogen technology for aerospace applications because sodium/sulfur batteries have two to three times the specific energy of nickel/hydrogen batteries. Sodium/nickel chloride is a relatively new variation of the sodium/beta technology and was being developed mainly for electric-vehicle applications. There has not been nearly the effort on this chemistry as on the sodium/sulfur battery.

Sodium/sulfur and sodium/metal chloride technologies are similar in that sodium is the negative electrode material and beta-alumina ceramic is the electrolyte. The solid electrolyte serves as the separator and produces 100% coulombic efficiency. Applications are needed in which the battery is operated regularly. Sodium/nickel chloride cells have a higher open-circuit voltage, can operate at lower temperatures, and contain a less corrosive positive electrode than sodium/sulfur cells. Nevertheless, sodium/nickel chloride cells are projected to be more expensive and have lower power density than sodium/sulfur cells.

The lithium/iron sulfide rechargeable battery system is another high-temperature system and must be operated above 400°C so that the salt mixture (LiCl-KCl) used as an electrolyte remains molten. The negative electrode is lithium, which is alloyed with aluminum or silicon, and the positive electrode can be either iron monosulfide or iron disulfide. No development is being performed on these technologies at this time.

37.4.3 Ambient-Temperature Lithium Batteries

Rechargeable lithium batteries, which operate at or near ambient temperature, have been and continue to be developed because of their advantageous energy density and charge retention compared to conventional aqueous batteries. The lithium-ion version of this chemistry has been commercialized for consumer electronic and other portable equipment in small button and prismatic cylindrical sizes. The attractive characteristics of rechargeable lithium batteries make them promising candidates for aerospace, electric vehicles, and other applications requiring high-energy batteries. As discussed elsewhere in the Handbook, high energy- and power-densities have been achieved with rechargeable lithium cells, despite the low conductivity of the organic and polymer electrolytes that are used to ensure compatibility with the other components of the lithium cell. Scaling up to the sizes and power levels while achieving the cycle life required for electric vehicles and maintaining the high degree of safety needed for all batteries remains a challenge.

A number of different approaches are being taken in the design of rechargeable lithium batteries. The rechargeable lithium cell that can deliver the highest energy density uses metallic lithium for the negative electrode, a solid inorganic intercalation material for the positive electrode, and an organic liquid electrolyte. Manganese dioxide appears to be the best material for the positive electrode based on performance, cost, and toxicity. Poor cycle life and safety,

however, are concerns with this type of cell because the porous, high-surface-area lithium that is plated during recharge is highly reactive and susceptible to forming dendrites which could cause internal short-circuiting.

Another approach is the use of a solid polymer electrolyte. These electrolytes are considered to have a safety advantage over the liquid electrolyte because of their lower reactivity with lithium and the absence of a volatile and sometimes flammable electrolyte. These electrolytes, however, have a lower conductivity that must be compensated for by using thinner electrodes and separators and by having larger electrode areas.

The approach that has been commercialized successfully is the "lithium-ion" cell. This cell uses a lithiated carbon material in place of metallic lithium. A lithiated transition metal intercalation compound is used for the positive active material, and the electrolyte is either a liquid aprotic organic solution or a solid polymer electrolyte. Lithium ions move back and forth between the positive and negative electrodes during charge and discharge. As metallic lithium is not present in the cell, lithium-ion cells are less chemically reactive and are safer and have a longer cycle life than other options.²⁷

For EVs, EHV's and electric utility energy storage, safety, cost, availability, and reliability as well as battery performance and ease of manufacture will be the most important considerations in the final choices of cell and battery design and components.

37.5 REFUELABLE BATTERIES AND FUEL CELLS- AN ALTERNATIVE TO ADVANCED RECHARGEABLE BATTERIES

Another category of aqueous battery systems is the metal-air battery. These batteries are noted for their high specific energy as they utilize ambient air as the positive active material, and light metals, most commonly aluminum or zinc, as the negative active material. Except for the iron/air battery, on which earlier development work for EV applications has now been abandoned, metal-air batteries have either limited capability for recharge, as for zinc/air, or they cannot be electrically recharged at all, as in the case of the aluminum/air system.

