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TECHNOLOGICAL REVIEW

Recent trends in the storage battery industry of Japan

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This review summarizes the trends in the battery industry of Japan and in particular examines the recent developments of conventional and new types of power sources.

Introduction

The economic growth and expansion of recent years has resulted in a rapid increase in production in many manufacturing industries. There has been a desire to exploit new markets and as a consequence of this expansion, Japan has become one of the world's leading battery manufacturing countries. Table 1 [1], shows the annual volume of lead–acid and alkaline storage batteries produced in Japan during the period 1965 to 1969.

Associated with this growth, considerable improvements have been made in the technological field. For example, the energy density of most types of power source has been significantly increased and a range of maintenance free systems has been developed to satisfy a variety of new applications. Improvements in high performance batteries suitable for use on electric vehicles have attracted attention due to public concern over the pollution caused by car exhaust fumes and due to the desire to use electric power during the off-peak periods. This review summarizes the trends in the battery industry of Japan and in particular examines the recent developments of conventional and new types of power sources.

1. Lead acid storage batteries

Since 1859, when Plante invented the lead-acid battery, the system has been used on a wide and increasing variety of applications. The main uses are on automobiles for starting, lighting and ignition, as a motive power supply on railway and marine applications, and to fulfil stationary requirements, such as emergency power supplies.

1.1. *Automotive batteries*

These represent approximately 80% of the total output of Japanese lead-acid batteries. Because of the large numbers involved, mass production techniques have been developed and most production processes have been fully automated. The exception is certain parts of the assembly process which still require manual operation. Amongst the recent important changes in the manufacturing processes ar::

(a) A method of producing lead oxide from lead by a molten flow process.
(b) Automatic casting machines for the production of lead grids.
(c) A combined automatic paste mixing and paste application unit.
(d) Stacking machines for automatically assembling the plate groups and separators.
(e) Automatic techniques for producing and handling battery components from the element lead burning process to the assembly stage.
(f) Automation of the container formation process.
(g) Improved methods of heat sealing the cover to the container and sealing the intercell connectors in the plastic cell walls.

Table 1. Production of storage batteries (data from Storage Battery Association)

	Classification	1965		1966		1967		1968		1969	
		Amount of Lead (kg)	*Sales (1000 dollar)*	*Amount of Lead (kg)*	*Sales (1000 dollar)*	*Amount of Lead (kg)*	*Sales (1000 dollar)*	*Amount of Lead (kg)*	*Sales (1000 dollar)*	*Amount of Lead (kg)*	*Sales (1000 dollar)*
Lead–Acid Storage Batteries	Motor tricycles and cars	46,943,076	59,284	66,127,331	83,635	82,374,000	104,340	99,358,000	125,808	106,123,000	134,762
	Motor cycle	5,372,913	8,957	6,100,613	10,168	6,298,000	10,498	6,371,000	10,615	7,320,000	12,317
	Stationary battery	4,138,282	9,125	4,621,605	10,210	5,213,000	11,509	4,979,000	11,015	6,208,000	13,519
	Portable battery	902,203	1,731	1,010,883	1,962	1,099,000	2,128	1,220,000	2,436	1,350,000	2,562
	Marine battery	392,690	813	461,962	956	450,000	933	680,000	1,378	758,000	1,117
	Motive power traction battery	1,762,551	3,314	2,398,789	4,529	3,176,000	5,962	4,010,000	7,231	5,094,000	7,156
	Railway battery	1,058,350	1,248	1,376,707	1,702	1,679,000	2,212	2,236,000	3,180	2,194,000	3,194
	The others	864,730	2,532	698,183	2,256	792,000	3,650	1,245,000	12,741	1,921,000	4,692
	Total	61,434,795	87,004	82,796,071	115,418	101,081,000	141,232	120,099,000	174,424	130,968,000	179,319
Alkaline Storage Batteries	Pocket type		3,396		3,452		4,400		5,078		6,057
	Sintered type		1,849		2,662		3,556		4,755		7,493
	The others		34		12		9		3		19
	Total		5,279		6,126		7,965		9,836		13,569

In the field of material usage, the increasing price of antimony has resulted in the development of low antimony alloys for use in battery grids. The improvement in grid casting techniques and the use of A.C. generators on most automobile charging equipment has enabled the thickness of negative plates to be reduced to 1 mm. Improvements in plastics technology has resulted in changes in battery containers and lids. For example, both acrylonitrile styrenes and acrylonitrile-butadiene styrene have been used for containers and lids. Lightweight thin wall polypropylene containers and lids which have high impact strengths are now used commercially. The impact resistance of polypropylene compared with various other plastic materials and hard rubber is given in Fig. 1. It can be seen that polypropylene has excellent low impact strengths at low temperatures. The only effective way to seal polypropylene containers is by heat-sealing and mass production techniques have been developed in recent years. Furthermore, with these materials a liquid tight seal can be made between the male and female connectors of adjacent cells, thereby producing a 'through-the-partition connector', with a considerable improvement in the voltage characteristics and starting capability of the battery. This design also uses less lead and correspondingly reduces the weight of the battery. A comparison of the effect of various intercell connection designs on the voltage characteristics of batteries at high current discharge rates is shown in Fig. 2.

