INVITED PAPER

Lithium-Ion Battery Systems

This paper presents a comprehensive review of the state of the art of commercially available lithium-ion battery technologies with emphasis on energy storage applications.

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ABSTRACT | The production of lithium-ion (Li-ion) batteries has been continually increasing since their first introduction into the market in 1991 because of their excellent performance, which is related to their high specific energy, energy density, specific power, efficiency, and long life. Li-ion batteries were first used for consumer electronics products such as mobile phones, camcorders, and laptop computers, followed by automotive applications that emerged during the last decade and are still expanding, and finally industrial applications including energy storage. There are four promising cell chemistries considered for energy storage applications: 1) $LiMn_2O_4$/graphite cell chemistry uses low-cost materials that are naturally abundant; 2) $LiNi_{1-X-Y2}Co_XAl_YO_2$/graphite cell chemistry has high specific energy and long life; 3) $LiFePO_4$/graphite (or carbon) cell chemistry has good safety characteristics; and 4) $Li_4Ti_5O_{12}$ is used as the negative electrode material in Li-ion batteries with long life and good safety features. However, each of the cell chemistries has some disadvantages, and the development of these technologies is still in progress. Therefore, it is too early to predict which cell chemistry will be the main candidate for energy storage applications, and we have to remain vigilant with respect to trends in technological progress and also consider changes in economic and social conditions before this can be determined.

KEYWORDS | Battery; cell chemistry; energy density; energy storage; life; lithium–iron phosphate; lithium manganite; lithium titanate; lithium ion; specific energy

I. INTRODUCTION

Lithium-ion (Li-ion) batteries are one of the most popular batteries in the world today due to the worldwide use of mobile phones and laptop computers. The commercialization of these batteries started in 1991 in Japan [1], [2]; however, their history is not as long as conventional batteries such as lead–acid batteries which have been manufactured for one and a half centuries. There are two reasons why Li-ion batteries have become the major type in such a short period: their excellent performance and timely advent to meet the growing market of consumer electronic products such as camcorders, mobile phones, and laptop computers. From the first decade of the 21st century, automotive application began [3], [4] and the market is still in the growth phase [5], [6], while application in the consumer electronics products is rather saturated. Another new industrial application is emerging in energy storage, which is expected to have significant growth. This paper covers a brief introduction to Li-ion battery technology, some examples of Li-ion battery development for energy storage applications, and some comments on future prospects.

Although there are many participant companies involved in Li-ion battery technology for energy storage around the world, there is only a limited volume of technical information presented in public media such as conference presentations and journal publications. Therefore, the information reported in this review may not be sufficient to satisfy all readers; however, most of the key points and major technologies will be covered to provide readers with a full understanding of the current map of this technology.

A. Outline of Lithium-Ion Batteries

The definition of Li-ion batteries is not completely authorized. However, it is commonly admitted that a battery that utilizes insertion reactions for both positive and negative electrodes with Li ions as charge carriers can be called a Li-ion battery.[1] In accordance with this definition, there are many types of cell chemistries for Li-ion batteries, so that the term Li-ion battery does not denote a single-cell chemistry, such as lead acid or nickel

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[1] Originally the term was defined as a battery utilizing intercalation reactions; however, the definition was expanded to include batteries based not only on intercalation, but also on other insertion reactions.

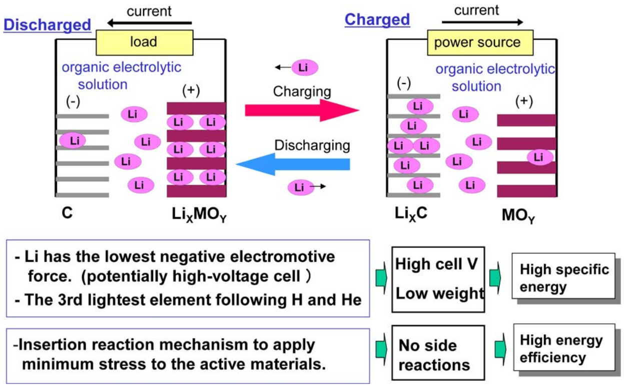

Fig. 1. ***Principle and features of Li-ion batteries.***

cadmium, but expresses a family of cell chemistries within the scope of the definition.

Fig. 1 shows the principle and features of Li-ion batteries, which are very simple: during the charge process, the positive electrode (cathode)[2] releases Li ions to the negative electrode (anode),[3] and in the discharge process, the negative electrode supplies the positive electrode with Li ions. Most Li-ion batteries use carbon materials such as graphite and hard carbon as the anode active material. Some metal oxides, such as lithium titanate ($Li_4Ti_5O_{12}$) [7] and niobium pentoxide (Nb_2O_5) [8], can also be used as an anode active material. These anode active materials accept Li ions when charged and release them during discharge, reactions that are referred to as insertion and extraction reactions. The reaction potentials for these materials are much lower than that of standard hydrogen electrodes; therefore, the electrolyte should be stable even at these lower potentials. This is the reason why organic electrolytes that consist of organic solvents and lithium salts are used for Li-ion batteries rather than aqueous electrolytes.

The cathode active materials should contain elemental lithium in the composition to provide a Li-ion source for cell reactions with the conventional anode active materials. Lithium cobaltate ($LiCoO_2$) was used as the cathode active material during the first stage of Li-ion battery commercialization. A similar compound, $LiNiO_2$, had also been studied intensively; however, it was not used because of its thermal instability. Substituted derivatives of this compound, formulated as $LiM_xNi_{1-x}O_2$ (M: metal element other than nickel such as Co, Mn, Al, Mg), were developed instead and used in several applications.

The features of Li-ion batteries are as follows:

1) high single-cell voltage;
2) high specific energy;
3) high energy efficiency;
4) long life.

