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Up-to-Date Development of Lithium-Ion Batteries in Japan

Key Words: Lithium-ion batteries, lithium polymer batteries, high-energy density, layered compounds, intercalation, polymer electrolytes, electric vehicles, load leveling

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Batteries have never attracted as much attention as they do today.

From the invention of “electric piles” by Volta in 1800 [1], batteries have a long history. Plante developed lead-acid batteries in 1859. Leclanche invented dry cells in the 1860s. Jungner invented nickel-cadmium (Ni-Cd) batteries in 1899. For the last two centuries, many types of primary and secondary batteries [2] have been developed and are now available as shown in Table 1 [3, 4]. It is surprising that old-type batteries developed in the nineteenth century are still used at the forefront of electronic devices and energy storage. In this respect, people in the twenty-first century should appreciate the great achievement of electrochemists in the last two centuries.

Nevertheless, batteries have never attracted as much attention as they do today. This is due to the rapid development of portable electronic devices, such as cellular phones, camcorders, and mobile computers. The demand for lightweight and small-sized secondary batteries for these portable electronic devices has accelerated the development of batteries with high-energy densities. Much effort had been devoted throughout the world to satisfy this demand, and small-sized secondary lithium-ion batteries (LIBs) came onto the market in 1991 in Japan. A lineup of commercially available LIBs is shown in Fig. 1. They have higher energy densities than any other commercially available secondary batteries, such as lead-acid, Ni-Cd, and nickel-metal hydride (Ni-MH) batteries. The volumetric and gravimetric energy densities of the latest LIBs reach 400 Wh dm⁻³ and 150 Wh kg⁻¹, respectively [5, 6]. Since their commercialization in 1991, LIBs have spread to a variety of portable electronic devices at an amazingly rapid pace. It might be said that now almost all Japanese people enjoy the benefits of LIBs. For example, at the end of March 2001, registered cellular phones, in which LIBs are exclusively used as a power source, exceeded 66.7 million [7]. This number is equal to about a half of the population of Japan. Furthermore, the high energy density of LIBs has stimulated their scaling up for use in electric vehicles (EVs) and dispersed energy storage systems for load leveling [8]. Hybrid electric vehicles (HEVs) using LIBs, which are capable of reducing CO₂ in exhaust gas by 50%, have been commercialized in Japan since 2000 (Fig. 2) [9, 10].

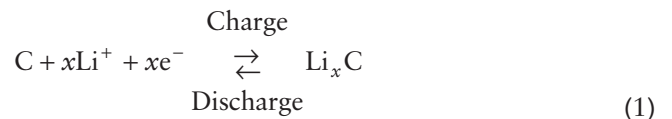
Here we review the up-to-date development of LIBs, focusing mainly on the situation in Japan. The materials, constructions, and performance of the latest commercially available LIBs, including lithium polymer batteries, which have come onto the market only fairly recently, are described in the first half of this article. We then discuss the recent trends in the development of battery materials for LIBs as well as those of large-scale LIBs.

LIBs

Battery Reactions

Commercially available LIBs generally employ carbon as a negative electrode, LiCoO₂ as a positive electrode, and a lithium salt dissolved in nonaqueous solvent as an electrolyte [11]. Figure 3 shows the principle of LIBs. The electrode reactions at the negative and positive electrodes [12] are described as

(Negative electrode)



(Positive electrode)

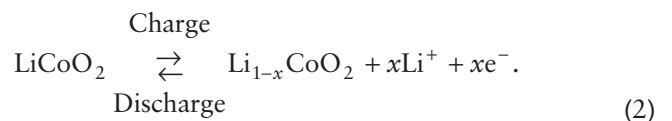
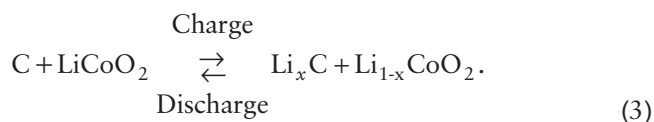


Table I. Commercially Available Primary and Secondary Batteries [3, 4].

Primary/ Secondary	Type	Components			Nominal Cell Voltage / V
		Negative Electrode	Electrolyte*	Positive Electrode	
Primary	Zinc-carbon (Leclanché)	Zn	NH ₄ Cl + ZnCl ₂ (aq)	MnO ₂	1.5
	Alkaline	Zn	KOH or NaOH (aq)	MnO ₂	1.5
	Zinc-silver oxide	Zn	KOH or NaOH (aq)	AgO ₂	1.55
	Zinc-air	Zn	KOH or NaOH (aq)	Air	1.4
	Lithium-manganese dioxide	Li	LiClO ₄ (org)	MnO ₂	3.0
	Lithium-carbon monofluoride	Li	LiBF ₄ (or)	(CF) _n	3.0
Secondary	Lead-acid	Pb	H ₂ SO ₄ (aq)	PbO ₂	2.0
	Nickel-cadmium	Cd	KOH (aq)	NiOOH	1.2
	Nickel-metal hydride	M-H	KOH (aq)	NiOOH	1.2
	Lithium-ion	C	LiPF ₆ (org)	LiCoO ₂	3.6-3.7
	Lithium polymer	C	LiPF ₆ , Li-imide (gel)	LiCoO ₂	3.6-3.7

* (aq): aqueous solution; (org): organic solution; (gel): gel electrolyte.

Both negative and positive electrodes are layered compounds, as shown in Fig. 3. During charging, the trivalent cobalt ion in LiCoO₂ is oxidized to tetravalent at the positive electrode and the resulting positive charge is compensated by deintercalation of the lithium ion into the solution, while the lithium ion in the solution is reductively intercalated between the layers of carbonaceous materials at the negative electrode. The reverse reactions take place during discharging. The overall battery reactions of LIBs are thus written as



Only the lithium ion moves back and forth between the positive and negative electrode upon charging and discharging, which gives rise to a potential difference of about 4 V between the two electrodes. The name, “lithium-ion” batteries, came from this simple mechanism, that is, the transfer of lithium ion between the electrodes.

The advantages of LIBs over conventional secondary batteries are: 1) high gravimetric and volumetric energy densities, 2) high operating voltages, 3) low self-discharge rates,

4) no memory effects, 5) wide temperature ranges of operation, and 6) quick-charge acceptance, as described in the following sections.

Materials

As was seen above, the positive electrode must contain lithium ions in its lattice when prepared. Many kinds of lithium-transition metal-oxides have been proposed as positive electrodes so far. These include LiCoO₂, LiNiO₂, LiMn₂O₄, etc. Of these, lithium cobalt oxide LiCoO₂ is almost exclusively used in small-sized LIBs because of its excellent cycleability and the ease of material preparation [13, 14]. The crystal structure of LiCoO₂ is shown in Fig. 4. LiCoO₂ has a

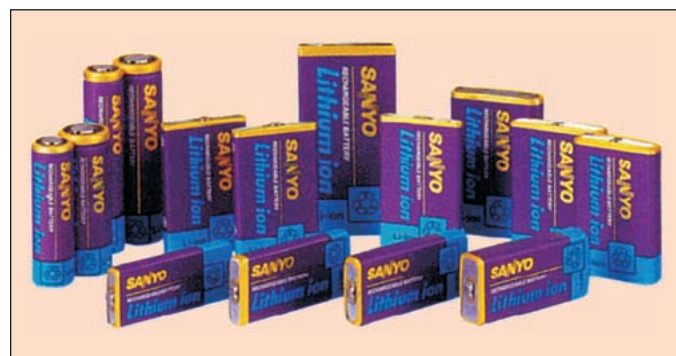


Fig. 1. A lineup of commercially available lithium-ion batteries [27].

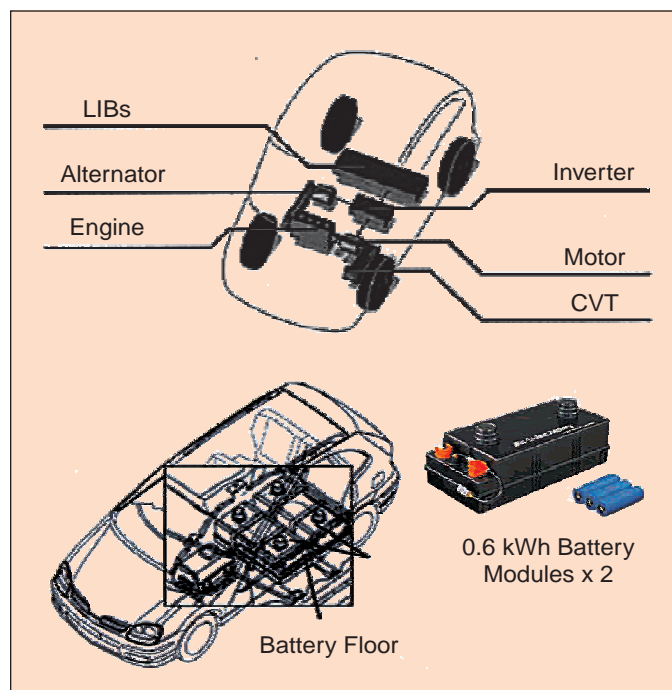


Fig. 2. Components of an internal combustion engine/lithium-ion battery hybrid electric vehicle [9, 10].

