# Lithium-Ion Batteries

Masaki Yoshio • Ralph J. Brodd • Akiya Kozawa
Editors

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# Foreword

## My Way to Lithium-Ion Batteries

**Yoshio Nishi**

I have been engaged in research and development (R&D) on novel materials for electronic appliances for 40 years since I joined Sony Corporation in 1966. I started my scientific career in Sony as a researcher of zinc-air batteries. After 8 years in R&D on electrochemistry, my research field was shifted against my will to electroacoustic materials, specifically diaphragm materials for electroacoustic transducers including loudspeakers, headphones, and microphones. My R&D work also extended to cabinet materials for speaker systems. This about-face was uncomfortable for me at first, but it forced me to devote myself to the investigation of various classes of materials unfamiliar to me, covering pulp and paper, metals (i.e., Ti, Al, Be), ceramics (B4C, TiN, BN, SiC), carbonaceous materials (carbon fibers, intrinsic carbon, artificial diamond), reinforcing fibers for FRP (carbon fibers, aromatic polyamide fibers, glass fibers, SiC fibers, superdrawn polyethylene fibers), organic polymers (polyamides, polyethylene, polypropylene, polymethylpentene, polyimides, polysulfones, polyetherimides, polyethersulfones, PET), boards (plywood, particle board), resin composites (bulk molding compounds, resin concretes, artificial marble), and so on. I also was engaged in development of piezoelectric loudspeakers employing poly(vinylidene difluoride) (PVdF).The remarkably successful output from my R&D activities in those days were organic polymer whiskers and bacterial cellulose. The former was the first organic whisker in the world discovered by M. Iguchi,[1] which is composed of polyoxymethylene (POM). Organic whiskers have favorable properties for speaker diaphragms, namely, a high Young's modulus and low density. Sony made the joint developmental work with Dr. Iguchi on POM whiskers and succeeded in their mass production on a small scale and in their application to speaker diaphragms through the development of composite materials with the whisker and polyethylene.[2]

Bacterial cellulose is biosynthesized by the help of *Acetobacter xylinum* cultivated in media containing monosaccharides or disaccharides. We developed headphone diaphragms composed of bacterial cellulose sheets that had a high specific elastic modulus comparable to aluminum and titanium foils with low specific gravity.[3] The Technical Award was given for this work from the Agrochemical Society of Japan.

After 12 years of work on electroacoustic materials, I resumed investigating novel electrochemical cells in 1986. My efforts were focused on cells with

nonaqueous electrolytes, especially on those making use of carbon-lithium alloy anodes. In 1990, Sony announced that novel high-powered rechargeable cells were completed. $LiCoO_2$ was used as a cathode-active material and a tailor-made carbonaceous material was developed as an anode. Lithium was inserted in this carbon anode when a cell was charged and lithium was extracted from the anode during discharge. We gave the name of *lithium-ion battery* or LIB to this battery system. My accumulated experience in a wide range of advanced materials described above was greatly helpful in my new R&D activities, because LIB required various sophisticated materials including ceramics (i.e., $LiCoO_2$), carbonaceous materials (i.e., anodes), polymer films (i.e., separators), adhesives (i.e., binders for cathode and anode materials), and organic solvents (i.e., electrolytes).

In the case of POM synthesis, for example, it was necessary to control the moisture content in the solution of raw materials to a very low level (a few ppm)[2] and I could turn this technique to advantage when I made up nonaqueous electrolytes in which water content must be as low as possible. Biaxially drawn polyethylene microporous film was adopted as a separator and this material was analogous to superdrawn polyethylene fibers described above. As a binder for active electrode materials, PVdF was used, which was familiar to me as a piezoelectric speaker material.