Li-ion batteries have high single-cell voltages around 3–4 V, which is due to the lower potentials of the anode active materials. The high specific energies are dependent on the higher cell voltages, because a specific energy is the product of the cell voltage and the specific capacity, where 3–4 V is an extraordinarily high cell voltage for secondary batteries; the specific energies for Li-ion batteries are 1.5 times as large as that for nickel–metal hydride batteries, of which the single-cell voltage is only 1.2 V, despite having specific capacities greater than those of Li-ion batteries. The high charge–discharge efficiencies, which are the product of the Coulombic (electric current) and voltage efficiencies, are due to high Coulombic efficiency because of the simple cell reactions without any side reactions, and high voltage efficiency, which is also attributed to the high single-cell voltage. The reason why a high single-cell voltage results in high voltage efficiency is as follows. The voltage efficiency is the quotient of the operating voltage divided by the open circuit voltage. If we suppose two cells, A with a higher open circuit voltage V_A than B with V_B, which have the same voltage loss X, the efficiency for A will be larger than that for B

$$(V_A - X)/V_A > (V_B - X)/V_B, \qquad \text{where } V_A > V_B.$$

The long life character is attributed to simple cell reactions without side reactions and to insertion reactions without any significant morphological changes in the active materials during normal charge–discharge cycles. This situation is quite different from that of conventional secondary batteries such as the lead–acid battery, where the cell reaction involves dissolution–deposition and represents complete morphological changes during charge–discharge cycles.

Another significant feature of Li-ion batteries is the use of an organic electrolyte, which consists of aprotic polar organic solvents and a lithium salt. The electrolyte enables the high voltages involved with Li-ion batteries. However, electrolyte combustibility causes safety issues. Therefore, it is a key technology for Li-ion batteries to minimize the cause and effect of electrolyte combustibility without sacrificing performance.

The status of Li-ion batteries with respect to other secondary batteries is shown in Fig. 2. Li-ion batteries are located in a dominant position over the other conventional secondary batteries and occupy a wide area, because the

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[2] The definition of positive electrode is different from that of cathode, so their meanings in the field of secondary batteries become identical only during the discharge process. However, the author uses the term cathode instead of positive electrode to comply with conventional usage.

[3] Although the author also knows that the term negative electrode is not equivalent to anode, the term anode is used instead of negative electrode for the same reason.

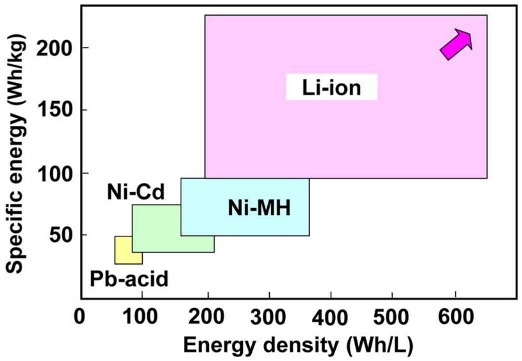


Fig. 2. *Comparison of secondary batteries.*

Table 1 Shapes and Features of Li-Ion Cells

Shape	cylindrical	prismatic	flat (pouch)
Electrode arrangement	wound	wound	stacked
Cross section			
Casing	can	can	Al-laminate
Mechanical strength	++	+	±
Specific energy	+	+	++
Heat radiation	±	+	+
Energy density in module	+	++	+

term Li-ion battery does not denote single-cell chemistry, but covers a wide range of cell chemistries. There is a possibility that new cell chemistries could be developed in the future, which would further expand the area in the figure.

Many cell chemistries can be included in Li-ion batteries and several tens are studied in detail; however, only a limited number of the Li-ion battery cell chemistries have been commercialized so far. The anode active materials being used for mass production are graphite, hard carbon, soft carbon, and lithium titanate. The cathode active materials employed are $LiCoO_2$, $LiM_xNi_{1-x}O_2$, $LiMn_2O_4$, and $LiFePO_4$. Combination of the four anode materials and the four cathode materials leads to 16 possibilities, although there are many further variations in each of these anode and cathode materials. However, not all 16 combinations are used in production.

B. Cell-to-Battery System

A single cell consists of two electrodes, an anode and a cathode, a separator between the electrodes, electrolytic solution (or electrolyte) absorbed in the separator, and a cell case to contain all the cell components. The electrodes are usually formed on an electrode substrate of metal foil, copper for anodes and aluminum for cathodes, by coating a slurry composed of an active material, a conductive material, a binder, and a solvent such as N-methyl pyrrolidone (NMP) or water. The separator is typically a microporous sheet of an organic polymer material such as polyethylene, polypropylene, or a hybrid of both [9], [10].

There are several types of external shapes and internal structures applied to commercial single cells: cylindrical, prismatic, and flat shapes, and wound (or jelly roll) and stacked structures of electrode assemblies consisting of an anode, a separator, and a cathode. The cell case materials are metal such as stainless steel or aluminum for cylindrical or prismatic cans, or an aluminum–laminate film for pouch cells. The cell cases have several functions, although they are merely containers. The most important are sealing the internal materials from moisture and oxygen in the exterior, which corrode Li-ion batteries, and insulation of the positive and negative terminals for individual cells. The other important functions are to allocate a safety vent to relieve internal pressure under abuse conditions, and to maintain mechanical strength for the unit of a battery module. However, these two functions are not provided for by the pouch-type cells using aluminum–laminate film [11]. Table 1 briefly summarizes the three types of cells. The scores shown as ++, +, and ± are not necessarily fixed; therefore, some of these may vary as the technology continues to progress. All these cell types have their own advantages and disadvantages; therefore, a cell type is selected in accordance with the cell design or design requirement with respect to the application of the battery.

There is another different cell type that does not use a liquid electrolyte, but rather a gel electrolyte that consists of an organic electrolyte absorbed into an organic polymer material [12]. The features of this type of cell are asserted to be no leakage, because there is no free liquid electrolyte, and thus reduced combustibility. The casing for this type of cell is typically an aluminum–laminate sheet to form a pouch cell. Therefore, the performance is not so different from other pouch-type cells, and a limited number of battery manufacturers are producing these types of cells for applications other than consumer electronics products. Consequently, they will not be specifically discussed in this paper.

The practical application of Li-ion batteries involves integration into battery systems that comprise many cells along with cell controllers, a battery controller, fans, various sensors, and other battery system parts, because the voltage of a single cell is limited to less than 5 V and the capacity is usually less than 100 Ah, i.e., the energy is much less than 1 kWh [11]. Otherwise, cells with extremely large capacities would need to be constructed to meet the capacity requirements of an application, which is not realistic.