A more recent development is the water activated dry charged battery. In this system, the electrolyte consists of a colloidal solution of sulphuric acid in a plastic bag. After pouring water into the container, the bag is broken and the battery can be used for operation immediately. No preliminary charge is required and since water is the only material to be added, it is an easy and convenient method of activation.

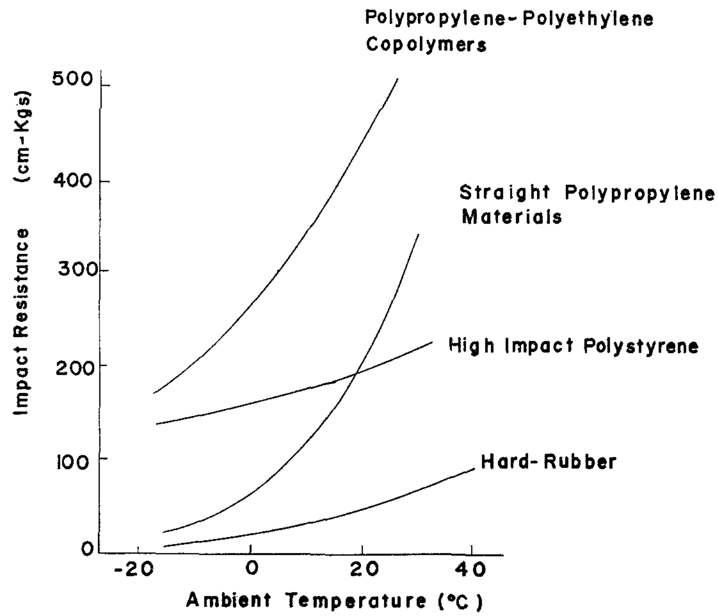

Fig. 1. Impact comparison.

1.2. *Batteries for portable equipment* [2]

Nickel–cadmium alkaline storage batteries are widely used in cordless appliances, such as portable electric and electronic equipment. In recent years, lead acid batteries have also been used in this application. These are widely known as 'gel-cell' batteries, and although they will not give the long cycle life associated with alkaline batteries, they are much cheaper. For example, most 'gel-cells' will give between 50 to 300 cycles, but are about one-fifth or one-sixth of the price of the equivalent alkaline cell. Table 2 gives a comparison of various types of batteries made by different manufacturers. Sizes in the range 3–8 Ah are available and the design usually consists of three cells in a monobloc container. As well as the use of gelled electrolyte to eliminate spillage, lead–calcium alloys are usually used to minimize self-discharge and to reduce the loss of water. Fig. 3 shows the change in capacity during a typical cycle life duty of these batteries. Fig. 4 shows the residual capacity of batteries made with lead–calcium and antimonial alloys after prolonged storage and enables the self-discharge rates to be compared.

The improved shelf-life is an important characteristic of this type of battery and various manufacturers have developed their own particular expertise and know-how for improving this feature.

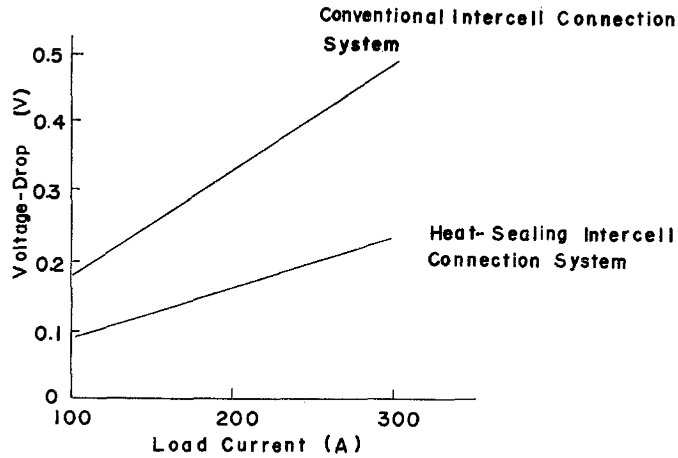

Fig. 2. Comparison of the newest and conventional intercell connection system with respect to voltage drop characteristics.