The anode-active material is one of the most important items in LIB. The oldest description about carbon/lithium-negative electrodes appeared, as far as I know, in the German Patent filed in August 7, 1978,[4] in which it was described that "Bei derartigen galvanischen Elementen kann das Leichmetall der negativen Elektrode aus Be, Mg, Ca, B, Al, Sc, C, Si, As oder aus einer überwiegend aus diesen Leichtmetallen aufgebauten Leichtmetallegierung oder aber aus Lithiumlegierungen der genannten Stoff bestehen." Since then, considerable patents and papers referred to carbon/lithium electrodes.[5–8]

In regard to positive electrodes, we had developed $AgNiO_2$ as a cathode-active material in silver oxide cells.[9] An Ag insertion-extraction was observed in NiO2 layers during charge-discharge reactions. By analogy with this phenomenon, a bright idea occurred to us that $LiMO_2$ (M = Ni, Co, etc.) could be used as cathode-active materials in lithium cells. J. B. Goodenough et al., however, previously showed us that $LiCoO_2$ and $LiNiO_2$ cathodes can be reversibly charged and discharged in aprotic solvents in metallic lithium/$LiMO_2$ cells.[10] From these facts, it might be said that the LIB system itself was not an original invention but a novel combination of already known technologies.

In my opinion, the most important thing in developing electrochemical cells is to create a means for confining all the materials (cathode and anode active materials, electrolytes, separators, current collectors, etc.) in a limited and enclosed space, and for enabling energy as large as possible to be brought out without any safety problems. We completed this goal and succeeded in introducing LIB to practical use in 1991.[12]

The first-generation cells had energy densities of 200 Wh $dm^{-3}$ and 80 Wh $kg^{-1}$, only slightly greater than those of nickel-metal hydride (NiMH) cells of those days.[13] LIB performance has been improved continuously since then, and now energy densities reach 560 Wh $dm^{-3}$ and 210 Wh $kg^{-1}$ or more.

We started R&D on LIB with gel electrolytes in 1988 prior to the commercialization of LIB and put them into the market in 1998. They have comparable performances to conventional LIB and gravimetric energy densities are higher than those of LIB because polymer films can be utilized as enclosure materials instead of metallic cans.14 I believe that the advent of LIB has realized the so-called ubiquitous era. LIB has made it possible for people to utilize mobile equipment for a longer time out of doors. And in Japan, almost a billion LIBs are manufactured annually at the present time.

Since I started my R&D activities in Sony, it has been my eager dream to use and enjoy a new product in which a novel material or a device that I developed myself is made use of. At last in 1976, a new hi-fi loudspeaker system with a novel diaphragm which I developed was put on the market and I wanted to buy and use it. To my regret, however, the price was too high for me: 2-million yen! I succeeded in introducing audio equipment constantly into the market in which my novel materials were adopted including organic polymer whiskers, superdrawn polyethylene, artificial diamonds, and so on. These products also were too expensive for me. In 1988, a headphone was commercialized in which bacterial cellulose was used as diaphragms and I expected that I could buy this because a headset usually was much cheaper than a speaker. But I was at a loss for words to hear that the price of this headset was 360-thousand yen.

From the price point of view, LIB is much cheaper than a loudspeaker and the price is acceptable to me. Unfortunately, however, independent batteries are of no use. I must purchase expensive mobile gear such as notebook computers, cellular phones, digital cameras, and so forth.

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# Introduction: Development of Lithium-Ion Batteries

**Masaki Yoshio, Akiya Kozawa, and Ralph J. Brodd**

## 1 Introduction

In response to the need for better batteries, the lithium-ion battery (LIB) was conceived and developed in Japan by Asahi Kasei Co.[1] and first commercialized by Sony Co.[2] in 1991, followed by A&T Battery Co. (a joint company of Toshiba Battery and Asahi Kasei Co.) in 1992. The LIB was accepted immediately because of its high-energy density, good performance, and no memory effect as occurred with nickel–cadmium (Ni–Cd) or nickel-hydride (Ni–MH) batteries. LIBs have been used mainly for portable electronics, especially cellular phones and notebook computers. Recently, the application area has been extended to power tools and battery-assisted electric bicycles. Several companies are working to adapt the lithium-ion system for use in hybrid electric vehicles to replace the Ni–MH.