II. CONSUMER ELECTRONICS APPLICATIONS

The first introduction of Li-ion batteries was in mobile phone applications, followed by camcorders and laptop computers and other personal information technology (IT) instruments [13]. The cell chemistry used for such applications started with $LiCoO_2$/hard carbon, then hard carbon was replaced by graphite to increase the packing capacity in a certain volume of cells such as the 18 650 (18 mm in diameter and 65 mm long) cell. $LiCoO_2$ was later mixed with compounds from the $LiM_xNi_{1-x}O_2$ family materials to decrease the amount of cobalt to reduce cost and increase the packing capacity. More recently, only the $LiM_xNi_{1-x}O_2$ family of materials has been used instead of $LiCoO_2$ for some types of Li-ion batteries.

The portability requirement of mobile products has meant that the total energies for the batteries, approximately proportional to the product mass, are typically less than 100 Wh. Therefore, the single-cell sizes are not so large; the most popular is the 18 650 type with a capacity of 2–4 Ah [14], dependent on the specifications. The capacities of cells used for mobile phones, which are small prismatic or flat cells, now exceed those of 18 650 cells because of their increased sizes and load.

The most important requirement for the performance of these Li-ion batteries is the energy density, so that such portable electronics devices can be driven for as long as possible. The high rate discharge capability and the calendar life requirements are not so intense; 3 C rate and a three to five year life are sufficient. Although cost considerations are essential, the cost per watthour is not always sufficiently low, because the total capacity of the batteries for such devices is relatively small. The battery control system is rather simple because of the simple function required for the power sources of such devices.

III. AUTOMOTIVE APPLICATIONS

The features of automobiles are mass production, integration of a large number of parts, long life up to ten years, reliability and safety under various environmental and driving conditions, and ultimate cost reduction; automobiles are large and long-life commodities that are used everywhere, anytime by a large cross section of people. Consequently, the requirements for automotive batteries will be very severe for this reason.

Automotive Li-ion batteries are different from automotive lead–acid batteries that function for starting, lighting, and ignition. They are used as traction power sources in hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and electric vehicles (EVs) [11]. This application is still in a younger phase than that for consumer electronics applications; therefore, most of the technology is based on the preceding batteries. However, there are some specific differences between automotive and consumer electronics applications.

The anode and cathode active materials are slightly different from those of batteries produced for consumer electronics products. Most HEV batteries employ $LiM_xNi_{1-x}O_2$/hard carbon chemistry because of the high power characteristics and smaller sizes, so that the material cost is not a large proportion of the total HEV battery system cost. In contrast, EV batteries commonly adopt $LiMn_2O_4$/graphite chemistry to reduce the material cost due to their larger size.

The reason why the HEV battery requirements are quite different from those for EV batteries is as follows. An HEV does not require energy, but power, because plenty of energy is stored in the fuel tank, although the battery should be capable of providing energy for the entire vehicle for a short time on some occasions, even though the total energy is as small as 1–2 kWh [15]. However, an EV does not require power, but energy, because there is nothing to store energy in, other than the battery in the car. Therefore, the cell size and design are considerably different between these batteries, while other requirements of the car battery system such as the lifetime, safety, reliability, and cost are almost the same.

One of the most notable differences between Li-ion batteries for automotive and consumer electronics applications is the system control technology, which supports the optimal and safe operation of the multicell systems. Battery control systems typically form a layer structure of cell controllers and a battery controller. The cell controller is used to monitor individual cells, report the information to the battery controller, and receive and implement commands from the battery controller. The battery controller gathers information from the cell controllers and sensors, calculates the input/output power capabilities, state of charge (SOC), and state of health (SOH), determines the ON/OFF state of the battery system, commands cell capacity balance to the cell controllers, and communicates with other vehicle system controllers. These complicated and heavy control system configurations and functions guarantee the safe, highly efficient, reliable, and long-life operation of the battery and vehicle systems.

Another important feature for this application is the system design technology, including the electrical, mechanical, and thermal design. The goal of the electrical design is to maintain electrical safety, even under serious abuse conditions, to prevent overcharge, overdischarge, overcurrent, overpower, leak current, short circuit, and electric shock. The parts that operate for this purpose include the current sensors, voltage sensors, leak detectors, disconnect switches, contactors, fuses, and input/output control systems.

The mechanical design is intended to guarantee sufficient mechanical strength under the conditions assumed to be applied to the battery system, such as shock, vibration, and thermal expansion. Although metal case cells have sufficient mechanical strength to be integrated

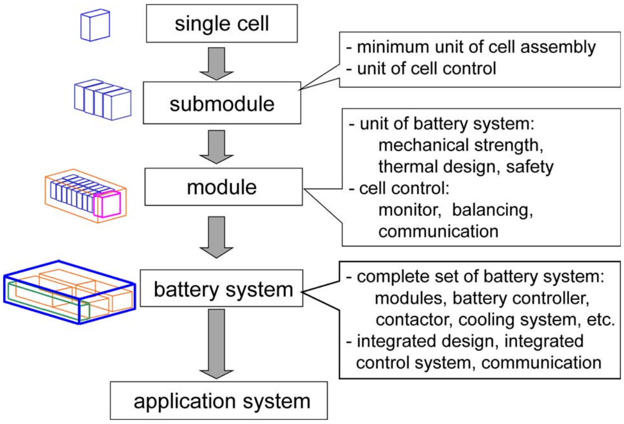


Fig. 3. ***Layer structure of the battery system.***

into modules or packs, pouch-type cells have minimal strength and thus require additional reinforcement.

Thermal design is important to maintain the battery temperature within a required temperature range to suppress battery degradation and prevent thermal runaway. Thermal management is implemented by the removal of excessive heat by cooling with air or a coolant. This requires control of not only the average or total temperature, but also the temperature distribution. Controlled temperature distribution is necessary to minimize differences in performance among individual cells to achieve the best performance of the battery, and to prevent the uneven degradation of cells in the module that would otherwise shorten the module lifetime.