1.3. *Stationary batteries*

In recent years a range of batteries which do not require maintenance (i.e. water addition), during service has been developed for stationary applications and are frequently used at power stations. There are basically two types. The semi-sealed type which contains a catalyst to combine the evolved gases and a hermetically sealed version which contains an auxiliary electrode to ionize the evolved gases. The first type is illustrated in Fig. 5 showing a vent assembly which contains a microporous ceramic material impregnated with the catalyst [3, 4]. The vent has a small air inlet, so that under conditions where excess hydrogen gas is evolved, water may be produced from oxygen supplied via the inlet. A modification of this system which consists of a heated catalyst bed to improve its efficiency is also in use [5]. The loss of water from a battery system using a catalyst is shown in Fig. 6. An obvious advantage of this system is that conventional batteries can be modified easily by changing the vent structure to one which contains a catalyst.

The principle of the auxiliary electrode-recombination technique is illustrated in Fig. 7. [6]. The efficiency of the recombination depends upon the potential of the auxiliary electrode and the relationship between the oxygen ionizing current and the potential of the oxygen electrode is shown in Fig. 8. Similarly, the relationship between the potential of the hydrogen electrode and the hydrogen ionizing current is shown in Fig. 9. The loss of water from a battery containing auxiliary electrodes is shown in Fig. 10.

Batteries of this kind are in use at 300 locations to supply emergency or auxiliary power for control instruments at sub-stations and in radio and telephone communications. A rectified constant voltage supply is used for charging the batteries at a float voltage of 2·15 to 2·22 V with a maximum recharge voltage of 2·3 to 2·4 V.

1.4. *Batteries for electric vehicles*

The Japanese Committee on Transportation

Table 2. Compact and light weight sealed type lead–acid storage batteries

Manufacturer	*Model*	*Normal capacity (output)*	*Weight*	*Dimensions (mm)*	*Normal life (cycles)*	*Characteristics of electrolyte*	*Grid alloys*	*Construction*
Company A	NP3-6	6 V–3 Ah/10HR (18 Wh)	700 g	46 × 69 × 104	Over 150	Acid solution	⊕Pb–Sb ⊖Pb–Sb	Semi-sealed Liquid-tight Vent element assembly
Company B	POR	6 V–3·5 Ah/10HR (21 Wh)	860 g	48 × 70 × 102	80	Gelled solution	⊕Pb–Sb ⊖Pb–Sb	Semi-sealed Rubber valve unit
Company C	SC4-6	6 V–4 Ah/10HR (24 Wh)	750 g	48 × 70 × 102	150	Gelled solution	⊕Pb–Sb ⊖Pb–Ca	Semi-sealed Rubber valve unit
Company D	TY-356C	6 V–3 Ah/10HR (18 Wh)	660 g	33 × 60 × 120	150	Gelled solution	⊕Pb–Ca ⊖Pb–Ca	Semi-sealed Rubber valve unit
Company E	GA6-7	6 V–7 Ah/10HR (42 Wh)	1560 g	59 × 119 × 135	150	Gelled solution	⊕Pb–Ca ⊖Pb–Ca	Semi-sealed Rubber valve unit

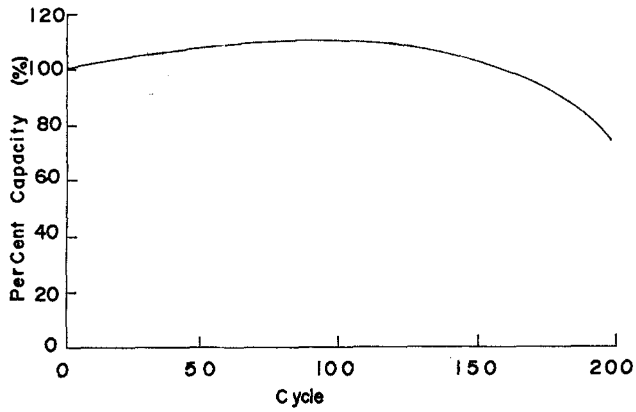

Fig. 3. Repeated cycle life of charging and discharging of square-shape compact and light weight lead–acid storage batteries.

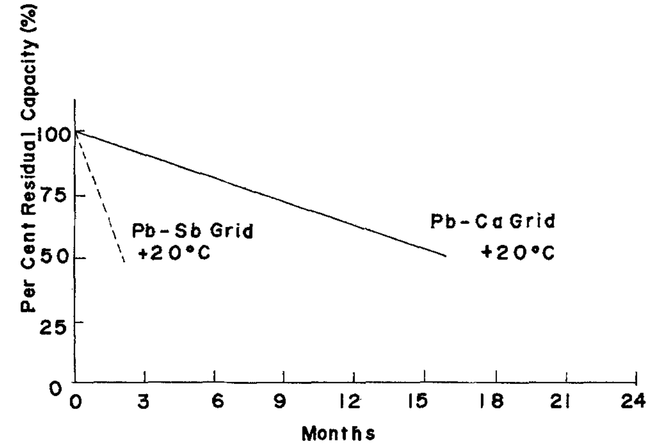

Fig. 4 .Lead calcium–lead antimony grid alloys comparisons on self-discharge.

