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Overview of Batteries

■1-1 History of Batteries

In 1791 Galvani who is the biologist of Bologna University discovered animal electricity from the phenomenon “muscle of flog is contracted by contact of metal”. And then in 1800 Volta who is the physicist in Italy found out the phenomenon “it generated voltage and could get continuously electricity that two different kind of metals were soaked into electrolyte” and invented famous Volta cell. This was the 1st cell that went out into the world. After that Davy and many other people carried out various experiments of electrolysis by using Volta cell. In 1831 Faraday found out the Faraday’s law and fundamental electrochemistry was established. Furthermore Daniel cell and another cells were developed and in 1868 Leclanche invented Leclanche cell that was the prototype of current dry cell. This cell was improved in active materials and structure, and still using in wide area as convenient and light weight primary source of electric energy.

On the other hand in 1859 Plante invented lead acid battery and here came rechargeable battery. This battery is different from previous primary batteries and has a merit of rechargeable. This fact, along with improvements to the electrical generator developed in 1866, allowed lead storage batteries to play a leading roll in electrical energy storage applications. And it was the start of storing of electric energy. Even now this battery used as starter power of car and many applications and is typical secondary battery as well known.

Following of lead acid battery, in 1899 Jungner and in 1901 Edison and et al developed alkaline rechargeable battery using alkaline electrolyte. Jungner battery was using Nickel as a cathode and Cadmium as an anode. And Edison battery was using Nickel as a cathode and Iron as an anode. Since the materials for alkaline batteries were expensive in comparison with those for dry or lead storage batteries, their practical applications were severely limited. In recent years, however, Jungner ’s Nickel-Cadmium battery has undergone intensified development using improved materials and manufacturing techniques to achieve a superior level of performance. The first major basic improvement to the Nickel-Cadmium battery was the result of a new sintered plate invented by Shlecht and Ackermann in 1932. The conventional plate employed a system under which the active materials were packed into a metal container called a pocket or tube. With Ackermann ’s method, however, the active materials are placed inside a porous nickel electrode formed by sintering nickel powder. Through the use of these sintered pole plates, Nickel-Cadmium battery characteristics were significantly enhanced. In particular, there was a large improvement in the high-rate discharge characteristics and service life was dramatically increased. In 1947 Neumann

realized sealed Nickel Cadmium rechargeable battery. It made open the new field as consumer secondary battery because of it was controlled demerits of secondary battery such as gas generation and leakage during charge and discharge.

We SANYO had been paying attention to technology of sealed battery early and in 1961 we developed Nickel Cadmium rechargeable battery(brand name ; Cadnica) by our original technology. Cadnica battery has been adopted to various cordless applications such as emergency light, radio control car or power tool and contributed to pioneer the small rechargeable market. With the development of a wide variety of cordless devices utilizing CADNICA batteries, along with various signals and emergency lights that use these batteries as a reliable emergency power source, CADNICA batteries are enjoying a wide application range that is still expanding.

A large variety of CADNICA batteries have been developed to meet a wide range of user needs, ranging from low current level uses like emergency power sources for semiconductor memories to very high power applications such as cordless drills, etc.

Furthermore, in 1990 we had developed and started to selling Nickel Metal Hydride battery to meet market requirement as high capacity in the first of the world. Nickel Metal Hydride rechargeable battery(brand name : Twicell) is one of alkaline rechargeable battery using Nickel Oxide as a cathode and Hydrogen Absorbing Alloy as an anode. It make use of electrochemical reversible reaction that hydrogen absorb into and release from alloy. Twicell is high performance battery that its capacity is about twice of normal Cadnica.

And then Lithium-ion battery was came. Using of Lithium metal as an anode can get maximum energy density in theory. In end of 1950's it took up Lithium for the project of military and space use battery for the first time and Thionyl Chloride Lithium primary battery was developed for military.

On the other hand, in Japan carbon fluoride lithium battery and manganese dioxide lithium battery were commercialized respectively in 1973 and 1975. The reactions of these batteries are out of previous electrochemical theory and it is much significance that the reactions were made clear by cooperation of industrial and academic fields. After that Japanese companies and universities have the important role in development of new batteries.

After high energy Lithium primary battery was developed it was expected more realization of lithium rechargeable battery and research and development were done more harder in all over the world. As the results, in 1979 lithium and transition metal complex oxide was find out for a cathode and in 1981 graphite cathode was find out. At those time basic technology of Lithium-ion battery was established.