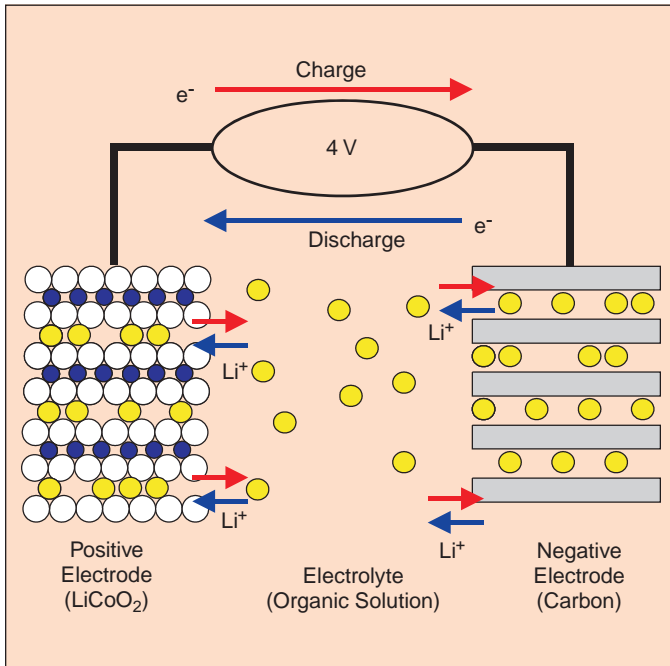


Fig. 3. Principle of lithium-ion batteries.

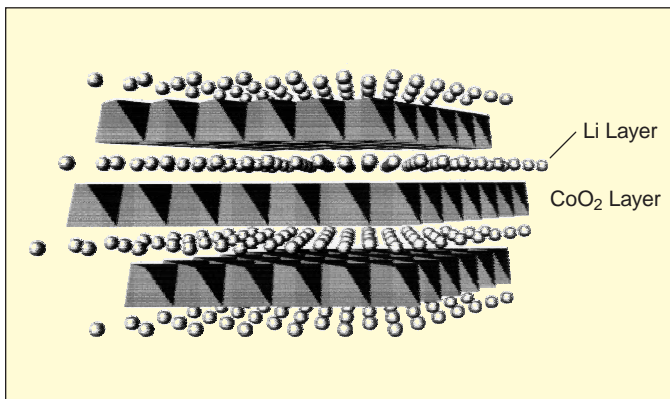


Fig. 4. Crystal structure of LiCoO_2 .

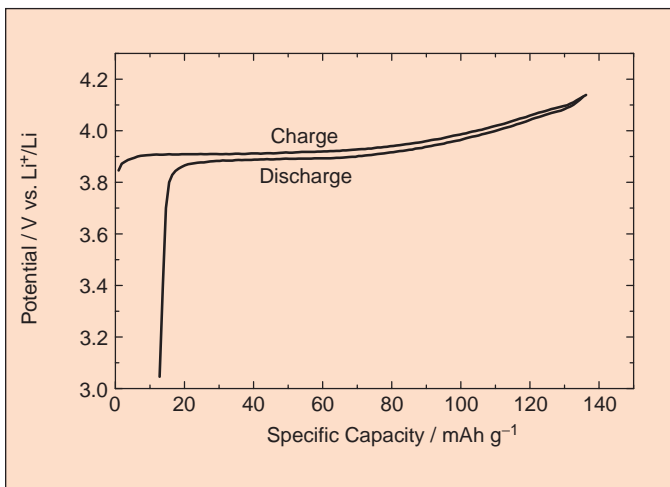


Fig. 5. Typical charge/discharge profiles of LiCoO_2 positive electrode between 3.0 and 4.15 V in $1 \text{ mol dm}^{-3} \text{ LiClO}_4\text{-PC}$ [15].

layered rock salt ($\alpha\text{-NaFeO}_2$ type) structure. Lithium ions reside between the CoO_2 layers consisting CoO_6 octahedra. Figure 5 shows typical charge/discharge profiles of LiCoO_2 [15]. Lithium deintercalation (charging) and intercalation (discharging) take place at high potentials of about 4 V against a metallic lithium electrode (Li^+/Li). LiCoO_2 shows excellent cycleability when cycled in the composition range $0.5 < x < 1.0$ in Li_xCoO_2 . Lithium deintercalation beyond this range deteriorates the layered structure of LiCoO_2 , and results in a poor cycleability. Only half of the theoretical capacity (274 mAh g^{-1}) thus can be used in practical cells.

As negative electrodes, carbonaceous materials are used in commercially available LIBs [16]. Graphite is a typical carbonaceous material that consists of hexagonal sheets of sp^2 -carbon atoms (called graphene sheets), weakly bonded together by van der Waals forces into an ABABAB... stacking, as shown in Fig. 6(a). Not only lithium ions, but also many kinds of ions and molecules can be intercalated between graphite sheets, and the resulting complexes are called “graphite intercalation compounds” (GICs) [17]. The important and characteristic property of GICs is the staging phenomenon, which is characterized by intercalate layers that are periodically arranged in the matrix of graphite sheets, as shown in Fig. 6(b). The stage structure of GICs is designated in terms of the stage index n , which denotes the number of graphene sheets between adjacent intercalate layers. Stage-1 Li-GIC is a fully lithiated state with a composition of LiC_6 , which restricts the specific capacity of graphite negative electrodes to 372 mAh g^{-1} .

Typical charge/discharge profiles of graphite are shown in Fig. 7. The intercalation and deintercalation of lithium ions take place with flat charge/discharge profiles at a very low potential ($< 0.25 \text{ V}$) that is close to the Li^+/Li half cell potential. X-ray diffraction (XRD) [18, 19] and Raman [20] studies have revealed that the following stage transformations successively take place during charging and discharging:

Dilute stage-1	\leftrightarrow	Stage-4	(ca. 210 mV)
Stage-2L	\leftrightarrow	Stage-2	(ca. 120 mV)
Stage-2	\leftrightarrow	Stage-1	(ca. 90 mV)

where dilute Stage-1 denotes a phase in which lithium is intercalated uniformly within the host and Stage-2L denotes a liquid-like Stage-2 phase that has no in-plane ordering [18]. As shown in Fig. 7, the charge consumed during the first charging (ca. 400 mAh g^{-1}) is not fully recovered on the following discharging. The lost capacity is called “irreversible capacity” (Q_{irr}), 65 mA h g^{-1} in Fig. 7, and is seen only in the first cycle. It is widely believed that the irreversible capacity is consumed by solvent decomposition followed by protective surface film formation on graphite [16]. The surface film is often called “solid electrolyte interface (SEI).” The SEI suppresses further solvent decomposition, but through this film lithium ion can be intercalated within a graphite negative electrode; that is, the presence of the SEI layer is a requisite for graphite negative electrodes to be used in commercially available cells. The

mechanism for SEI formation has been extensively studied in order to obtain a good SEI layer at a minimum irreversible capacity [21, 22]. In the second cycle and later, the irreversible capacity disappears and a specific capacity in the range 300-350 mAh g⁻¹ is usually obtained with a coulombic efficiency > 99%. Less graphitized carbons such as cokes were used as negative electrodes in the early 1990s; however, graphite is currently employed in almost all LIBs because of its higher specific capacity.