Techniques in an interim report to the Ministry of Transportation in July 1970, stated that the regulations for the exhaust of fumes from internal

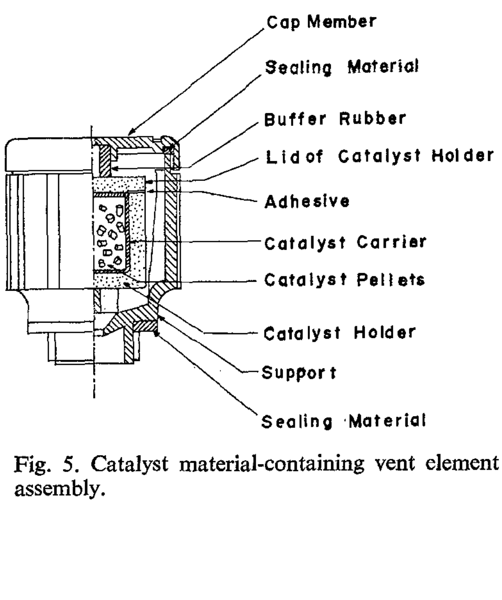

Fig. 5. Catalyst material-containing vent element assembly.

combustion and diesel engines should be reviewed frequently during the period 1973 and 1975. As a consequence, the Committee on Industrial Structure in a report to the Ministry of Trade and Industry in August 1970 stated that it was desirable that pollution-free, safety cars should be developed to meet the new regulations.

Considerable efforts are now being made to increase the number of electrically powered vehicles in Japan and the Ministry of Trade and Industry has recommended that electric vehicle development be one of the major projects of the Agency of Industrial Science and Technology. The project started in 1971, and has a budget of about 5 billion yen, (£5,833,380), to develop battery powered systems over the next five years. Hybrids of internal combustion engines and batteries are excluded. Five types of vehicle are scheduled for development by the end of

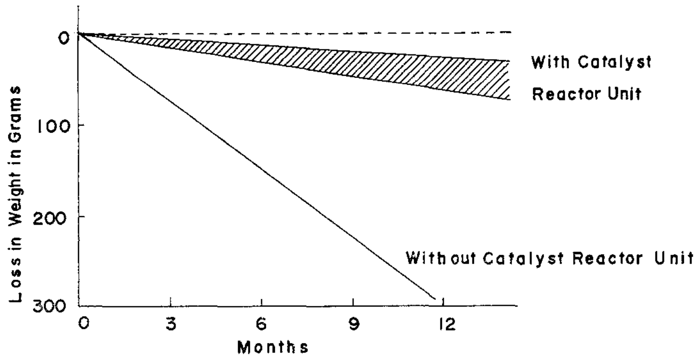

Fig. 6. Electrolyte circulation efficiency in catalyst-activated gas recombination battery system.

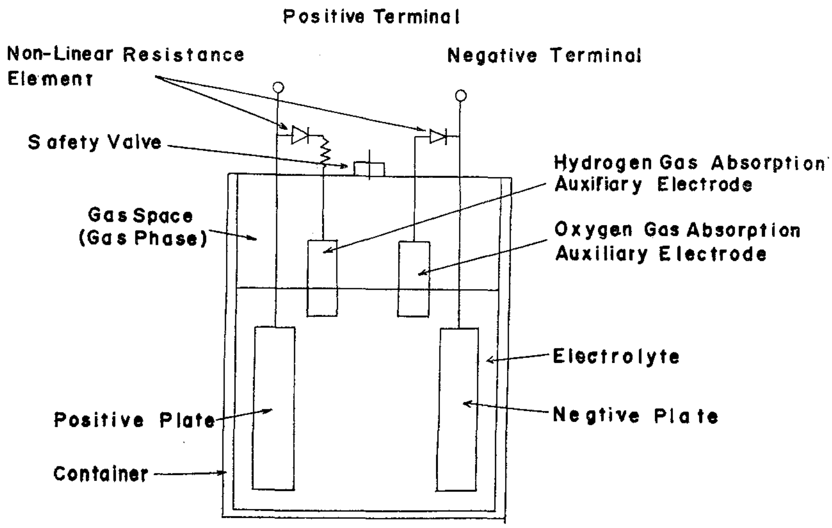

Fig. 7. Auxiliary electrode–gas recombination battery system.