The zinc/air system is commercially available as a primary battery. For EV and other applications it is being developed as a "mechanically" rechargeable battery where the discharged electrode is physically removed and replaced with a fresh one. There are efforts underway at Evonyx, Metallic Power and elsewhere on this approach. Recycling or recharging of the reaction product is done remotely from the battery. There was a significant effort in the 1980s and 1990s to develop an aluminum/air battery with mechanical recharging²⁸, but this work has been mostly abandoned.

Fuel cells can in a sense be regarded as refuelable batteries, and are being considered for use in portable electronic equipment. As a result, they also are discussed later in the Handbook.

TABLE 37.1 USABC Criteria for Performance of Electric Vehicle Batteries

	<u>Mid-term</u>	<u>Long-term</u>
Specific energy, Wh/kg (C/3 discharge rate)	80 (100 desired)	200
Energy density, Wh/L (C/3 discharge rate)	137	300
Specific power, W/kg (80% DOD/30 s)	150 (200 desired)	400
Power density, W/L	250	600
Life, years	5	10
Cycle life, cycles (80% DOD)	600	1000
Ultimate price, \$/kWh	<\$150	<\$100
Operating environment	-30 to 65°C	-40 to 85°C
Recharge time, h	<6	3-6
Continuous discharge in 1 h, % (no failure)	75 (of rated energy capacity)	75
Power and capacity degradation, % of rated specifications	20	20
Efficiency, % C/3 discharge, 6-h charge	75	80
Self-discharge	<15%/48 h	< 15 %/month
Maintenance	No maintenance (service by qualified personnel only)	No maintenance (as mid-term)
Thermal loss at 3.2 W/kWh (for high-temperature batteries)	15% of capacity per 48-h period	15 % of capacity per 48-h period
Abuse resistance	Tolerant (minimized by on-board controls)	Tolerant (minimized by on-board controls)
Specified by contractor: packaging constraints; environmental impact; safety; recyclability; reliability; overcharge/overcharge tolerance		
SOURCE: Ref. 1.		

TABLE 37.2 PNGV Technical Targets* for Power-Assisted (targets shown in parentheses) and for Dual-Mode Electric Hybrid Vehicle Batteries. Targets are shown for a 400V battery system.

Characteristics	Units	Calendar Year		
		2000	2004	2006
18-second power/energy ratio	W/Wh	(83) 27	(83) 27	(83) 27
Specific energy	Wh/kg	(8) 23	(8) 23	(10) 24
Energy density	Wh/liter	(9) 38	(9) 38	(12) 42
Cycle life**	Thousand of cycles	(200) 120	(200) 120	(200) 120
Calendar life	Years	(5) 5	(10) 10	(10) 10
Cost***	\$/kWh	(1670) 555	(1000) 333	(800) 265

* From Reference 3

** For cycles corresponding to the minimum excursion of state-of-charge during an urban driving cycle

*** Based on cost per available energy

TABLE 37.3 Utility Energy Storage Applications and Corresponding Requirements

	Energy Capacity, MWh	Average discharge time, h	Maximum discharge rate, MW
Load leveling	>40	4-8	>10
Spinning Reserve	<30	0.5-1	<60
Frequency regulation	<5	0.25-0.75	<20
Power quality	<1	0.05-0.25	<20
Substation applications, transformer deferral, feeder or customer peak shaving, etc.	<10	1-3	<10
Renewables	<1	4-6	<0.25

TABLE 37.4 *Operating Characteristics for Photovoltaic Systems*

Characteristic	Value	Comments
System:		
Storage capacity	0.05-1000 kWh	
Voltage	6-250 V dc	
Battery:		
Capacity	30-2000+ Ah	
Charge rate	C/15-C/500	Charge regulation mechanisms: on-off, constant-voltage, pulse-width-modulated, multi-step
Discharge rate	C/5-C/300	27% of systems discharge battery at C/150 46% of systems discharge battery at C/100 15% of systems discharge battery at C/200
Average daily DOD (depth of discharge)	1-30%	Dependent on economics and battery chemistry
Temperature range	-40° to 60°C	Geographically dependent
Average life	4 years	For <350-Ah cells
	7-10 years	For >350-Ah cells
Average cost	\$67/kWh	For flooded/vented lead-acid
	\$97/kWh	For gelled/sealed lead-acid

SOURCE: Data from Ref. 4.