Electrolyte solutions are indispensable for batteries because they carry lithium ions between the positive and negative electrodes. An aqueous electrolyte solution cannot be used in LIBs because its potential window is limited within 2 V at maximum by the decomposition of water, that is, hydrogen and oxygen evolution. Hence, nonaqueous (organic) electrolyte solutions, which are much more stable against the high terminal voltage of about 4 V, are used in LIBs. Typical organic solvents used in LIBs are summarized in Table II. [23, 24]. Cyclic esters and lactones—such as ethylene carbonate (EC), propylene carbonate (PC), and γ -butyrolactone (GBL)—have a high dielectric constant and a high viscosity. On the other hand, aliphatic esters and ethers—such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethoxyethane (DME), and tetrahydrofuran (THF)—have a low dielectric constant and a low viscosity. Commercially available LIBs usually employ a mixed solvent system that is based on a viscous solvent with a high dielectric constant and a less viscous solvent. The high dielectric constant promotes dissociation of lithium salts and the low viscosity enhances the movement of lithium ions. Highly graphitized carbons are degraded upon charging in PC-based solutions [25], so that EC-based solutions are exclusively used in LIBs using graphite as negative electrodes. A lithium salt is dissolved in these mixed solvents to obtain ionic conductivity. Typical lithium salts and their conductivities in various solvent systems are summarized in Table III [26]. As shown in Table III, LiPF₆ shows the highest ionic conductivity, and is most widely used in practical cells.

Commercially Available LIBs

Figure 8 shows the cell structures of cylindrical and prismatic LIBs [27]. The powder of LiCoO₂ is mixed with a conductive filler, e.g., acetylene black, and a binder, e.g., poly(vinylidene difluoride). A thin layer of the mixture (100-150 μ m in thickness) is coated on an aluminum foil current collector to form a positive electrode. In a similar manner, a thin layer of a graphite powder/binder mixture is coated on a copper current collector to form a negative electrode. A porous separator (25 μ m in thickness) made of polyethylene or polypropylene is sandwiched between the positive and negative electrodes. They are rolled up spirally and inserted in a steel casing (negative can). An organic electrolyte solution containing a lithium salt is injected in the casing and sealed with a positive cap. For safety, a pressure valve and a PTC (positive temperature coefficient) element are provided to release gas inside the cell should high pres-

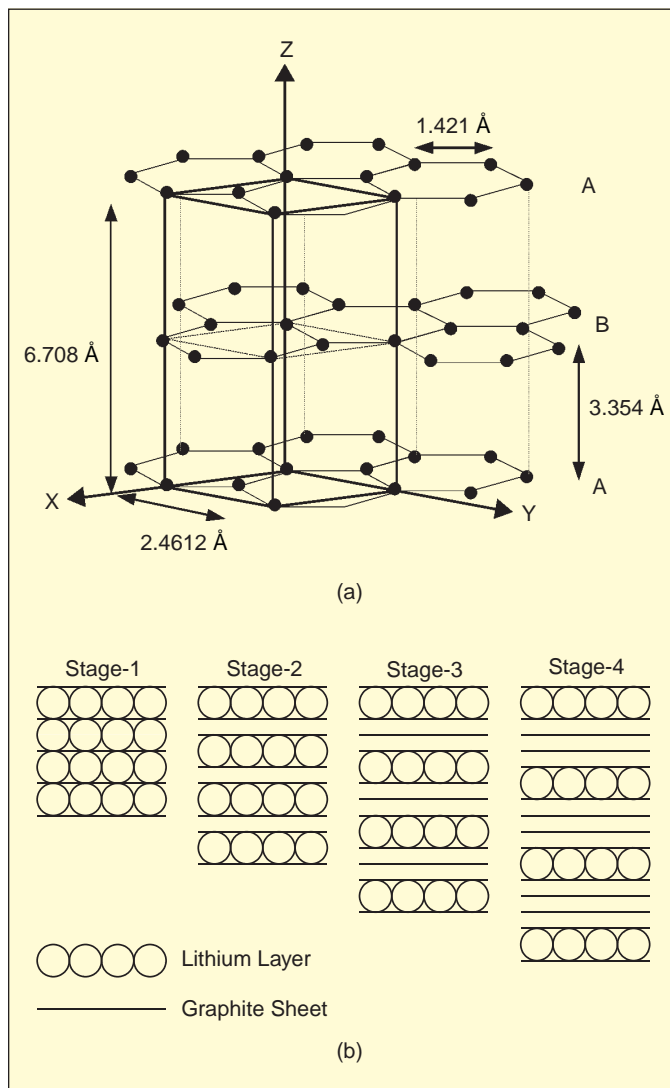


Fig. 6. (a) Crystal structure of graphite and (b) stage structures of graphite intercalation compounds.

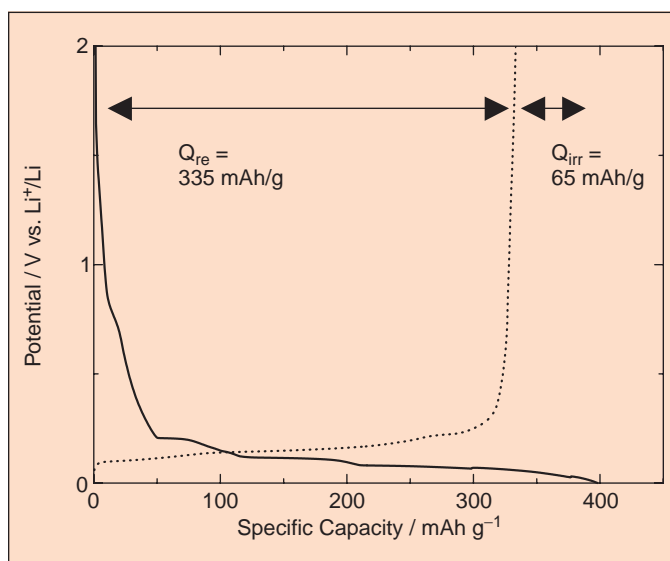


Fig. 7. Typical charge/discharge profile of graphite negative electrode between 0.0 and 2.0 V in 1 mol dm⁻³ LiClO₄-EC/DEC (1:1 by volume).

Table II. Characteristics of Organic Solvents in LIBs [23, 24].

Solvent	Melting Point / °C	Boiling Point / °C	Dielectric Constant at 25 °C / -	Viscosity at 25 °C / cP	Donor Number / -
Ethylene carbonate (EC)	39-40	248	89.6 ^a	1.86 ^a	16.4
Propylene Carbonate (PC)	-49.2	241.7	64.4	2.53	15.1
γ-Butyrolactone (GBL)	42	206	39.1	1.751	-
Dimethyl carbonate (DMC)	0.5	90-91	-	0.59	-
Diethyl carbonate (DEC)	-43	126.8	2.82	0.748	-
Ethyl Methyl carbonate (EMC)	-55	108	2.9	0.65	-
1,2-Dimethoxyethane (DME)	-58	84.7	7.2	0.455	24
Tetrahydrofuran (THF)	-108.5	65	7.25 ^b	0.46 ^b	20
Methyl Formate (MF)	-99	31.5	8.5	0.33	-

^a at 40 °C and ^b at 30 °C.

surization by gas evolution occur and to shut down the current upon thermal runaway, respectively. Cylindrical cells are used in camcorders, portable computers, etc. whereas prismatic cells in smaller portable electronic devices such as cellular phones. Some types of prismatic cells use aluminum as a negative casing instead of steel, which reduces the weight of the cells by about 30%. The energy density of LIBs has been improved every year. A two-fold increase in energy density was achieved in the last 10 years, and LIBs with the volumetric and gravimetric energy densities greater than 400 Wh dm⁻³ and 150 Wh kg⁻¹, respectively, are now available as mentioned earlier.

Figures 9(a) and (b) show typical discharge characteristics of a cylindrical LIB (type 18650, outer diameter: 18 mm, height: 65 mm, weight: 41 g) [27]. The nominal terminal voltage and capacity are 3.7 V and 1700 mAh, respectively. Even at a high discharge rate of 2 C mA [28], 95% of the capacity can be obtained at room temperature. The ionic conductivity of nonaqueous electrolyte solutions is lower than two orders of magnitude compared to that of aqueous solutions; however, the low conductivity is made up for by using thin and large-area electrodes stuffed into a limited space. In addition, LIBs can be

used over a wide temperature range, -20 to 60 °C, as shown in Fig. 9(b). Commercially available LIBs retain 70-80% of the initial capacity even after 300 cycles, and more than 500 cycles of charging and discharging can be attained [27]. The self-discharge rate of LIBs is typically 35% per year at room temperature, which is much slower than that of Ni-Cd or Ni-MH cells. Figure 10 shows a charging profile of the 18650 cells [27]. LIBs are typically charged at a constant current to a predetermined cell voltage, and then at the constant voltage, which is called constant current/constant voltage (CC/CV) charging. The final voltage is usually set at 4.1-4.2 V, which depends on the combination of the positive and negative electrode materials. Overcharge beyond this limit may lead to combustion or explosion so that the cells should be charged with their exclusive chargers. It takes a few hours for LIBs to be fully charged, while about 90% of capacity could be charged in an hour.