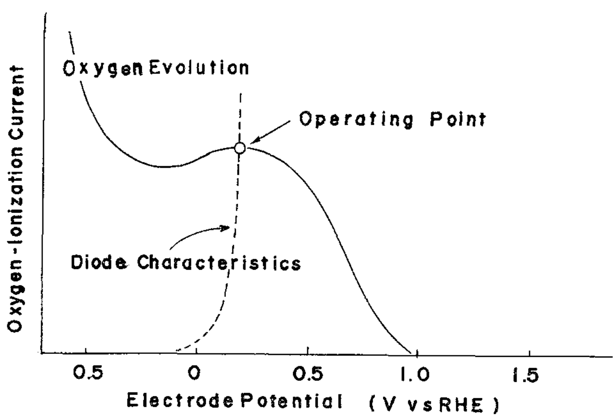

Fig. 8. Relation between electrode potential of oxygen gas absorption auxiliary electrode and oxygen-ionization current.

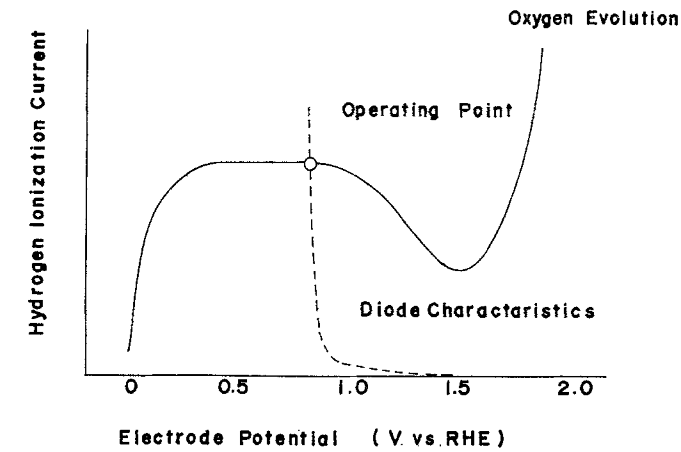

Fig. 9. Relation between electrode potential of hydrogen gas absorption auxiliary electrode and hydrogen ionization current.

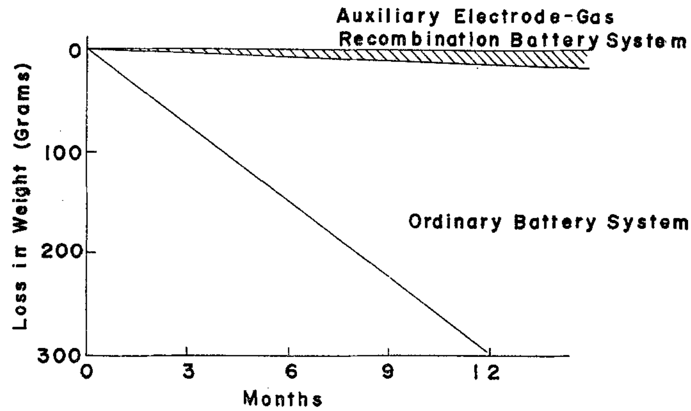

Fig. 10. Circulation efficiency of auxiliary electrode–gas recombination battery system.

Table 3. Test car development goal (by the end of 1974) (data by the agency of industrial science and technology of Japan)

Field of use	For short distance Truck type Midget class	Light class	For business use Automobile van type Midget class	Light class	Route bus Bus type Large class
Passenger+load	2 passengers+ 200 kg	2 passengers+ 1000 kg	4 or 2 passengers and 100 kg	5 or 3 passengers and 300 kg	60 to 80 passengers
Gross weight (kg)	1100 (approx.)	3500 (approx.)	100 (approx.)	200 (approx.)	15,000 (approx.)
Maximum speed (km/h)	Above 70	Above 70	Above 80	Above 80	Above 60
Range of distance without recharging	130–150	180–200	130–150	180–200	230–250
Rate of acceleration (0–30 km/h) (sec.)	Less than 5	Less than 5	Less than 4	Less than 3	Less than 8
Ability of climb (speed at a slope of 6°) (km/h)	Above 40	Above 40	Above 40	Above 40	Above 40

March 1974. These are summarized in Table 3. It is expected that the projects will be complete by the end of March 1976.

The success of these developments, of course, depends primarily upon the characteristics of the power source. Lead–acid batteries for this application must have an energy density of at least 60 Wh./Kg. and a life of 300 to 400 cycles. With the newer types of power source the objective is an energy density of 100 Wh/Kg and a life of 300 to 500 cycles. The three types of power source selected for further development are the zinc–air, sodium–sulphur and iron–air battery.