TABLE 37.5 *Index of Rechargeable Battery Systems and Refuelable Technologies Chapters in this Handbook*

	Chapter
Conventional battery systems	
Lead-acid	24 and 25
Nickel/iron *	30
Nickel/hydrogen *	32
Nickel/cadmium	26
Nickel/zinc	29
Nickel/metal hydride	33
Zinc/silver oxide **	31
Aqueous batteries	
Metal/air	38
Iron/air **	?
Zinc/air	38
Flow Batteries	
Zinc/chlorine **	This chapter
Zinc/bromine	39
Iron/chromium redox **	This chapter
Vanadium-redox	This chapter
Polysulfide/bromine redox (Regenesys)	This chapter
High-temperature batteries	
Lithium/sulfur **	41
Lithium-aluminum/iron sulfide	41
Lithium-aluminum/iron disulfide **	41
Sodium/sulfur	40
Sodium/metal chloride **	40
Lithium ambient-temperature batteries	
Liquid electrolyte **	?
Lithium-ion	?
Lithium-polymer	?
Refuelable systems	
Fuel cells ***	?
Zinc/air batteries	?
Aluminum/air batteries	This chapter
Lithium/air batteries **	?

* No longer considered suitable for target applications.

** No significant work underway on this system.

*** Portable fuel cells are discussed in Chapter 42. Fuel cells for EVs and electricity generation not treated in the Handbook.

TABLE 37.6 Organizations with Major Development Projects on Advanced Rechargeable Batteries for EVs/EHVs and/or Electric Utility Storage

Private Sector

Organization, Country	Major Funders of Work	Advanced Batteries/Application of Interest
Avestor, Canada	Avestor (Hydro-Quebec), DOE	Lithium-polymer/EV, EHV, utility storage
Innogy, United Kingdom	Innogy (formerly National Power)	Regenesys: Polysulfide/bromine redox (flow)/utility storage
NGK, Japan	Tokyo Electric Power Co., NGK	Sodium/sulfur/utility storage
Ovonics Powercell, USA, Austria	USABC, DOE Powercell, DOE	Nickel/metal hydride/EV, EHV Zinc/bromine/utility storage
Saft, France, USA	Saft, DOE	Nickel/metal hydride/EV, EHV Lithium-ion/EV, EHV, utility storage, telecomm
Sony Energetic, Japan	Sony	Lithium ion/EV
Sumitomo Electric, Japan	Sumitomo Elec., Kansai Electric Power Co.	Vanadium-redox (flow) battery/utility storage
ZBB, USA, Australia	DOE, ZBB	Zinc/bromine/utility storage

Universities & U.S. DOE National Laboratories

Organization	Main Programmatic Interest
Argonne National Laboratory	Batteries for EV, EHV Lithium/iron sulfide battery R&D
Case Western Reserve University	Basic battery and fuel cell research for EVs and EHVs
Lawrence Berkeley Laboratory	Basic battery research for all applications
Lawrence Livermore National Laboratory	Basic battery research for advanced applications
Sandia National Laboratories	Batteries and other advanced technologies for Utility storage systems and EHV
Texas A&M University	Basic battery and fuel cell research for EVs and EHVs