Lithium Polymer Batteries

Gel Electrolytes

Portable electronic devices, especially cellular phones, are becoming immensely popular in Japan, which imposes a demand for even smaller secondary batteries. However, it is widely recognized that a critical thickness is 4 mm for LIBs using metal cans as casings. In 1999, the limit of 4 mm was overcome by lithium polymer batteries (LPBs) using polymer electrolytes [29] and aluminum/resin-laminated films (~100 μm in thickness) as casings.

The major difference between LIBs and LPBs is that the latter use polymer electrolytes instead of liquid electrolyte solutions in the former. Polymer electrolytes used in commercially available LPBs are so called “gel electrolytes.” They are composed of an electrochemically inactive polymer matrix swollen by a lithium salt solution in a compatible solvent, and are further classified as “homogeneous gels” and “porous gels.” At high temperatures they flow like liquid, but below a glass transition temperature (T_g) they behave as rubber, as shown in Fig. 11. A suitable choice of a lithium salt and a solvent system can attain a high conductiv-

Table III. Ionic Conductivity of Various Electrolyte Solutions [26].

Salt*	Ionic conductivity ** / mS cm ⁻¹				
	PC	GBL	PC/DME	GBL/DME	PC/EMC
		(1:1 mol)	(1:1 mol)	(1:1 mol)	
LiBF ₄	3.4	7.5	9.7	9.4	3.3
LiClO ₄	5.6	10.9	13.9	15.0	5.7
LiPF ₆	5.8	10.9	15.9	18.3	8.8
LiAsF ₆	5.7	11.5	15.6	18.1	9.2
LiCF ₃ SO ₃	1.7	4.3	6.5	6.8	1.7
LiN(CF ₃ SO ₂) ₂	5.1	9.4	13.4	15.6	7.1
LiC ₄ F ₉ SO ₃	1.1	3.3	5.1	5.3	1.3

* Concentration: 1 mol dm⁻³

** PC: propylene carbonate; GBL: γ-Butyrolactone; DME: dimethyl ether; EMC: ethyl methyl carbonate

ity (10^{-3} - 10^{-2} S cm^{-1}), which is comparable with that of a liquid electrolyte solution.

Homogeneous gels are prepared by polymerizing a mixture of a monomer and a liquid electrolyte solution. The poly-

mer matrix completely dissolves in the liquid electrolyte solution in homogeneous gels. Typical matrix polymers used in homogeneous gels are poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), and poly(methyl methacrylate) (PMMA). In contrast, porous gels are prepared using a phase separation of a polymer matrix in a solvent system. The resulting porous matrix is soaked in a liquid electrolyte solution to form a solid gel. Microscopically the crystalline part of the polymer matrix forms a framework of the gel, while the amorphous part dissolves the electrolyte solution. Co-polymer of vinylidene difluoride and hexafluoropropylene P(VdF-HFP), which was developed by Bellcore [30], is a typical polymer matrix for porous gels. Both types of gel electrolytes are now employed in commercially available LPBs.

The main advantage of LPBs is the absence of free solvents. Figure 12 compares the amounts of evaporated solvent when a gel electrolyte and a porous separator containing a liquid electrolyte solution were heated to various temperatures [31]. Evaporation of solvent is much lower from the gel electrolyte. Consequently, the use of gel electrolytes results in a decrease in internal pressure and suppresses the expansion of the battery casing, which enables the use of mechanically weak aluminum/resin laminated films as casings of LPBs. In addition, the absence of free solvents greatly improves the safety and reliability of the cells.

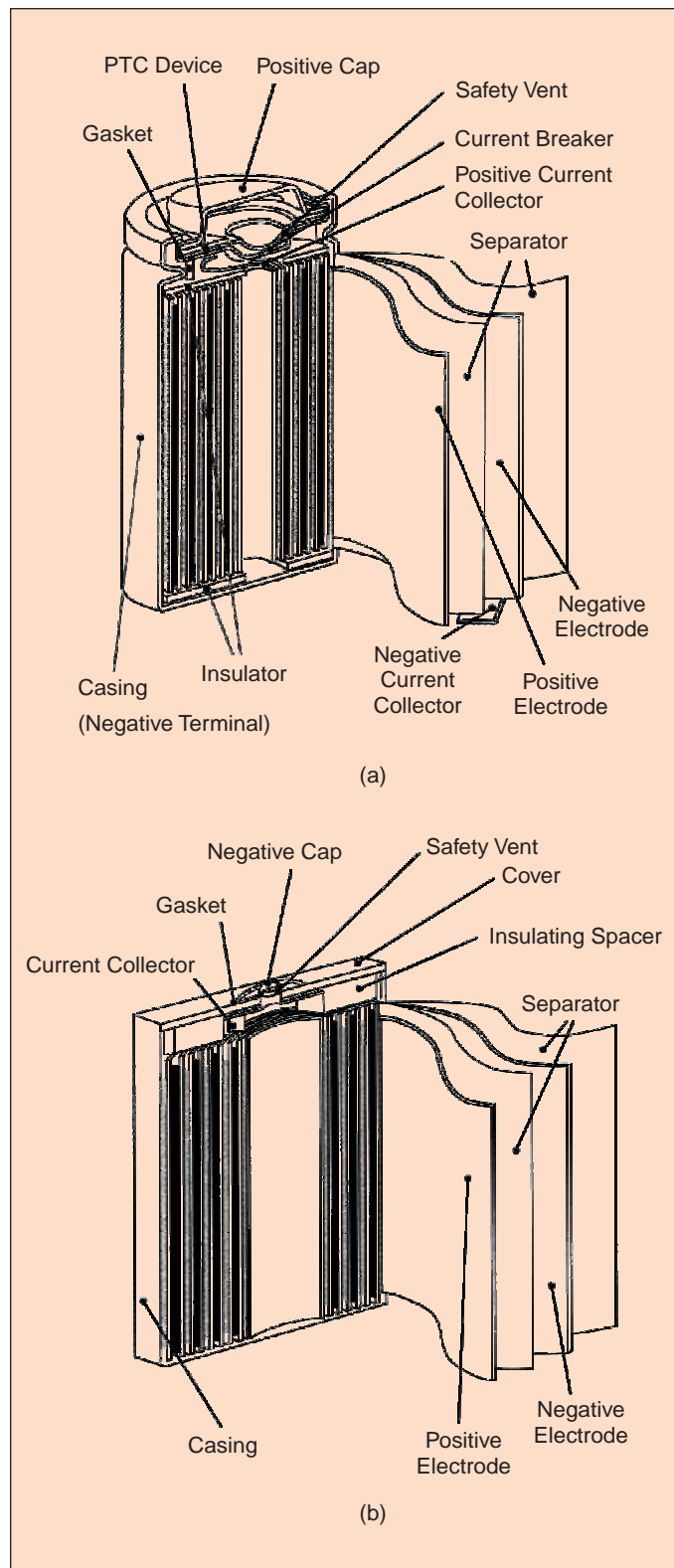


Fig. 8 Cell structures of (a) cylindrical and (b) prismatic lithium-ion batteries [27].

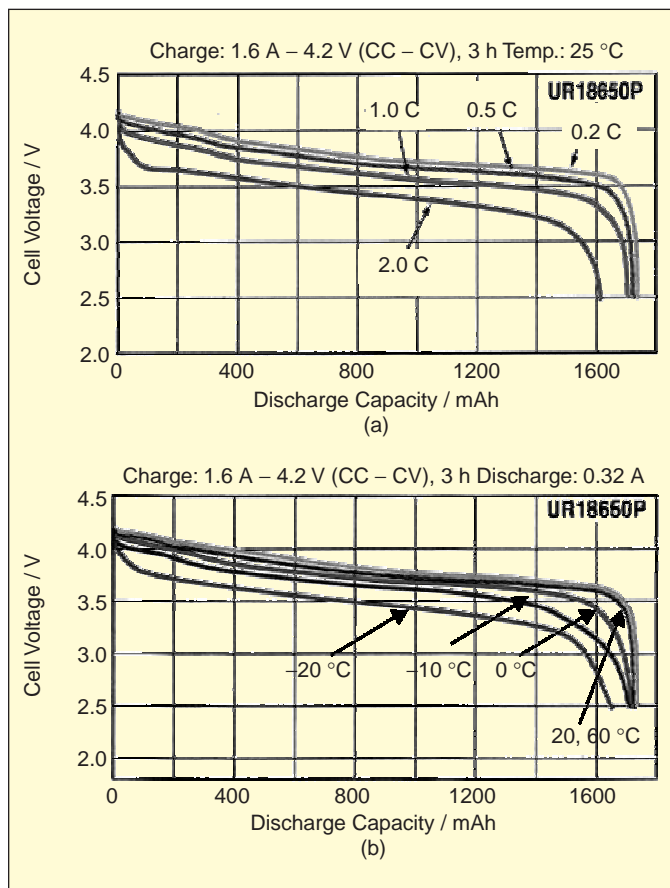


Fig. 9. Performance of a lithium-ion battery (type 18650, outer diameter: 18 mm, height: 65 mm, weight: 41 g). (a) Rate capability and (b) temperature dependence [27].