The energy density of lead–acid batteries has been increased considerably by the use of thinner plates, improved active material and a monobloc type construction. Multi-layer positive electrodes and electrolyte circulation systems are now being examined with the aim of producing a marketable product in three years' time. At the present time, the lead–acid battery is superior to any other system economically and in terms of reliability, but increases in the energy density may only be possible as a result of some sacrifice in these areas. There is, however, clearly a limit to the extent by which the energy density can be increased and the research into new power sources is being carried out in parallel with the development of the lead accumulator.

2. Alkaline storage batteries

The nickel–cadmium battery is the most widely used alkaline system. Others, namely nickel–iron and silver–zinc batteries are limited in their application as a result of their price or performance.

2.1. *Jungner batteries*

These usually contain cadmium pocket type cathodes in place of the iron cathode used in the Edison battery. The plates are about 2 mm thick and the battery has good high rate discharge characteristics. They can be charged more efficiently, have improved low temperature characteristics and are widely used in such devices as mining lamps and stand-by emergency lighting because of the low maintenance that is required and long operating life.

2.2. *Sintered nickel–cadmium batteries*

The nickel–cadmium batteries were invented in Germany during World War II and mass production started in Japan in 1962. Since that time production has increased rapidly, particularly in the case of the sealed nickel–cadmium batteries that are used in electronic devices, fire alarms and emergency pilot lamps. The increasing number of cordless appliances such as stroboscopes, electric shavers, tape recorders, portable television sets, has resulted in a rapid increase in the production of this type of battery in recent years. Hermetically-sealed Ni-Cd rechargeable batteries encased in ceramic materials are also used in space satellites.

In September, 1971, the first Japanese Science Satellite, (Shinsei 1971-080-A), was launched into earth orbit. This was a joint venture with NASA and the Aeronautical Research Institute of the University of Tokyo. The satellite contained a ceramic hermetically-sealed Ni-Cd rechargeable battery, built at Furukawa and consisting of 15 WS 103 cells. It is charged during daylight periods by a solar cell and supplies all power requirements during the night. Fig. 11 shows the performance characteristics during the first two weeks after launch.

The sintered nickel–cadmium battery is more costly than the lead–acid battery. Furthermore, the production processes are more sophisticated and tighter control during production is required to ensure the correct degree of sintering and impregnation. Improvements are continually being made in the production techniques. The most recent are the use of nickel-plated iron in place of nickel, the development of battery plates which have greater porosity at the surface of the active material, the use of mixtures of carbonyl nickel powder and binder, and a method of applying the nickel powder to the sintering frame using a slurry of powder and binder. The whole process of sintering and impregnation can now be carried out continuously. More recent developments are those concerned with operation of the battery. In particular, using an auxiliary electrode of

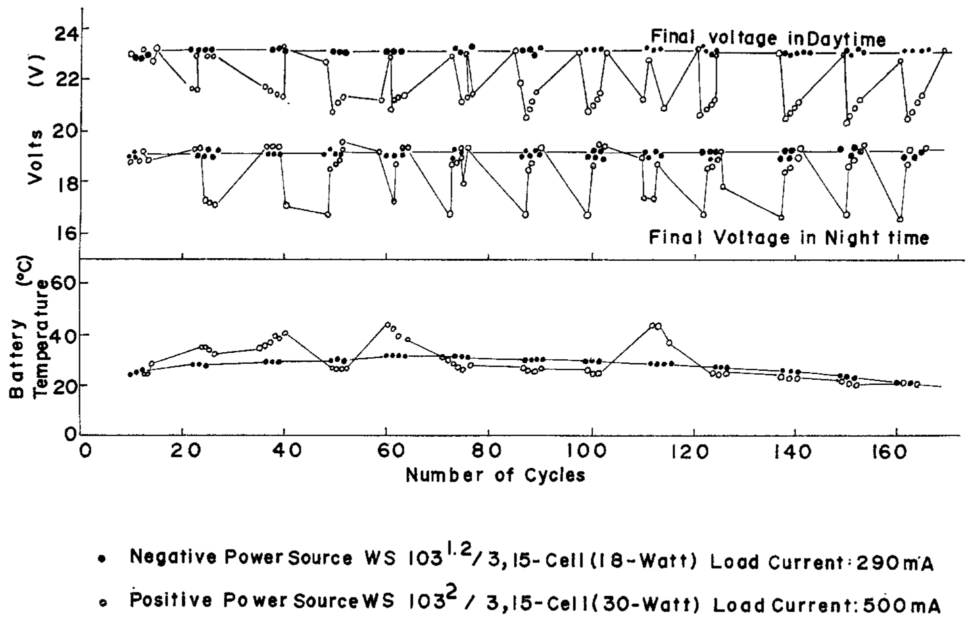

Fig. 11. Operating condition of batteries in flight; ● negative power source WS $103^{1\cdot 2}$/3,15-cell (18 W) load current: 290 mA. ○ positive power source WS 103^{2}/3,15-cell (30 W) load current: 500 mA.

platinum impregnated carbon, [7, 8, 9] batteries can be re-charged at very high current rates. Using sensitive voltage switches of the Joggle type, the charging time can be reduced still further, by having high charge acceptance with little gas evolution [10]. Boost charging is also possible using a coulometer controlled charge system.