In the first stage of development lithium metal was investigated as an anode, but there are problems of charge discharge efficiency and cycle life. To clear these problems lithium rechargeable battery using alloy anode was developed in 1980's. We also developed coin type manganese dioxide lithium rechargeable battery using lithium-aluminum alloy anode in 1989. It has been using for memory back up battery.

But development of battery for power supply to portable applications that have big capacity and it can discharge at high load had gotten behind. In 1989 cylindrical lithium secondary battery using lithium metal anode was made practical. But, it did not spread because there was safety issue on lithium metal. To solve these issues, it was developed that lithium secondary battery (Lithium-ion battery) did not using Lithium metal but carbon material (cokes) absorbing lithium ion for anode in 1989. It dose not generate dendrite so it is safety and has good cycle life because of lithium metal free.

Lithium-ion battery is a new chemistry and using carbon material that can absorb lithium ion as an anode, lithium and transition metal complex oxide as a cathode and organic solvent dissolving lithium salt as an electrolyte. The voltage is 3 times higher than that of nickel cadmium or nickel metal hydride and gravimetric energy density is twice.

We SANYO started to research and development of Lithium-ion battery from early and applied graphite anode for the patent. And we commercialized cylindrical Lithium-ion battery that had flat discharge characteristics came from graphite technology in 1994, then we commercialized light weight prismatic type using aluminum can as a pioneer. As the result we could improve energy density greatly in the consumer rechargeable battery field. Cylindrical type are mainly used for power supply of camcorder or notebook PC and prismatic type for cellular phone. It could make portable applications smaller and lighter. It is said that Lithium-ion battery is very much suitable for potable applications.

History of battery can say in another words that is improvement of treatment and energy exchange efficiency. The role of battery become more important as changing of generation, especially in the recent situation of the rapid growth of electronics fields and feature demands of energy battery seems to be more important.

SANYO have three chemistry of battery that of Cadnica, Twicell and Lithium-ion and these battery will improve still more then these battery will have much demands taking each advantages.

Table 1-1: The History of Batteries

1600	Gilbert (England)	● Establishment of the basics of electricity
1700		
1791	Galvani (Italy)	● Discovery of animal electricity
1800	Volta (Italy)	● Invention of the voltaic cell
1800		
1831	Faraday (England)	● Formulation of Faraday s Law
1836	Daniell (England)	● Invention of the Daniell cell
1840	Armstrong (England)	● Invention of the water-powered generator
1859	Planté (France)	● Invention of the lead storage battery
1866	Siemens (Germany)	● Innovative improvements to the generator
1868	Leclanché (France)	● Invention of the Leclanché battery
1888	Gassner (USA)	● Completion of the dry cell
1899	Jungner (Sweden)	● Invention of the Nickel-Cadmium storage battery
1900		
1901	Edison (USA)	● Invention of the nickel-alkali storage battery
1932	Shlecht-Ackermann (Germany)	● Invention of sintered plate
1947	Neumann (France)	● Successful complete sealing of the Nickel-Cadmium battery
1962		● First practical use of Sanyo CADNICA batteries
1977		● First practical use of Sanyo lithium(MnO_2-Li)batteries
1982		● First practical use of Sanyo amorphous solar cells (AMORTON)
1989		● First practical use of Sanyo lithium(Li-Mn)secondary battery
1990		● First practical use of Sanyo Nickel-Metal hydride rechargeable batteries(TWICELL)

■1-2 Classification of Batteries

There are many kind of batteries. The role of all batteries is exchanging of energy. That is to say battery is the device to exchange energy form chemical of physical to electrical. The battery that use chemical reaction is called chemical battery and the battery that use physical change is called physical battery.

There are three types of chemical battery such as primary batteries that can only one time use, secondary(rechargeable) batteries that can use repetitive by recharge and fuel cells that can continuously use if energy supply from outside.

Following figure shows the grouping of main consumer batteries according to above mentioned rules. Within secondary batteries it is called that acid secondary battery as using acid electrolyte alkaline secondary battery.

Table 1-2 and 1-3 shows summarization of performances for main commercialized chemical batteries.