TABLE 37.7 Comparative Background Data for Rechargeable Battery Technologies^a

Technology	Open-circuit voltage, V	Approx. Closed-circuit, voltage, ^b V	Theoretical specific capacity ^c , Ah/kg	Theoretical specific energy ^c , Wh/kg	Operating temperature, °C	Recharge time, h	Self-discharge, % per month @ 20°C
Lead-acid	2.1	1.98	120	252	-20 to 50	8-24	3
Nickel/cadmium	1.35	1.20	181	244	-40 to 60	1-16	10
Nickel/iron	1.4	1.20	224	314	-10 to 60	5	25
Nickel/hydrogen	1.5	1.20	289	434	-10 to 30	1-24	60
Nickel/metal hydride	1.35	1.20	206	278	-30 to 65	1-2	30
Nickel/zinc	1.73	1.60	215	372	-20 to 50	8	15
Zinc/silver oxide	1.85	1.55	283	524	-20 to 60	8-18	5
Zinc/bromine	1.83	1.60	238	429	10 to 50	-	12-15 ^d
Regensys (polysulfide/bromine)	1.5	1.2	27	41	10-50	8-12	5-10
Vanadium-Redox	1.4	1.25	21	29	10-50	6-10	5-10
Zinc/air	1.6	1.1	825 ^e	1320 ^e	0 to 45	-	-
Aluminum/air	2.73	1.4	2980 ^e	8135 ^e	10 to 60	-	-
Iron/air	1.3	1.0	960 ^e	1250 ^e	-20 to 45	-	15
Sodium/sulfur	2.08	2.0	375	755	300 to 350	5-6	-
Sodium/nickel chloride	2.58	2.47	305	787	250 to 350	3-6	-
Lithium-aluminum/iron monosulfide	1.33	1.30	345	459	375 to 500	5-8	-
Lithium-aluminum/iron disulfide	1.73	1.68	285	490	375 to 450	5-8	-
Li-C/LiCoO ₂	3-4	3-4	100	360	-20 to 60	-	-
Li-C/LiNi _{1-x} Co _x O ₂	3-4	3-4	-	-	-20 to 45	2.5	<3.5
Li-C/LiMn ₂ O ₄ - polymer elect.	3-4	3-4	105	400	-20 to 60	3	<2.5

^a A source for comparative data on batteries is NAVSEA Battery Doc. NAVSEA-AH-300, July 1993.¹⁰

^b At C/5 rate.

^c Calculated values based on the electrochemical cell reactions and the mass of active material.

^d Finite self-discharge. This value applies if electrolyte is not circulating. Self-discharge is limited to only that bromine in the cell stacks.

^e Based on metal negative electrode only.

TABLE 37.8 Comparative Data for Rechargeable Battery Technologies^a for Current & Emerging Applications

Technology	Cycle life, ^b cycles	Config-uration	Specific energy, ^c Wh/kg	Energy density, ^c Wh/L	Specific power, ^d W/kg	Applications	Advantages/disadvantages
Lead-acid	800	Cell	35	80	200	Electric/hybrid vehicles, utility energy storage, consumer	Commercially available, no maintenance/low specific energy
Nickel/cadmium	1000	Cell	35	80	260	Electric/hybrid vehicles, aerospace, consumer	Commercially available/low energy, high cost
Nickel/metal hydride	900	Battery	65	220	850	Electric/hybrid vehicles, aerospace, consumer	High specific power/high cost
Nickel/iron	1000	Cell	30	60	100	Industrial	Commercially available/high maintenance, significant H ₂ evolution
Nickel/hydrogen	2000	Cell	55	60	100	Aerospace, military	Long life/very high cost, high self-discharge
Zinc/silver oxide	40-50	Cell	90	180	500	Aerospace, military, consumer	High specific energy and power/high cost, very short life
Zinc/bromine	1250	Battery	65	60	90	Utility energy storage	Low cost/low specific energy density
Zinc/air	Mech. Rech.	Battery	150	160	95	Industrial	Mod. specific energy/short life, low sp. power
Regensys (polysulfide/bromine)	2000	Battery	20	20	-	Utility energy storage	Very large scale
Vanadium-redox	3000	Battery	10	10	-	Utility energy storage	Very large scale
Sodium/sulfur	1500	Cell	170	345	250	Utility energy storage	High specific energy and energy density/high temperature
	1000	Battery	115	170	240		
Li-C/LiCoO ₂	600	Cell	155	410	-	Consumer, electric/hybrid vehicles, utility storage	High specific energy/uncertain cost
Li-C/LiNi _{1-x} Co _x O ₂	400	Cell	140	300	-	Consumer, electric/hybrid vehicles	High specific energy
Li-C/LiMn ₂ O ₄ - polymer electrolyte	600	Cell	140	300	-	Consumer, Electric/hybrid vehicles	High specific energy/development needed

^a A source for comparative data on batteries and projections of future performance is NAVSEA-AH-300, July 1993.¹⁰

^b At approximately the C/5 rate to 80% of rated capacity.