Auxiliary electrodes to assist in gas recombination are also used in the larger type of vented nickel–cadmium battery. It is anticipated that this type of battery will be used with automatic constant voltage chargers as a maintenance free system on computers and in control units at power stations, sub-stations etc.

2.3 *Silver–zinc batteries* [11, 12, 13]

The silver–zinc battery has the highest energy density of all the commercially available batteries. The decrease in cell voltage during operation is small and high rate discharges are possible. Because of their compact and light-weight nature, they are used in rockets, missiles and torpedoes and in a variety of portable and cordless applications. The life of these batteries has been improved by better control of the manufacturing processes and charge equipment. On a 25% depth of discharge schedule, cycle lives of 2,500 cycles are possible. The annual production at the present time is only small with batteries to the value of 100 million yen (£116,760), being produced in Japan in 1969. Production is expected to increase gradually during the next few years. Silver–cadmium batteries are not made in Japan at the present time.

3. New batteries

In recent years significant progress has been made in the development of new power sources such as fuel cells, zinc–air systems etc. Some of these are now commercially available.

3.1. *New types of secondary battery*

Amongst those currently under development are the sealed type sodium–sulphur battery and two types of zinc–air battery, i.e. with and without electrolyte circulation [14]. The zinc–air and the iron–air system are widely recognized as having energy densities which potentially could meet the demands of heavy duty equipment. Fig. 12 shows a zinc–air battery

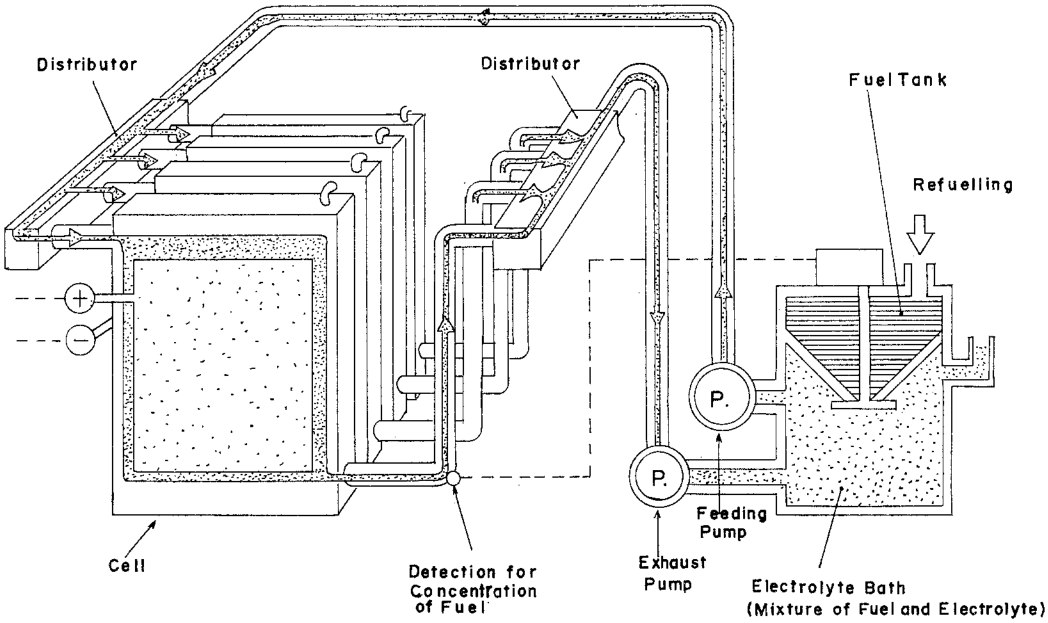

Fig. 12. Sony's metal electrode-containing fuel cell system construction.

system that is currently being developed by the Sony Corporation [15].