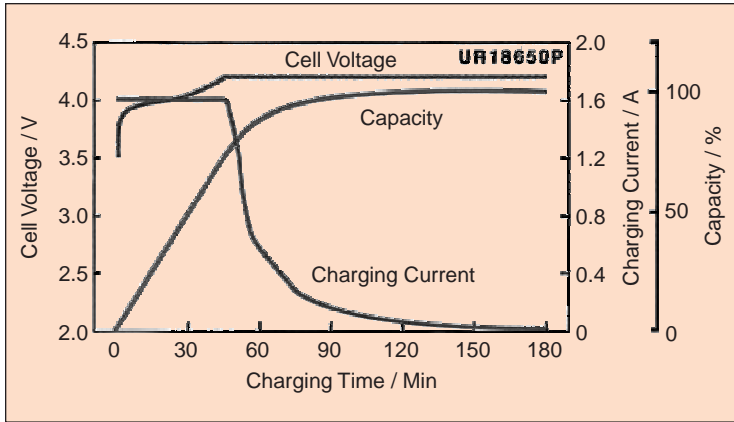


Fig. 10. Constant current/constant voltage charging for a lithium-ion battery (Type 18650) [27].

Commercially Available LPBs

Figure 13 shows an LPB and its construction [32]. LiCoO_2 and carbons are commonly used as positive and negative electrode materials, respectively, in LPBs. For porous gel-type LPBs, the positive and negative electrodes and a polymer matrix layer are rolled up and inserted in an aluminum/resin-laminated film casing. A liquid electrolyte solution is then injected to form a gel electrolyte. A polyolefin microporous separator and/or fine ceramic filler, such as SiO_2 , are often added to improve the mechanical strength. For the preparation of homogeneous gel-type LPBs, a polyolefin microporous separator is sandwiched between the positive and negative electrodes. They are rolled up and inserted in a laminated film casing. After a mixture of a monomer and an electrolyte solution are injected in the cas-



Fig. 11. Photograph of a homogeneous gel electrolyte. [Courtesy of Sanyo Electronic Co.]

ing, thermal polymerization is carried out to form a gel polymer in the cell.

Figure 14 shows discharge characteristics of a typical LPB (type: 363562, size: $35 \times 62 \times 3.6$ mm, weight: 13.5 g; nominal capacity: 570 mAh). The discharge characteristics at high rates and at low temperatures, which are considered to be weak points of LPBs, have been improved to levels comparable with those of LIBs. The gravimetric and volumetric energy densities of the LPB are 156 Wh kg^{-1} and 270 Wh dm^{-3} , respectively. The results of safety tests are not found in the literature; however, the absence of free solvents undoubtedly improves the safety of LPBs. Most of LPBs are currently manufactured for use as power sources of cellular phones that become thinner and lighter every year in Japan.

Recent Development of Battery Materials

Negative Electrode Materials

As mentioned earlier, graphite is most widely used as a negative electrode in LIBs. In addition to graphite, many kinds of carbonaceous materials such as carbon black, activated carbon, carbon fiber, and cokes are manufactured and have been tested as negative electrodes. The electrochemical characteristics of carbonaceous materials depend on the morphology, the crystallinity, the orientation of crystallites, etc. Pyrolyzed carbons are classified as “soft carbons (graphitizable carbons)” and “hard carbons (nongraphitizable carbons)” [16]. Figure 15 shows relationships between the specific capacity and heat-treatment temperature (HTT) of soft and hard carbons [33]. In Fig. 15, two types of carbons have attracted attention because they exhibit higher specific capacities than those of highly graphitized carbons heat-treated at temperatures > 2400 °C. One is soft carbons heat-treated at temperatures below 1000 °C, which show a specific capacity in the range $500\text{-}1000 \text{ mAh g}^{-1}$ [34, 35]. Typical charge/discharge profiles are shown in Fig. 16(a) [36]. This kind of soft carbon is characterized by a large hysteresis in their potential pro-

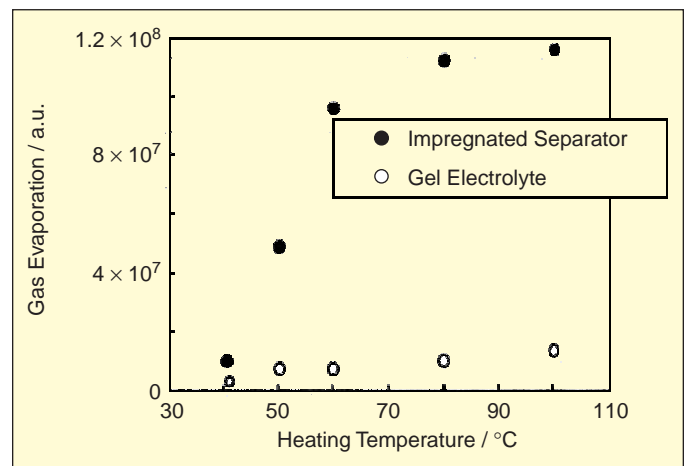


Fig. 12. Amounts of evaporated solvent from a gel electrolyte and a porous separator containing a liquid electrolyte solution plotted against heating temperature [31].

files. The presence of the hysteresis leads to a loss of stored electrical energy, which is dissipated as heat during charge/discharge cycles. Another drawback is poor cycleability, and the capacity decreases to a half of the initial capacity in several cycles. Various models explaining their high capacity have been suggested so far. These include lithium intercalation between graphene sheets with an in-plane LiC_2 structure [37], lithium doping within nanoscopic cavities [38], formation of ionic complexes like lithium naphthalene [39], a chemical reaction between inserted lithium atoms and the hydrogen-terminated edges of hexagonal carbon fragments [40], etc. However, the mechanism for the high capacity is still controversial.

The other type of the high-capacity carbons are hard carbons heat treated at $\sim 1000^\circ\text{C}$, which exhibits a specific capacity in the range $500\text{--}700\text{ mAh g}^{-1}$. Hard carbons pyrolyzed from petroleum pitch, poly(furfuryl alcohol), and phenolic resins belong to this category. This type of hard car-

bon is characterized by the presence of a low and large potential plateau at about 0.05 V in their charge/discharge profiles as shown in Fig. 16(b) [41]. It seems that the high capacity is brought about by Li-cluster formation in nanopores formed by small graphene sheets ($\sim 2.5\text{ nm}$) in the hard carbons [42], which is called a “house of card” model [43].

Lithium metal is the most attractive alternative material as a negative electrode in LIBs because of its low electrode potential (-3.045 V vs. standard hydrogen electrode) and its high specific capacity (3860 mAh g^{-1}). In fact, lithium metal has been widely used as a negative electrode in primary lithium cells for more than 20 years. The R&D of secondary batteries using lithium metal began in 1970s, and secondary Li/MoS₂ cells were once commercialized in 1987 for cellular phones. In secondary cells, however, prolonged charge/discharge cycling causes dendrite formation of the lithium metal, which results in poor safety and cycleability. Because of the safety problems, all the manufactured Li/MoS₂ cells were recalled in 1989. The key to suppress dendritic deposi-