Fig. 3 illustrates the layer structure of an automotive battery system along with the functions described here. Although this figure shows the battery the system structure for an automotive application, it is also applicable to energy storage battery systems. The automotive battery system technology is thus a good basis and reference for the development of energy storage Li-ion battery system technology.

IV. ENERGY STORAGE APPLICATIONS

Other than the two major categories of Li-ion battery applications outlined in Section III, another important category remains: industrial applications. The term industrial application covers a wide area of applications from those for do it yourself (DIY) power tools to specialty applications such as space, aviation, and military. Among these, the so-called energy storage applications occupy a significant area [11].

Energy storage applications are classified into the following three types:

1) for grid stabilization to cope with energy generation from natural sources, such as wind turbines and solar cells;
2) uninterruptible power supply (UPS) for emergency incidents to be installed at large social facilities, such as telecommunication stations, data centers, and hospitals;
3) home use to manage the energy consumption with/without the introduction of power generation systems such as solar cells and wind turbines.

The total battery system capacity would generally be in the order of 1) > 2) > 3).

Such applications are still in an early phase; nevertheless, the technology has been given much attention recently due to the increasing severity in the struggle between energy and environmental issues, and the technical and business success of Li-ion batteries. The amount of battery production for such applications is still limited, despite the increased attention and positive expectations.

The features of Li-ion battery systems to be applied to energy storage applications are condensed into the following:

1) large energy capacities from several kilowatt hours to several tens of megawatt hours;
2) large numbers of cells;
3) importance of the control system.

The scale of energy storage systems ranges from that for domestic energy storage and management to that for leveling of the output of a large-sized wind farm or photovoltaic generation; therefore, the battery system sizes cover a wide distribution. Large size requires a system to consist of a large number of moderate-sized cells because it is not realistic to manufacture large format cells to meet the size requirements of each system. Many cells must be well concerted for the system to operate safely and efficiently without errors for a long time; therefore, the control systems have become much more significant for energy storage applications than for other smaller applications such as consumer electronics products or even automobiles. The control systems for large-sized systems have also become more complicated, multilayered structures, than those employed for automotive applications discussed in Section III.

The materials used in cells for energy storage applications are not special, but there are some differences from those used for other applications such as consumer electronics and automobiles. The large size of the battery system means a large weighting from materials in the total system cost, which leads to the selection of low-cost materials. Consequently, the cell chemistry of lithium manganite/natural graphite is thought to be the most promising for this application. However, other cell chemistries have also been proposed and adopted because no specific cell chemistry can completely satisfy all the requirements.

Three types of cells, cylindrical, prismatic, and pouch type, are used for energy storage applications, as with the other applications discussed before. The performance requirements for the batteries are not severe, but rather moderate. The energy density requirement is not so important for the wind farm and photovoltaic generation because of the extensive site area, but it becomes important for domestic and other indoor energy storage systems; high power less than 5 C rate, in most cases 3 C rate or less, is sufficient for real-world operation. On the other hand, long life of more than ten years is anticipated for wind and photovoltaic energy generation systems. The ultimate cost target will be the same level as pumped storage; however, it is too early to evaluate the comparison accurately.

In this section, four types of Li-ion batteries classified with the characteristic cathode or anode active materials will be introduced and discussed along with some examples of commercialized batteries: lithium manganite ($LiMn_2O_4$; LMO), lithium nickelate substituted with cobalt and aluminum ($LiNi_{1-x-y}Co_xAl_yO_2$; NCA), lithium iron phosphate ($LiFePO_4$; LFP), and lithium titanate ($Li_4Ti_5O_{12}$; LTO). LTO is the only anode active material among these.

A. LMO Type

LMO/graphite is the commonly adopted cell chemistry for EV applications and it is also promising for energy storage applications with respect to cost and natural abundance; however, there is the issue of manganese dissolution at high temperatures and higher potentials [16]–[18], which makes both the cathode and anode capacities decrease significantly [19]. The substitution of other metals in LMO, including lithium for manganese, were attempted to stabilize the material and certain level of improvement was achieved [17], [20], [21]. The addition of $LiM_xNi_{1-x}O_2$ explicitly suppressed manganese dissolution and the related effects [22], although the mechanism has not yet been clearly analyzed. Therefore, none of the so-called LMO cathodes for practical batteries consist of $LiMn_2O_4$ alone, but all of them contain some form of $LiM_xNi_{1-x}O_2$ along with $LiMn_2O_4$. The reversible specific capacity for LMO is around 100–110 Ah/kg, which is not larger than other cathode materials such as NCA and LFP, although the electrode potential for LMO is around 4.0 V versus Li/Li^+, which is somewhat higher than the others and may compensate for the capacity drawback slightly. Consequently, the key point for LMO is whether it will exceed the other materials in cost performance ($/Wh).

Two Japanese companies, GS Yuasa Corp. (Kyoto, Japan) and Mitsubishi Heavy Industries, Ltd. (MHI, Tokyo, Japan), have developed this type of battery. GS Yuasa has been developing various large format Li-ion batteries for automotive, space, aeronautic, and energy storage applications. Table 2 shows the specifications for a GS Yuasa energy storage battery module consisting of seven cells [23]–[25]. The single-cell case is a prismatic stainless steel can with flatly wound electrode assemblies inside. The cell chemistry is assumed to be LMO-based/graphite. From the specifications, the specific energy and specific discharge power can be calculated as 82 and 520 W/kg, of which the former is lower than those for EV batteries that have approximately 100 Wh/kg or more using a similar cell chemistry [5], [26], [27]. The cycle life for the LIM series cells is reported to be excellent: 70% of the initial capacity is kept after 3000 cycles with 1 C charge/1 C discharge load at 25°C [28]. A 1-MW class energy storage system was designed using the modules shown in Table 2. Table 3 shows the specifications of the 1-MWh/1-MW system [23], [29]. The system efficiency was reported to be 88%–90%; however, the conditions for this were not precisely specified. The system is to be integrated into much larger systems, as large as 20 MW.