^c At approximately the C/5 rate.

^d Short-duration pulse, fully charged to half-charged except sodium/sulfur, which is 50-80% charged. The values listed do not reflect the maximum that is achievable if batteries are purposely designed for high specific power.

TABLE 37.9 Comparative Data for Other Rechargeable Battery Technologies.^a of Interest

Technology	Cycle life, ^b cycles	Config-uration	Specific energy, ^c Wh/kg	Energy density, ^c Wh/L	Specific power, ^d W/kg	Advantages/disadvantages
Nickel/zinc	200	Cell	60	120	300	High specific energy/ high cost, short life
Aluminum/air	Mechanically rechargeable	Battery	200-250	150-200	-	High specific energy/ low specific power, not electrically rechargeable
Iron/air	300	Battery	65	100	-	Good life, low cost/ low voltage per cell, low coulombic efficiency on charge
Sodium/nickel chloride	2500	Cell	115	190	260	High specific energy/ high temperature
	1000	Battery	95	150	170	
Lithium/iron monosulfide	1000	Cell	130	220	240	High energy density/ low specific power, high temperature
Lithium/iron disulfide	1000	Cell	180	350	400	High specific energy and power/ high temperature

^a A source for comparative data on batteries and projections of future performance is NAVSEA-AH-300, July 1993.¹⁰

^b At C/5 rate to 80% of rated capacity.

^c At C/5 rate.

^d Short-duration pulse, fully charged to half-charged, except lithium/iron monosulfide and lithium/iron disulfide, which are 50-80% charged. The values listed do not reflect the maximum that is achievable if batteries are purposely designed for high specific power .

FIGURE 37.1 Typical cycle of dynamic stress test for electric-vehicle batteries. (From Ref. 2)

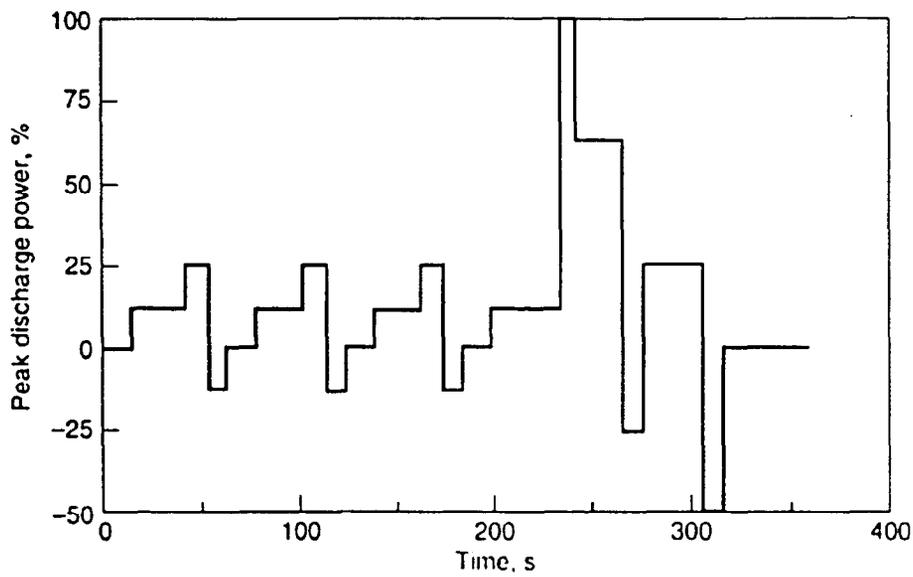


FIGURE 37.2 (a) Weekly load curve of electric-utility generation mix with energy storage. (b) Test regime typical of frequency regulation and spinning reserve application for electric utilities. (Courtesy of Sandia National Laboratories. See Ref. 4)