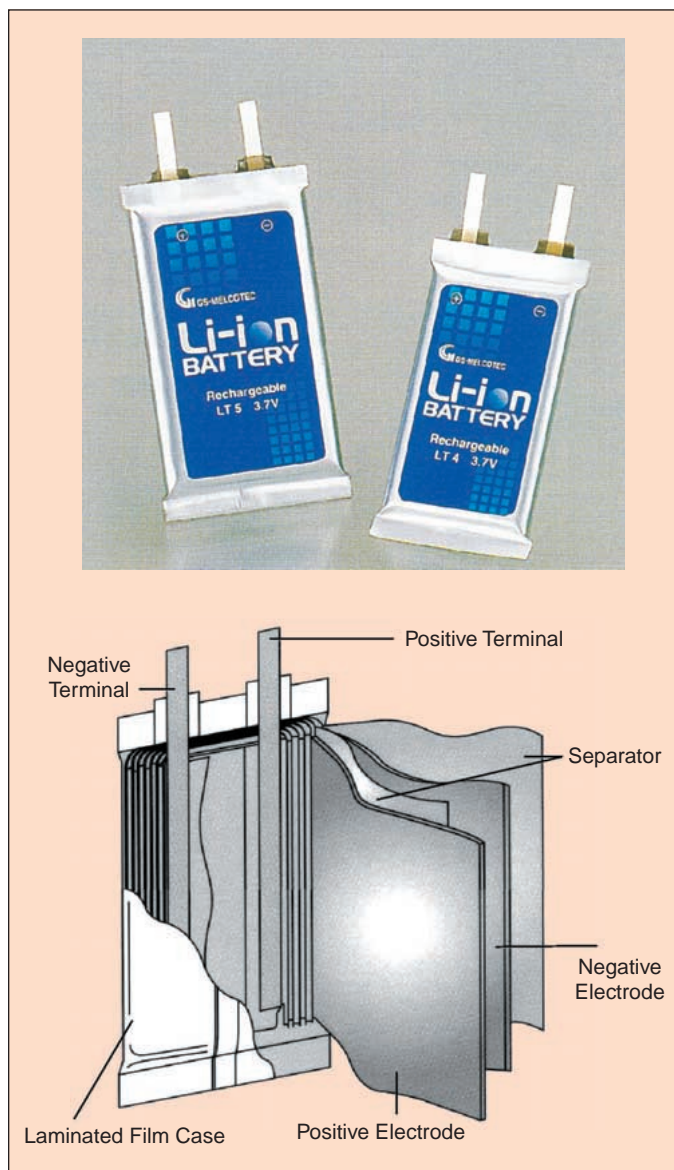


Fig. 13. Cell construction of a lithium polymer battery [32].

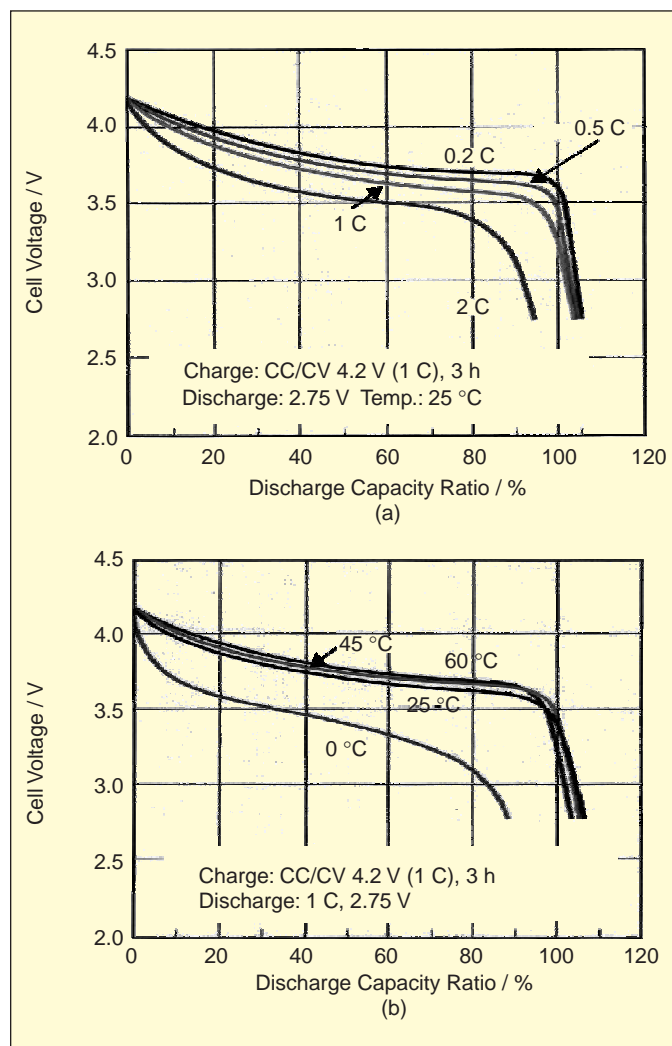


Fig. 14. Performance of a lithium polymer battery (type: 363562, size: $35 \times 62 \times 3.6\text{ mm}$, weight: 13.5 g ; nominal capacity: 570 mAh). (a) Rate capability and (b) temperature dependence [32].

tion of lithium metal is to control the SEI (solid electrolyte interface) layer formed on lithium metal. For this purpose, the composition and morphology of SEI have been studied extensively using a variety of analytical tools such as FT-IR [44], X-ray photoelectron microscopy (XPS) [45], and atomic force microscopy [46]. In spite of extensive efforts of many researchers, it will be some time before secondary lithium metal batteries are placed on the market.

Another class of potential negative electrodes are lithium-alloys and intermetallic compounds Li_xM (Mg, Ca, Al, Si, Ge, Sn, Pb, As, Sb, Bi, Pt, Ag, Au, Zn, Cd, Hg, etc.) that offer much higher specific capacities than graphite, e.g., 710 mAh g^{-1} for $\text{Li}_{4.4}\text{Sn}$ [47]. However, alloying causes a large volume change (i.e., 100-300%) and the resulting alloys are usually brittle. Lithium-alloy electrodes hence suffer from cracking and crumbling (pulverization), and deteriorate after only several charge/discharge cycles. A big breakthrough in lithium-alloy electrodes was proposed by Fuji Photo Film Co. in 1997 [48]. They developed tin-based amorphous composite oxide (TCO), $\text{SnB}_x\text{P}_y\text{O}_z$ [$x = 0.44-0.6$, $y = 0.6-0.4$, and $z = (2 + 3x + 5y)/2$], which exhibits a good

cycleability as well as a high specific capacity ($\sim 640 \text{ mAh g}^{-1}$). During the first charging, $\text{SnB}_x\text{P}_y\text{O}_z$ is first reduced to active Sn particles and an oxide matrix, and the Sn metal is alloyed with Li at lower potentials. The oxide matrix stabilizes the fine Sn particles, and greatly improves the cycleability. Stimulated by the success of TCO, lithium-alloy and related materials have received particular attention, and many kinds of improved alloys and intermetallic compounds have been proposed [47]. These include Sn-Sb [49], Sn-Fe(-C) [50], In-Sb [51], and Mg-Ge [52].

Lithium transition-metal nitrides ($\text{Li}_{3-x}\text{M}_x\text{N}$, M: Co, Ni, and Cu) are also potential candidates for negative electrode materials [53]. $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ shows a high capacity of 900 mAh g^{-1} at an average discharge potential of 0.7 V , and shows good cycleability [54]. Spinel $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is an interesting material as a negative electrode [55]. Although the discharge potential ($\sim 1.6 \text{ V}$) is not as low as other alternative negative electrodes, this material shows no volume change during charging and discharging, and hence is characterized by an excellent cycleability with a small capacity fade upon prolonged cycling.

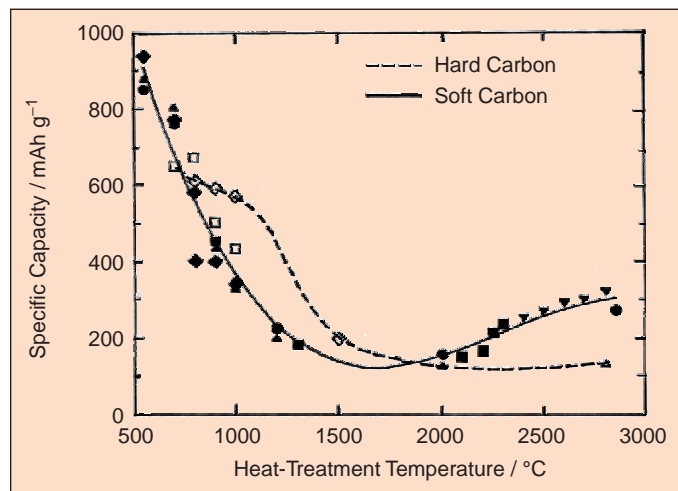


Fig. 15. Relationships between reversible specific capacity and heat-treated temperature (HTT) [33]. Closed and open data points show data obtained for soft and hard carbons, respectively.