Table 2 Specifications of the GS Yuasa Energy Storage Battery Module LIM50E-7G

Module arrangement	7 cells in series
Nominal capacity	47.5 Ah
Nominal voltage	25.9 V
Nominal energy	1.23 kWh
Max. discharge power	7.77 kW
Max. charge current	125 A (2.6 C)
Max. discharge current	300 A (6.3 C)
Dimensions (WxDxH)	180x412x135 (mm)
Mass	15 kg

MHI also developed Li-ion batteries with the LMO-based/graphite cell chemistry [30], [31]. The specifications for the industrial battery are shown in Table 4 [31]. The cell case is a prismatic aluminum can with a stacked electrode arrangement inside. It is also reported that the cycle life is more than 3500 cycles by reaching 85% of the initial capacity based on the cycle life test at 0.4 C rate, and that the discharge capacity at −15 °C was 80% of that at 25 °C. Fig. 4 and Table 5 show the appearance and brief specifications of the MHI energy storage system (ESS) of approximately 2200 cells, including ancillary facilities of 400 kWh–1000 kW [31].

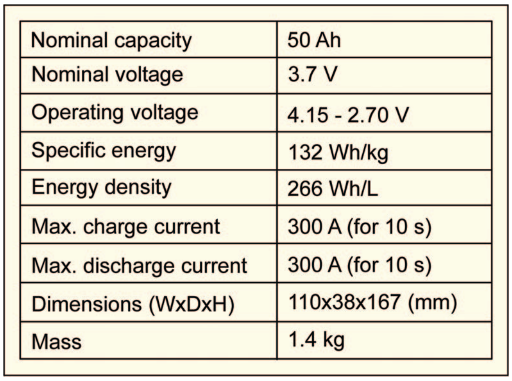
B. NCA Type

NCA belongs to the $LNiO_2$ family, which was originally expected to have greater capacity than lithium cobaltate ($LiCoO_2$, LCO) or LMO. However, the structural and

Table 3 Specifications of the GS Yuasa 1-MW Class Energy Storage System

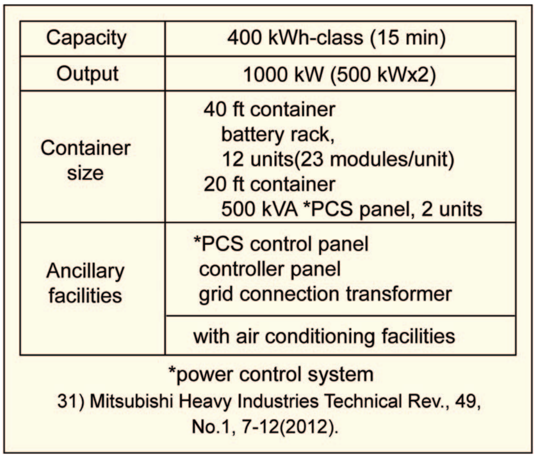
Module number	480 (12 cells / module)
Inverter capacity	1 MW
Battery capacity	1 MWh
Battery voltage	DC 500 V
Conversion efficiency	88–90% (system)
Response time	< 0.5 s

Table 4 Specifications of the MHI Energy Storage Li-Ion Cell P140



Nominal capacity	50 Ah
Nominal voltage	3.7 V
Operating voltage	4.15 - 2.70 V
Specific energy	132 Wh/kg
Energy density	266 Wh/L
Max. charge current	300 A (for 10 s)
Max. discharge current	300 A (for 10 s)
Dimensions (WxDxH)	110x38x167 (mm)
Mass	1.4 kg

Table 5 Specifications of the MHI Energy Storage System



Capacity	400 kWh-class (15 min)
Output	1000 kW (500 kWx2)
Container size	40 ft container battery rack, 12 units(23 modules/unit) 20 ft container 500 kVA *PCS panel, 2 units
Ancillary facilities	*PCS control panel controller panel grid connection transformer
	with air conditioning facilities

*power control system

31) Mitsubishi Heavy Industries Technical Rev., 49, No.1, 7-12(2012).

thermal stability of $LiNiO_2$ was not sufficient for use in commercial batteries. The partial substitution of nickel for various other metals has been attempted by many researchers [32]–[34]. Cobalt proved to be effective to stabilize the crystal structure in a single phase during the charge–discharge process [35], [36], and aluminum improved the thermal stability when charged and heated [37]. The reversible specific capacity for NCA is 150–180 Ah/kg, depending on the composition, although the average discharge potential is 3.75 V versus Li/Li^+, which is slightly lower than that of LCO.

Saft Groupe S. A. (Bagnolet, France) has been working on nickel-based cathode active materials for a long time [38], [39]. Saft first developed Li-ion batteries with the $LiNi_{1-x-y}Co_xAl_yO_2$/graphite cell chemistry for automotive and other specialty applications, including the space and military. Application was expanded to energy storage, and high energy densities were demonstrated with excellent life longevity of more than 1000 deep cycles [40], [41]. Figs. 5 and 6 show the cycle life and storage life test results [41]. The former is that based on the dynamic stress test (DST) pattern mode test developed for automotive battery cycle tests reflecting real driving [42], using 80% depth of discharge (DOD) at 20 °C, which shows much less degradation in energy up to 1000 cycles and more. The latter is the storage life test results at 100% SOC, which shows excellent stability at 20 °C and a slight loss as small as 4%, even at 40 °C storage for 22 months. Table 6 summarizes the specifications of the three types of Li-ion batteries proposed for energy storage applications, from the domestic use of kilowatthour class to grid stabilization of 100-kWh class [43]. All cells contain spirally wound electrode assemblies in cylindrical aluminum cans (54 mm in diameter, 222 mm long). Although they consist of the same cell chemistry and have the same dimensions and almost the same mass, the characteristics vary from the high energy of the VL 45E cell and the high energy and power of the VL 41M cell, to the high power of the VL 30P cell, which proves that Li-ion batteries are tunable to address a wide scope of requirements.