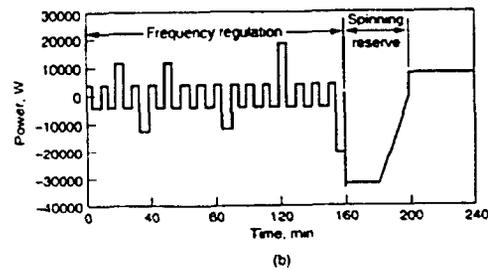
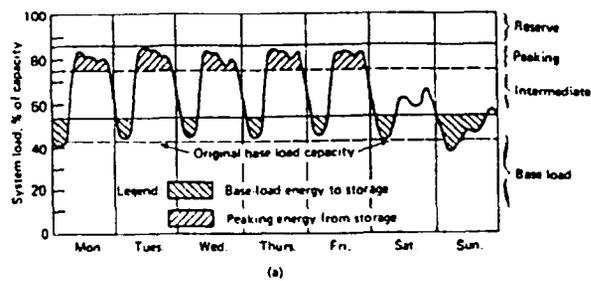


FIGURE 37.3 Plot of specific power vs. specific energy for various rechargeable battery technologies. (Courtesy of Sandia National Laboratories.)

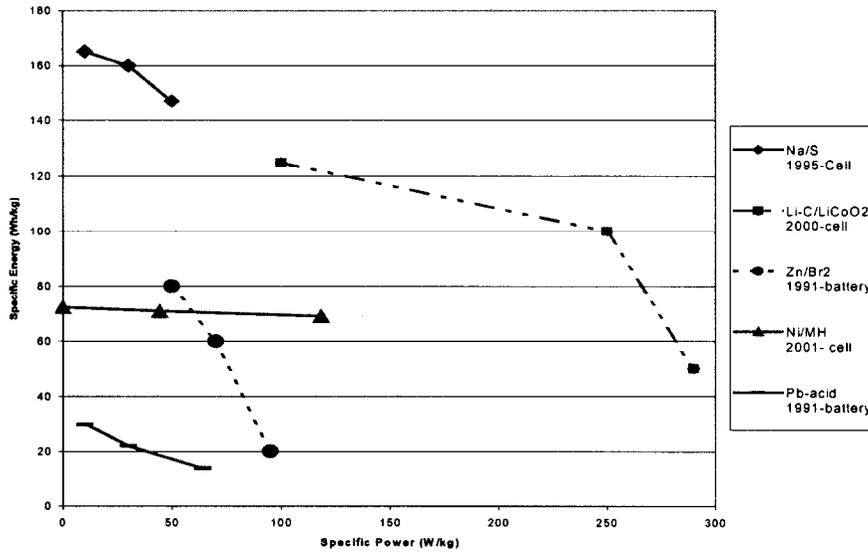


FIGURE 37.4 Block Diagram of Vanadium-Redox System