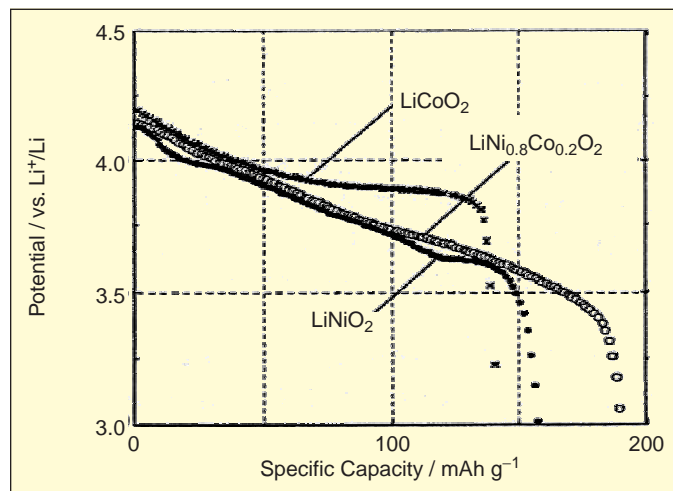


Fig. 17. Discharge curves of LiCoO_2 , LiNiO_2 , and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrodes [60].

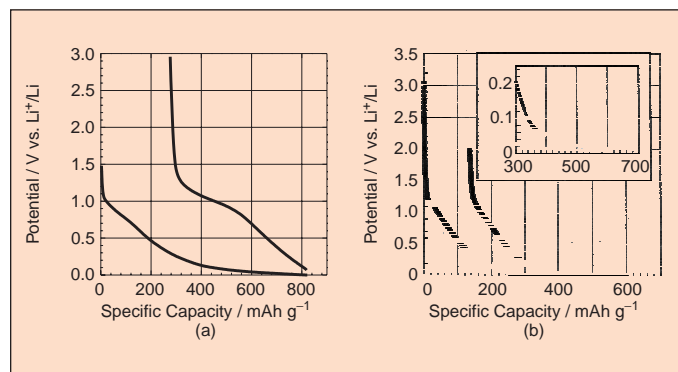


Fig. 16. Typical charge/discharge profiles of high-capacity (a) soft and (b) hard carbons. (a) mesocarbon microbeads heat-treated at $700 \text{ }^\circ\text{C}$ [36]; (b) petroleum-pitch-based pseudo-isotropic carbon [41].

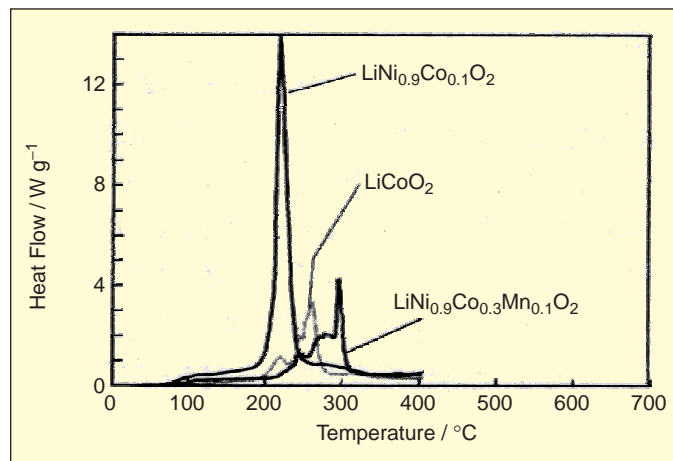


Fig. 18. Differential scanning calorimetry (DSC) curves of LiCoO_2 , $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$, and $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$ [61].

Positive Electrode Materials

As mentioned earlier, most small-sized LIBs employ LiCoO_2 as a positive electrode material. Nevertheless, the toxicity and the scarcity of cobalt resources, and the relatively low specific capacity ($\sim 140 \text{ mAh g}^{-1}$) have accelerated the development of alternative positive electrode materials with higher specific capacities and lower costs.

LiNiO_2 -based oxides are among the most promising candidates as 4-V class positive electrode materials [56, 57]. LiNiO_2 crystallizes in the same layered structure as LiCoO_2 . Lithium ion is reversibly extracted and inserted in the range $0.3 \leq x \leq 1.0$ in Li_xNiO_2 , and thereby LiNiO_2 offers a higher specific capacity ($\sim 200 \text{ mAh g}^{-1}$) than LiCoO_2 . Preparation of stoichiometric LiNiO_2 is very difficult because Ni^{3+} ions are unstable and tend to be reduced to Ni^{2+} ions, which occupy the Li^+ sites in the layered rock-salt structure. Even stoichiometric LiNiO_2 shows poor cycleability upon prolonged cycling. The structural instability of LiNiO_2 can be partly overcome by Co^{3+} doping ($\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$) [58, 59]. Figure 17 compares discharge curves of LiCoO_2 , LiNiO_2 , and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrodes [60]. A specific capacity of about 190 mAh g^{-1} can be achieved from the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrode. Figure 18 shows differential scanning calorimetry (DSC) curves of LiCoO_2 , $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$, and $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$ [61]. Singly doped $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ decomposes at about 200°C accompanied by a large exothermic heat. Such thermal instability is greatly improved by double doping of Co and Mn ions [62] as shown in Fig. 18. Doubly doped $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$ exhibits a specific capacity of 160 mAh g^{-1} with a good cycleability [63].

Manganese is an abundant natural resource and its toxicity is low, which makes spinel LiMn_2O_4 positive electrodes very attractive for use not only in small-sized cells, but also in large-scale LIBs [64-66]. The charge/discharge profiles of spinel LiMn_2O_4 are shown in Fig. 19. The practical capacity of LiMn_2O_4 in the 4-V region is around 130 mAh g^{-1} . Spinel LiMn_2O_4 electrodes suffer from a serious capacity fade upon prolonged charge/discharge cycling. Partial substitution of Mn^{3+} with Li^+ [67] or other transition metal ions, such as Cr^{3+} , Co^{3+} , and Ni^{2+} [68], is effective to suppress the capacity fade. It was reported that the presence of oxygen vacancies plays a major role in the capacity fade of undoped LiMn_2O_4 [69-71]. The partial substitution decreases oxygen vacancies, which improves the cycleability at room temperature. However, even doped spinel electrodes deteriorate at elevated temperatures ($\sim 60^\circ\text{C}$) accompanied by the dissolution of Mn ion [72]. It seems that the capacity fade at elevated temperatures is related to the presence of acid in the solution [72] and the structural instability of $\text{Li}_x\text{Mn}_2\text{O}_4$ at $x \sim 0.8$ [73].

It is worth mentioning that doped spinel electrodes ($\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$, M: Cr, Co, Ni, Cu, etc.) exhibit a capacity in the 5 V range in addition to that in the 4 V range [74-76]. The high voltages of these doped spinel electrodes result from high solid-state redox potentials of the dopants in the spinel framework. Unfortunately, the 5 V positive electrodes cannot

be used in LIBs at present because of a lack of electrolyte materials that are stable against the high potentials. Other types of 5 V positive electrodes such as inverse-spinel LiNiVO_4 [77] and olivine LiCoPO_4 [78] have been also reported.

Layered manganese dioxide, LiMnO_2 , has a lower working potential than the spinel electrodes, but shows a higher capacity ($\sim 200 \text{ mAh g}^{-1}$) [79]. The layered structure of pure LiMnO_2 tends to transform into the spinel structure on charge/discharge cycling, resulting in a rapid deterioration in performance. The transformation can be suppressed by partial substitution of Mn^{3+} by other metal cations, and thereby the performance can be greatly improved. Cr-doped $\text{Li}(\text{Cr}_{0.4}\text{Mn}_{0.4}\text{Li}_{0.2})\text{O}_2$ exhibits a specific capacity of 180 mAh g^{-1} at 55°C , and the transformation to spinel is not observed at least for 200 cycles [80]. However, the cycleability of these layered manganese oxides is still open to questions for practical use in LIBs.