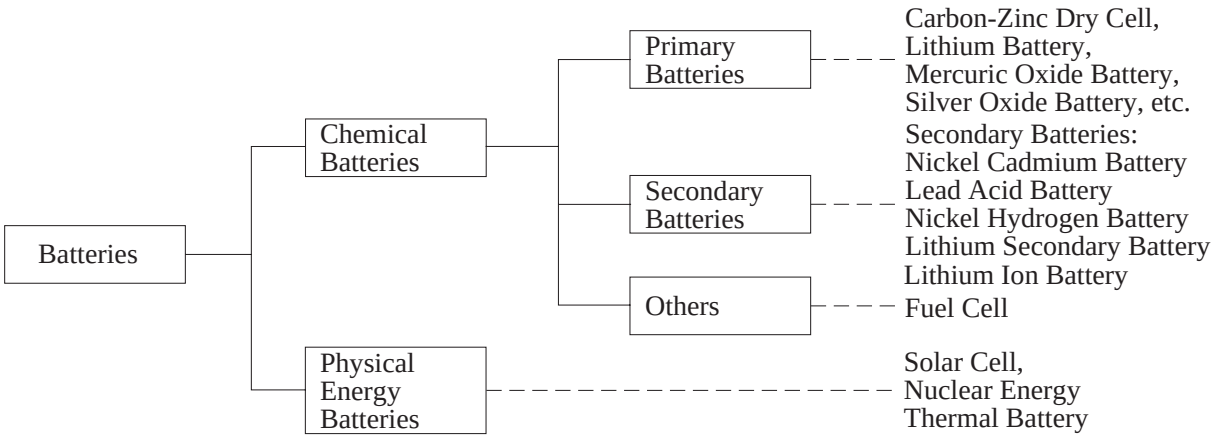

Table 1-2: Energy Density of Commonly used Batteries

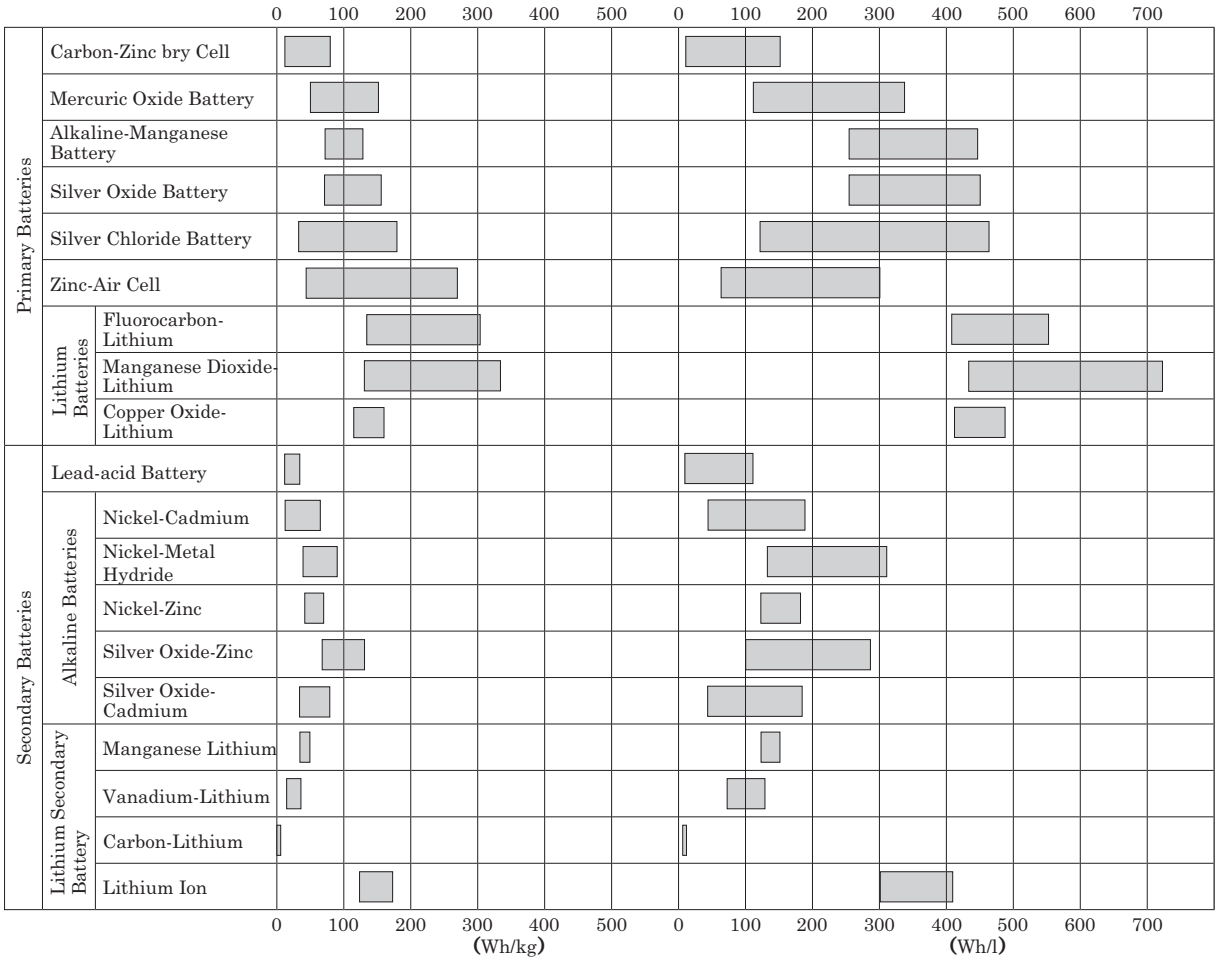

Table 1-3: Current characteristics of commonly used primary and secondary batteries

Category	Battery name		Composition			Rated voltage (V)	Self discharge rate at R.T. (%)	Discharge characteristics				Discharge cycle life(cycle)
			Active material of positive electrode	Electrolyte	Active material of negative electrode			High-rate discharge	Voltage stability	Temperature characteristics		
										Low temp.	High temp.	
Primary batteries	Carbon-zinc dry cell		MnO_2	NH_4Cl-$ZnCl_2$	Zn	1.5	10/year	B	C	C (Low-Temp. model available)	C	—
	Mercury oxide		HgO	KOH(ZnO)	Zn	1.3	5/year	C (intermittent) B ~ C	AA	C (Low-Temp. model available)	AA	—
	Alkaline-manganese		MnO_2	KOH(ZnO)	Zn	1.5	7/year	B	B~C	A	A	—
	Silver oxide		Ag_2O	KOH or NaOH(ZnO)	Zn	1.5	10/year	B	AA	A	A	—
	Silver chloride		AgCl	Saltwater	Mg	1.4	Storable for 3 ~ 5 years	AA	AA	AA	A	—
	Zinc air cell		Air (activated charcoal)	KOH(ZnO) or NH_4Cl	Zn	1.3	—	C	A	B	C	Negative Zn electrolyte replaceable