The sodium–sulphur battery operates at a temperature of 250–300°C. Molten sodium and sulphur are used as cathode and anode respectively, with a solid state electrolyte of a ceramic (β-alumina), which is selective to sodium ions only. Studies are currently being carried out in order to improve the electrolyte which must consist of a mechanically strong dense polycrystalline material to resist the stress and strain during assembly and operation, and must also withstand the corrosion caused by the metallic sodium and Na_2-S. The assembly process consists of joining the sodium reservoir of α-alumina to the β-alumina solid electrolyte, and connecting the collar of the reservoir to a stainless steel pipe which is the sodium inlet. Figure 13 shows one configuration of the battery [16]. Factors which must be taken into

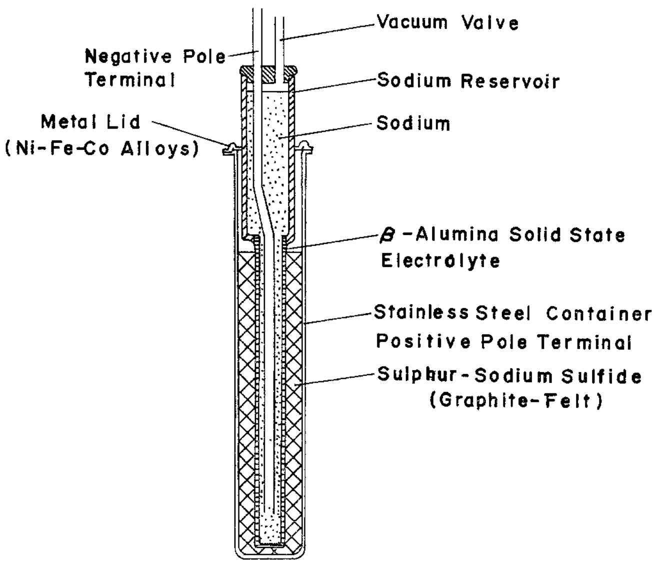

Fig. 13. Sodium–sulphur battery construction.

consideration when the system is used in electric vehicles are the pre-heating period which is necessary, the thermal insulation and the safety factor during emergencies.

The zinc–air and iron–air systems can operate at normal temperatures. Both types of zinc–air battery, i.e. with or without electrolyte circulation, are scheduled for development in the 5-year plan on the electric street vehicle. The major problems in this area are the passivation of zinc during discharge, the control of dendritic growth of zinc during charge and the removal of carbon dioxide from the air prior to its use.

Other light-weight systems containing non-aqueous electrolytes are being developed, using active metals selected from groups I-A and II-A of the Periodic Table as cathode, and halides of copper, nickel or silver as the anode. Propylene carbonate is usually the electrolyte. Studies are also being carried out on the lithium–metal halide storage battery. It is anticipated that many years of research are required in order to produce systems which have both high-energy density and long operating life. The basic research now under way consists of examination of the component materials for electrodes, electrolyte and a study of the method of depositing lithium on the electrode during charge.

3.2. *Fuel cells*

For the past ten years fuel cells have been undergoing development in Japan and commercial systems are now available. Seven methanol fuel cells were installed in a lighthouse in 1966, giving a 25 W supply. In 1967, 35 W fuel cells were installed in a rainfall telemeter station. The methanol cell is easy to operate, but has high fuel costs. Other problems are the low power density and the contamination of the electrolyte during service. On the other hand, the hydrazine fuel cell can be operated at high power densities and is also free from the deterioration of the electrolyte during service. It is anticipated that portable power sources will be used by the Japanese Agency as a maintenance free power source for use in remote areas. Early in 1970, 40 W and 50 W hydrazine fuel cells were placed in the television repeater stations of the Japanese Broadcasting Corporation at Kanaya and Kimata. Hydrogen fuel cells are capable of supplying up to several kilowatts of power, but they are too costly to operate. Recently oxygen–hydrogen fuel cells have been developed for use in submarines. The largest of this type which has been developed for trial purposes is a 9 kW unit. In the United States fuel cells with solid state electrolyte using natural gas and coal as the fuel are currently being investigated. There are few investigations in this area being carried out in Japan.

3.3. *Special batteries*

These include thermal and zinc–air primary batteries. The thermal batteries have been developed as a power source for the Nike-J in the Japanese fourth defence plan. The batteries of sealed type construction with an electrolyte which is a eutectic mixture of fusible salts. The batteries will operate between temperatures of $-50°C$ and $+70°C$ and can be used both for continuous and standby emergency power supply in communication systems.

The zinc–air primary cells which are interchangeable with conventional dry cells are expected to be marketed in the near future.

In comparison with other industries it is fair to say that the rate of technological change is slow. However, steady and regular improvements are continually being made over a wide field. Perhaps the most challenging development of recent years is the development of electrically powered street vehicles to overcome the environmental pollution problem. The extensive research and development now being carried out by the Japanese battery industry will face up to this challenge.

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