Electrolytes

The choice of the proper electrolyte is crucial in LIBs. Commercially available LIBs commonly employ an electrolyte solution of LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and an aliphatic carbonate such as dimethylcarbonate (DMC), diethylcarbonate (DEC), and ethyl methyl carbonate (EMC). Electrolyte solutions containing LiPF_6 show a high ionic conductivity ($\sim 10^{-2} \text{ S cm}^{-1}$) and high electrochemical stability against LiCoO_2 positive electrodes up to $\sim 4.5 \text{ V}$, and furthermore can provide a dense and uniform SEI (solid electrolyte interface) layer on graphite negative electrodes. However, its safety cannot be guaranteed upon thermal runaway because LiPF_6 decomposes gradually at about 100°C and extensively at 200°C . Novel lithium salts that show superior stability as well as high ionic conductivity have been reported recently. These include lithium imides [81] such as $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, and $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$, as well as lithium fluoroalkylphosphates such as $\text{LiPF}_{6-n}(\text{CF}_3)_n$ [82] and $\text{LiPF}_{6-n}(\text{C}_2\text{F}_5)_n$ [83]. The sensitivity towards hydrolysis is also suppressed to a

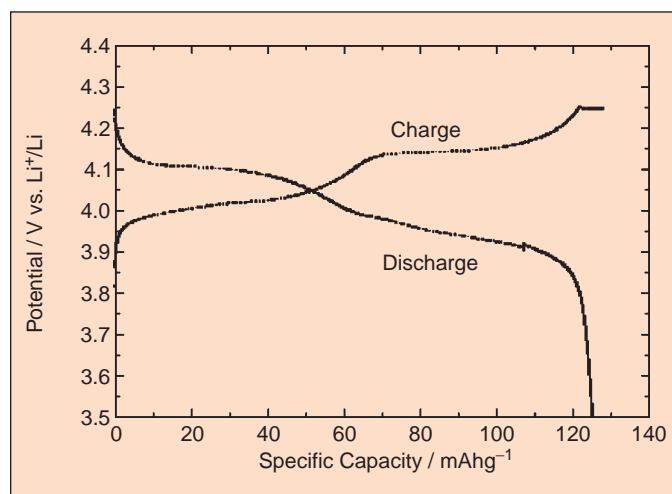


Fig. 19. Charge/discharge profiles of spinel LiMn_2O_4 electrode between 3.5 and 4.25 V (CC/CV) in 1 M LiPF_6 -EC/DMC (1:2 by volume).

Type	Stationary	EV application
Module capacity	2 kWh class	3 kWh class
Gravimetric energy density / Wh kg ⁻¹	120	150
Volumetric energy density / Wh dm ⁻³	240	300
Power density / Wh kg ⁻¹	-	400
Cycle life / cycles	3500	1000
Energy efficiency / %	> 90	> 85

great extent. It has been pointed out that the imide salts corrode aluminum current collectors in LIBs [84].

Another important issue to improve safety is the development of nonflammable solvents. In this respect, partially fluorinated solvents are attracting considerable attention because the electronegativity of the substituted fluorine atoms results in a low reactivity and a higher decomposition temperature [85] - [87]. For example, fluorinated esters such as methyl difluoroacetate exhibit a significant improvement in thermal stability when coexisting with lithium metal or Li_xCoO₂ [88]. Another advantage of fluorination is to expand liquidus ranges of solvents, which improves the ionic conductivity at low temperatures [89].

DRY POLYMER ELECTROLYTES

There are two types of polymer electrolytes. One is the "gel electrolyte" described earlier. The other type is called "dry polymer electrolyte," which consist only of a polymer and a lithium salt. Dry polymer electrolytes are based on a complex of PEO, which has sequential oxyethylene units, -(CH₂-CH₂-O)_n-, and a lithium salt such as LiClO₄, LiBF₄,

LiCF₃SO₃, LiN(SO₂CF₃)₂, etc. At room temperature, most of the dry polymer is crystallized, which results in a low ionic conductivity in the range 10⁻⁷-10⁻⁶ S cm⁻¹. Above a melting point at about 60 °C, segmental motion of the polymer chains is activated and the conductivity increases by three orders of magnitude. The suppression of crystallization is effective to improve the ionic conductivity. This has been realized by (i) cross-linking, (ii) co-polymerization, (iii) introduction of branched side chains [90], (iv) polymer alloying, and (v) inorganic filler addition [91].

In dry polymer electrolytes, lithium ions are strongly fixed by oxyethylene units so that anions move faster than lithium ions. This causes a depletion of lithium ions in the vicinity of an electrode at high current densities and may result in a large polarization. In this respect, single (lithium)-ion conductive dry polymer electrolytes are preferred for use in LPBs. Inorganic-organic hybrid polymers have been reported for single-ion conductors [92]. The potential window of PEO-based polymer electrolytes is limited to 3.7-3.8 V because of their instability against oxidation; hence, 3-V positive electrodes such as V₆O₁₃, Li₄Mn₅O₁₂ [93], and LiFePO₄ [94, 95] are used in lithium dry-polymer batteries.

Dry polymer electrolytes are completely free from volatile solvents, and hence their use improves the safety to a great extent. In addition, dry polymer electrolytes are likely to suppress the dendritic formation of lithium metal [96]. These features of dry polymer electrolytes are very profitable when used in large-scale batteries. In Japan, large-scale lithium dry-polymer batteries are being developed under a national project as described in the following section [97].

Large-Scale Batteries

Limitation on fossil resources and environmental considerations press our society to utilize energy resources more efficiently. In Japan, energy security issues are even more serious than those in other developed countries due to Japan's scarce resources. Utilization of natural energy resources such as sunshine, wind, wave, etc. is becoming important in our society. One of the problems in utilizing these natural energy resources is difficulty in expressing a resource as a stable supply of electricity. Development of large-scale batteries of high performance and long cycle life is essential to solve this problem. It is also important to level the load of electric power with rechargeable batteries for efficient operation of existing large-scale electric power plants.

Although modern cars emit far less toxic pollutants than their predecessors, their increasing number is resulting in a growing insistence to reduce automobile pollution. It is necessary to replace a significant number of the internal-combustion-engine vehicles with electric vehicles including pure (PEVs), hybrid (HEVs), and fuel cell (FCEVs) electric vehicles in the near future [98]. This has been accelerated by an ambitious requirement of the California Air Resource



Fig. 20. Photographs of (a, b) stationary-type (2 kW-class) and (c, d) EV-application-type (3 kW-class) battery modules and unit cells developed in the NSS Program. [Courtesy of New Energy and Industrial Technology Development Organization of Japan (NEDO)].

Board (CARB) [99]. Auto-manufacturers in the world are in fierce competition for developing their own electric vehicles. In response to this, national projects were established in the United States, Europe, and Japan, and have continued with the development of large-scale batteries for EVs.

In Japan, the Lithium Battery Energy Storage Technology Research Association (LIBES) began contracted research and development of large-scale LIBs of 20-30 kWh for use in dispersed battery energy storage systems and electric vehicles as part of the government's New Sunshine (NSS) Program [100, 101]. In 1997, the basic plan was revised [102] and great importance was placed on the development of high-performance battery modules of 2-3 kWh, as shown in Table IV [103, 104]. The modules are manufactured by combining several unit cells of 200-360 Wh. For example, 360 Wh unit cells with energy densities of 129 Wh kg⁻¹ and 288 Wh dm⁻³ have been already developed. The stationary-type and EV application-type battery modules and unit cells developed in the NSS Program are shown in Fig. 20. The revised plan emphasizes safety and low cost, as well as easy processing. In addition, battery technologies in the near future such as lithium dry-polymer batteries, lithium metal batteries, and nonflammable electrolytes are being developed with special emphasis in the NSS Program.

Conclusions

Since the commercialization in 1991, the production of LIBs has grown satisfactorily in Japan. In the next decade LIBs must meet diverse demands of the market. The rapid development of portable electronic devices imposes a demand for even smaller secondary batteries. Development of large-scale LIBs for EVs and energy storage systems is also a matter of great urgency in the twenty-first century. The energy density of LIBs has been doubled without changing the basic components since 1991. However, the improvement of the energy density has reached the limits, and now it seems to be the time for LIBs to evolve from the original components. Such evolution started with the commercialization of LPBs in 1999. Some of the alternative materials described in this review article are very promising, and in the first decade of the 21st century variety types of LIBs including large-scale batteries will be developed and commercially available not only in Japan, but also in all over the world.

Finally, safety is the most important issue in the development of LIBs although it is not described with special emphasis in this review article. One explosion somewhere in the world may plunge the whole market of LIBs into a serious situation, as was proved by the history of secondary lithium metal batteries.

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Zempachi Ogumi was born in 1945 and studied electrochemistry at Kyoto University, Japan. After received his Ph.D. degree in 1970, he worked at Fritz-Haber Institut der Max-Planck Gesellschaft in Berlin, Germany for one year. Since then, he has been at Kyoto University, and is now a professor. His current research interests include electrochemistry with an emphasis on materials for batteries, fuel cells, and solid-state ionics.

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