	Lithium		(CF)n	$LiBF_4$+ γ-butyrolactone	Li	3.0	0.5 ~ 1/year	B	A	A	A	—
			MnO_2	Propylene carbonate and other organic solvents	Li	3.0	0.5 ~ 1/year	A~B	A	A	A	—
			CuO	Propylene carbonate and other organic solvents	Li	1.5	0.5~ 1/year	B	A	A	A	—
Secondary batteries	Lead-acid battery		PbO_2	H_2SO_4	Pb	2.0	20/month	B	A~B	C	A	100~400
	Alkaline batteries	Nickel-cadmium	NiOOH	KOH	Cd	1.2	20/month	AA	A	A	A	500~5000
		Nickel-metal hydride	NiOOH	KOH	MH	1.2	30/month	AA	A	A	A	500~2000
		Nickel-zinc	NiOOH	KOH	Zn	1.6	30/month	AA	A	A	A	100~400
		Nickel-iron	NiOOH	KOH	Fe	1.2	20/month	B	A	C	AA	100~2000
		Silver oxide-zinc	AgO	KOH(ZnO)	Zn	1.5	30/month	AA	2 level portions	A	A	10~400
		Silver oxide-cadmium	AgO	KOH	Cd	1.1	25/year	AA	2 level portions	A	A	300~2000
	Lithium secondary batteries	Manganese-lithium	MnO_2	Organic solvent	Li-Al	3.0	2/year	A~B	A	A	A	50~3000
		Vanadium-lithium	V_2O_5	Organic solvent	Li-Al	3.0	2/year	A~B	A	A	A	50~2000
		Carbon-lithium	C	Organic solvent	Li alloy	3.0	5/year	C	C	C	C	2000
		Lithium ion	$LiCoO_2$	Organic solvent	Li-C	3.7	2/month	AA	A	A	A	500~1000