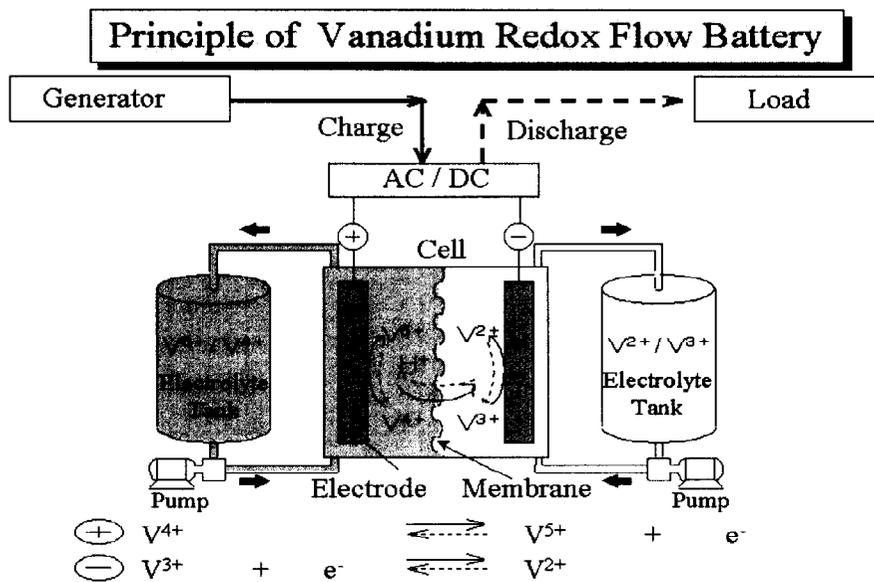


FIGURE 37.5 Vanadium-Redox Battery In Use

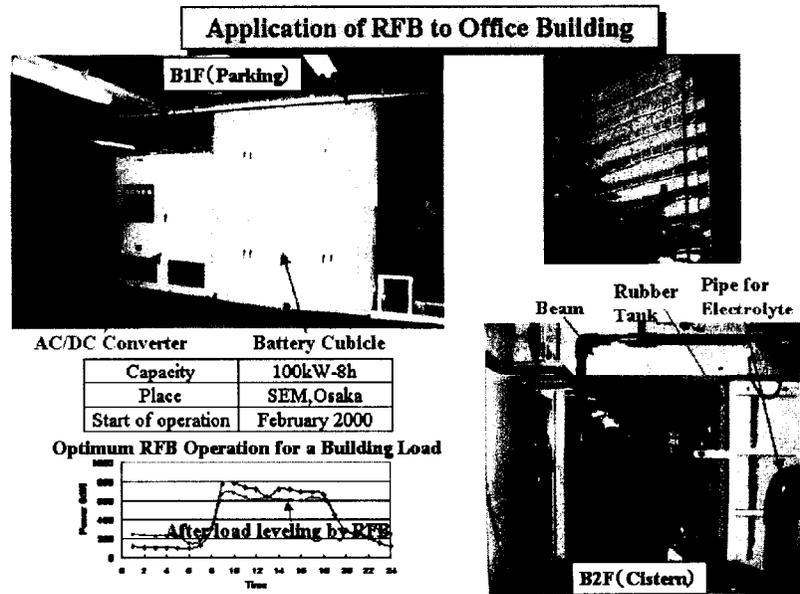
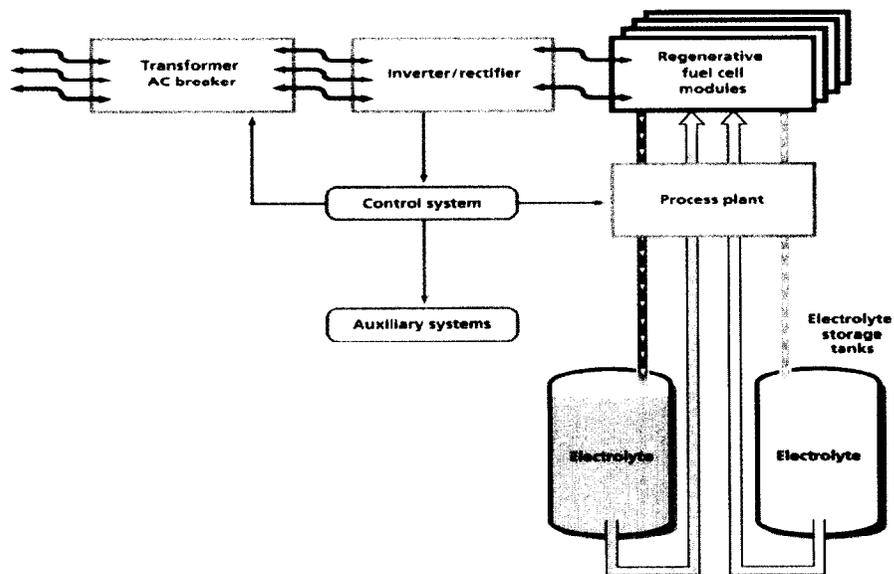


FIGURE 37.6 Block Diagram of Regenesys Energy Storage Plant (RFB=Redox Flow battery)
(From Ref 25)



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