In spite of the excellent performance, no major battery manufacturers other than Saft have adopted this cathode active material for the large format Li-ion batteries. The key point left for this type of Li-ion battery is the cost issue caused by the composition, which consists of nickel and cobalt as the major components. The ultimate cost reduction is dependent, to a great deal, on the production scale, which is always the same as for other cell chemistries. Therefore, the question of what will be the

Fig. 4. *MHI 1000-kW and 400-Wh class energy storage systems.*

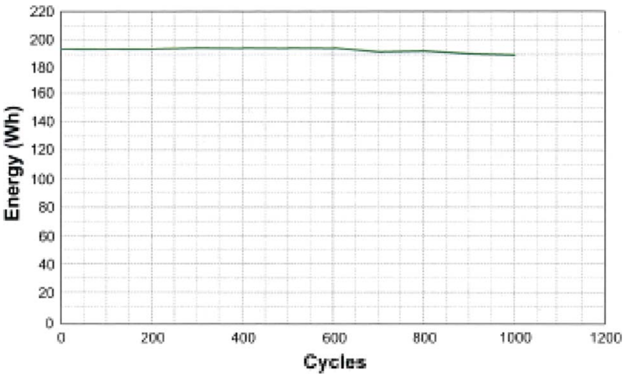


Fig. 5. *DST cycle life test result for Saft 45-Ah high energy cell.*

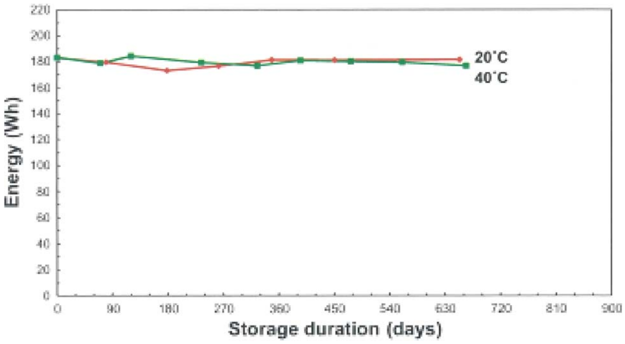


Fig. 6. *Storage life test results for Saft 45-Ah high energy cell at 100% SOC.*

major cell chemistry for energy storage applications is still unanswered.

C. LFP Type

LFP is a unique material, for it does not decompose easily with the simultaneous evolution of oxygen at high temperatures, which is quite different from other cathode active materials of double oxides of lithium and transition metals such as LCO and LMO. Therefore, excellent safety is expected with this type of Li-ion battery [44]. The discharge potential for the material is around 3.4 V versus Li/Li^+, which is around 0.3 V lower than that for other cathode active materials such as LCO, LMO, and NCA. The reaction mechanism is also different and is not a one-phase but a two-phase reaction between $LiFePO_4$ and $FePO_4$

$$LiFePO_4 \rightarrow FePO_4 + Li^+ + e^- \text{ (charge reaction).} \quad (1)$$

The reverse of (1) is the discharge reaction [44]. The charge/discharge potential curve is very flat at the same voltage around 3.4 V versus Li/Li^+ because of the two-phase reaction mechanism. The specific capacity calculated from reaction [1] is 169 Ah/kg and the reversible capacity reaches around 140 Ah/kg or more.

Table 6 Specifications of Saft Energy Storage Li-Ion Cells

Cell name	VL 45E	VL 41M	VL 30P
Nominal capacity (Ah)	45	41	30
Nominal voltage (V)	3.6	3.6	3.6
Operating voltage (V)	4.0 - 2.7	4.0 - 2.7	4.0 - 2.5
Specific energy (Wh/kg)	149	136	97
Energy density (Wh/L)	313	285	209
Specific power (W/kg)	664 (30 s)	794 (30 s)	1136 (30 s)
Max. disch. current (A)	250 (30 s)	300 (30 s)	500 (10 s)
Dimensions (r x H, mm)	54.3 x 222	54.3 x 222	54 x 222
Mass (kg)	1.07	1.07	1.1

Table 7 Comparison of LFP With Some Other Cathode Active Materials

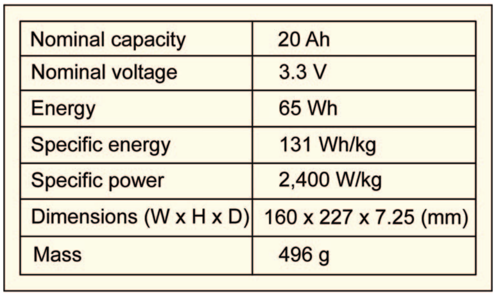
Material formula	Calculated capacity (Ah/kg)	*Average discharge voltage (V)	Density (g/cm^3)	*Specific energy (Wh/kg)	*Energy density (Wh/L)
Li_xCoO_2 (0.5<X<1)	137	3.7	5.1	507	2590
$Li_xMn_2O_4$ (0<X<1)	148	4.0	4.2	592	2490
Li_xFePO_4 (0<X<1)	169	3.4	3.6	575	2070

*values for cathode materials assuming anodes of 0 V vs. Li/Li^+

The disadvantage of this material is the low electronic conductivity, so that it is necessary to apply a carbon coating onto the powder to increase it. Another important point is particle size control, because the crystal structure of LFP allows Li ions to move along only one crystal axis direction (one-dimensionally); therefore, fine particles are required to increase the effective surface area and guarantee smooth Li-ion diffusion without prevention by crystal defects [45]. Table 7 shows a comparison of LFP with some other cathode active materials. Although the calculated specific capacity of LFP is larger than the others, the lower potential causes lower cell voltage and the lower density results in lower energy density than the other cathode active materials. This is the reason why LFP is not used for consumer electronics batteries, where the energy density is a crucially important characteristic. However, the long life and high rate charge/discharge capability of LFP have attracted much attention from battery manufacturers for industrial applications. Moreover, low cost and steady supply in the future were anticipated because the composition comprises abundant materials. Nevertheless, this does not simply correspond to the low cost, because the cost is controlled not only by the raw material cost but also by the process cost.

A123 Systems (Livonia, MI, USA) was one of the most active battery manufacturers producing LFP-type batteries in the world. For industrial applications, they first developed a 2-MW energy storage system that consisted of around 90 000 2.3-Ah cylindrical cells, which could deliver 2-MW power for 15 min, and they reported that the system could be integrated up to 200 MW [46]. They then developed a 20-Ah single cell as the unit of the energy storage systems [47], of which the specifications are shown in Table 8. The cell is called prismatic and the dimensions are 160 mm wide, 227 mm high, and 7.25 mm thick, which means a very thin cell. Presumably, it is a type of pouch cell inserted into a metal case. These single cells were connected in parallel and series to form the appropriate modules. An example is the 24-V/100-Ah

Table 8 Specifications of the A123 System Energy Storage Li-Ion Cell AMP 20



Nominal capacity	20 Ah
Nominal voltage	3.3 V
Energy	65 Wh
Specific energy	131 Wh/kg
Specific power	2,400 W/kg
Dimensions (W x H x D)	160 x 227 x 7.25 (mm)
Mass	496 g

module that consists of 40 cells, of which eight are in series and five in parallel. In this way, they are able to design battery systems to meet the required specifications and intend to substitute these battery systems for conventional lead–acid batteries used for UPS applications in telecommunication stations and data centers [47].

D. LTO Type

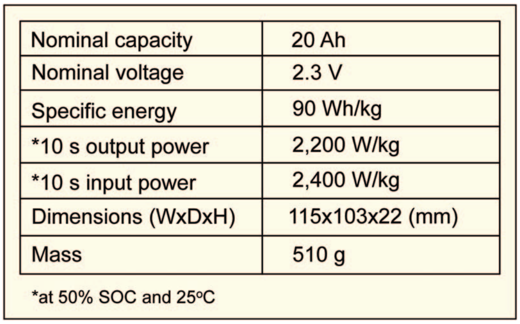
LTO is a type of spinel material which has a stiff 3-D structure, the same as LMO. The composition formula $Li_4Ti_5O_{12}$ can also be expressed as $Li_{4/3}Ti_{5/3}O_4$, where the charge reaction is

$$Li_{4/3}Ti_{5/3}O_4 + Li^+ + e^- \rightarrow Li_{7/3}Ti_{5/3}O_4. \qquad (2)$$

The reverse reaction of (2) is the discharge reaction [7]. The specific capacity calculated from reaction (2) is 165 Ah/kg, which is less than half of 372 Ah/kg for graphite, and the reversible capacity reaches around 150 Ah/kg or more. LTO scarcely shows any change in the lattice constants by the insertion of Li ion accompanying reduction [48], [49]. Therefore, the mechanical stress during charge–discharge cycle becomes very small, which suggests potentially long cycle life. High power capability is also expected [49].

Another significant feature of this material is the charge–discharge potential at around 1.5 V versus Li/Li^+. The high potential makes the cell voltage, coupled with typical cathode active materials, around 2.4 V, which is almost two thirds that of conventional Li-ion batteries used today, and consequently reduces the specific energy of the cell [50]. However, it does prevent lithium deposition, even under overcharge conditions or with longer cycling, which results in enhanced safety and long life [51]. Furthermore, a high potential anode scarcely causes reductive decomposition of the organic solvent at the interface with the organic electrolytic solution to form a solid electrolyte interphase (SEI) [52] that would increase the interface resistance at the surface, and this also supports the long life of the cell. A long cell life, such as ten years or more, is thus predicted [53], [54].

Table 9 Specifications of the Toshiba 20-Ah Class LTO/NCM Cell



Nominal capacity	20 Ah
Nominal voltage	2.3 V
Specific energy	90 Wh/kg
*10 s output power	2,200 W/kg
*10 s input power	2,400 W/kg
Dimensions (WxDxH)	115x103x22 (mm)
Mass	510 g

*at 50% SOC and 25ºC

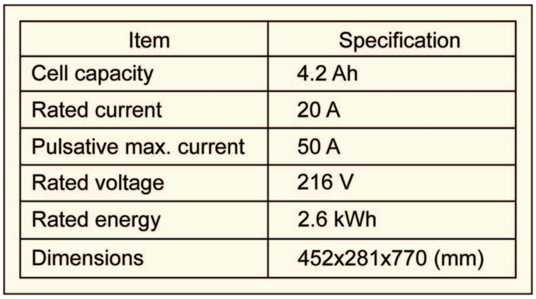
This type of battery seems to fit applications that demand much power, such as HEVs, while the long life also enables them to be used for energy storage applications. Intensive development of such batteries has been continued by two companies: Toshiba (Tokyo, Japan) and Altairnano (Reno, NV, USA).

Toshiba's LTO batteries are called SCiB, and Table 9 shows the specifications of the 20-Ah class cell developed for energy storage applications [53]. The abbreviation NCM denotes $LiNi_{1-x-y}Co_xMn_yO_2$ here, although it is typically used to indicate $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. A wound electrode assembly is contained in a prismatic aluminum case. The specific energy of 90 Wh/kg is not so high; however, the 10-s specific power is as high as 2200 W/kg. The short-circuit tolerance mechanism for these cells indicates that the rush current at the short-circuit point results in the formation of resistive LTO, which suppresses the propagation of rapid discharge [55]. The lifetime for the cell capacity to fade down to 80% of the initial is predicted to be 15 years, assuming 3 C rate cycles for 1.5 years and 100% SOC floating for the remaining time [53].

Toshiba developed two types of energy storage systems [56]: a 2.6-kWh format for domestic use and a 110-kWh format for utility grids. Both are summarized in Tables 10 and 11. The former uses small prismatic cells that are good for quick charge up to a 5-min charge [56], [57]. Those used for the latter are identical with those described in Table 9.

The Altairnano single cells are pouch-type cells that use aluminum–laminate sheet cases. Two types of cells were

Table 10 Specifications of the Toshiba Battery for Domestic Energy Storage Systems



Item	Specification
Cell capacity	4.2 Ah
Rated current	20 A
Pulsative max. current	50 A
Rated voltage	216 V
Rated energy	2.6 kWh
Dimensions	452x281x770 (mm)

Table 11 Specifications of the Toshiba Battery for Utility Grid Energy Storage Systems

Item	Specification
Cell capacity	20 Ah
Rated current	200 A
Pulsative max. current	1,000 A
Rated voltage	552 V
Rated energy	110 kWh
Dimensions	1.70x0.815x1.80 (m)

developed for stationary applications. Table 12 summarizes the specifications [58]. Both specifications are quite similar, except for the capacities and maximum charge rates. The cycle life was estimated on the basis of a single-cell test up to 9000 cycles [58], while the calendar life was estimated to be 25 years by extrapolation of single-cell tests conducted up to 3.3 years, i.e., a 7.6 times expansion [59]. A 1-MW energy storage system was built by integrating the 50-Ah cells; 56 cells form a module, and approximately 50 modules form the 1-MW/250-kWh system [58]. The battery charge–discharge efficiencies measured at 50% SOC were 97% for 250 kW and 91% for 1-MW discharge. Fig. 7 shows the appearance of a system that consists of two 1-MW units and a power control system (PCS) [59], which looks similar to that in Fig. 4, in that both have a trailer type appearance. The 1-MW system can be integrated up to 20 MW by increasing the number of connected systems [59].

Li-ion batteries that use LTO in the anodes have quite different performance from that of conventional Li-ion batteries with carbon material anodes, and have the advantages and disadvantages previously discussed. Whether the LTO-type Li-ion batteries will exceed the conventional types in the market will be determined by the market itself by taking both performance and cost into consideration.

E. Examples of Trial Introduction

Many trial introduction or field test programs of Li-ion batteries for energy storage applications are planned and implemented in many countries. However, it is difficult to introduce and review all of them one by one, so only two examples are given here.

Table 12 Specifications of the Altairnano LTO-Type Single Cells for Stationary Use

Cell product	Specific energy	Specific power	Max. charge rate	*Typical cycle life	*Typical calendar life
11 Ah energy cell	74 Wh/kg	1.1 kW/kg	10 C	>15,000 cycles	>25 years
50 Ah energy cell	72 Wh/kg	1.0 kW/kg	6 C	>15,000 cycles	>25 years

*time for the capacity to reach 80% of the initial value.

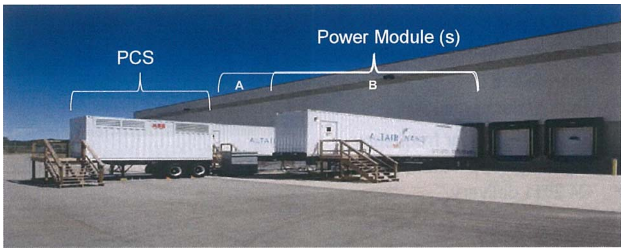


Fig. 7. ***Altairnano 2-MW energy storage system consisting of two 1-MW batteries and PCS.***

In the United States, there are many field trials for utility battery energy storage under testing [60], [61]. More than ten battery manufacturers, including those mentioned above and those that produce batteries other than Li ion, have been supplying batteries to these trials. The largest energy storage system among the trials was built for the Tehachapi Wind Farm in California. The capacity is 8 MW for 4 h or 32 MWh [62], [63], which is said to be the largest ever grid-connected Li-ion energy storage system. The batteries were supplied by LG Chem (Seoul, Korea) and the system is operated by Southern California Edison under partial support from the U.S. Department of Energy.

In China, there is also testing of Li-ion batteries for energy storage from photovoltaic and wind power generation at the Zhangbei Energy Storage Experimental Base in Hebei Province. The 1-MW/2-MWh and 3-MW/9-MWh Li-ion battery systems have already been built. There is also a plan to extend the battery capacity up to 14 MW/63 MWh [64].

These demonstration tests are anticipated to supply a great deal of data, to make further progress in technology, and to drive the introduction of the new technology. The provision of positive results is expected to accelerate investment into large-scale production by battery manufacturers, while negative results facilitate further progress of the technology. Such tests will enhance social recognition of this technology and its necessity.

V. FUTURE PROSPECTS

Many papers on new anode and cathode materials have been presented and published during the last decade. Silicon and tin are most popularly used for anodes. However, these materials cannot be employed as substitutes for carbon materials in energy storage applications yet, because their total performance including cost is still lower than that of carbon materials. $LiNi_{0.5}Mn_{1.5}O_4$ and $LiMO_2{-}Li_2MnO_3$ are expected to be the most promising cathode material in the near future. However, they are still in the developmental phase. Energy storage applications are large systems that consist of many cells, and thus much material, so that such applications are very sensitive to the material cost. Consequently, the introduction of these new materials will take some years for development, maturation, and supply at an appropriate cost.

Innovative batteries that are expected to exceed conventional Li-ion batteries are also attracting much attention in both the academic realm and industry. These batteries include lithium-metal-based batteries such as lithium-air and lithium-sulfur batteries, all solid batteries with solid state electrolytes, and those that use metals other than lithium, such as sodium, magnesium, aluminum, calcium, and zinc. Most of these are not new, but rather old and well-known cell chemistries; however, they have potentially high theoretical specific energies, although there remain many problems to be solved to approach practically high specific energies that would lead to commercialization. Therefore, it is likely that Li-ion batteries will prevail over other batteries, at least within a few decades, before some of these innovative batteries are commercialized.

The sizes of energy storage systems composed of Li-ion batteries are usually larger than those for other applications, and thus the total cost, which is proportional to the sizes, becomes larger and the weight of cost will be much more critical than that for other applications. For the purpose of cost reduction, production volume is one of the most important key points; therefore, the synergistic effect of volume production including as many applications as possible will contribute to significant cost reduction. Market expansion is also necessary to reduce the cost by extended large-scale production; however, the market will not expand before significant cost reduction, which is a chicken and egg relation. Therefore, timely and effective political leadership with incentive policies is anticipated and will also be crucial.

Such being the case, the future for this technology is still full of uncertainty and will be determined by not only technical but also other factors, because the situation of the technology has become much more important and complicated than before due to the recent global realization of energy and environmental issues. Therefore, R&D efforts on energy storage battery technology should not neglect economic and social factors from an international perspective in order to contribute to society through such technology. ■

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