## 2 History of Lithium Batteries

Today, the major battery systems are the rechargeable lead acid and the primary manganese dioxide-zinc. Both have a long history and are at an advanced state of technical maturity. The LIB is poised to challenge these established systems as the demand for higher-performance battery systems continues. Lithium has a low atomic number and a high electrode potential that results in significantly high-energy density for the LIB compared to lead and zinc in the traditional batteries. However, the development of new high-energy lithium systems has been neither simple nor easy. It has required a total system approach and the development of breakthrough technologies based on new anodes, cathodes, and nonaqueous electrolytes to continue the steady improvement of high-energy lithium battery systems.

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Lithium-metal anode primary batteries based on nonaqueous electrolytes such as propylene carbonate-lithium perchlorate and lithium negative electrodes were developed in the early 1970s, with Matsushita introducing a lithium-carbon monofluoride (Li-CFx) primary cell in 1973, followed by Sanyo which commercialized primary lithium-manganese dioxide primary cells (Li-MnO$_2$) in 1975. These cells were used for LED fishing floats, cameras, and memory backup applications. A strong research effort then was mounted to convert lithium primary cells into rechargeable cells with high energy density. Table 1 documents the various research efforts. In the 1970s and 1980s most efforts concentrated on inorganic cathode compounds. Conducting polymer materials such as polyacetylene were developed as possible negative and positive electrode materials. However, these polymer materials have less density than water, and the batteries made with these materials offered no competitive advantage when it is enlarged, except for the polyacene (PAS) battery. The low-density conducting polymer cathodes have found a use only for coin cells for memory backup.

The early rechargeable lithium cells were plagued with safety problems caused by the tendency of lithium-metal anodes to form dendrites and powder deposits on recharging. The use of the high-performance perchlorate electrolytes was discontinued for safety reasons due to dendrite formation and very reactive fine powder deposits during recharge. In 1989, Moli Energy had the heat generation related to lithium metal in an AA-size cell. There was a shift to Li-Al alloy anode for greater safety in coin cells. However, the metallurgy of the alloy proved unacceptable for wound AA-size cells. Tadiran developed a dioxolane-based electrolyte that spontaneously polymerized at temperatures above 110°C.[3] The polymerized electrolyte had high resistance and shut down cell operation to provide a safety measure for the cells. The lithium-metal rechargeable cells now are restricted mainly to small-capacity coin cells. An early blend of lithium battery that still is in use is based on the electrochemical system Li-Al-PAS. In conjunction with a small solar cell this type of battery provides a convenient and compact power sources which now is used widely for road sign nighttime illumination or similar applications in remote

**Table 1**  Various rechargeable lithium metal battery systems developed

| System | Voltage | Wh/kg | Wh/l | Company |
|---|---|---|---|---|
| Li/TiS2 | 2.1 | 130 | 280 | '78 Exxon |
| LiAl/TiS2 | | | | '79 Hitachi |
| Li/LiAlCl$_4$-SO$_2$/C | 3.2 | 63 | 208 | '81–85 Duracell |
| Li/V$_2$O$_5$ | 1.5 | 10 | 40 | '89 Tohsiba |
| Li/NbSe$_3$ | 2.0 | 95 | 250 | '83–86 Bell Lab |
| LiAl/Polyaniline | 3.0 | – | 180 | '87 Bridgestone |
| LiAl/Polypyrolle | 3.0 | – | 180 | '89 Kanebo |
| Li/Al/Polyacene | 3.0 | – | – | '91 Kanebo/Seiko |
| Li/MoS$_2$ | 1.8 | 52 | 140 | '87 MoLi |
| Li/CDMO(Li$x$MnO$_2$) | 3.0 | – | – | '89Sanyo |
| Li/Li$_{0.3}$MnO$_2$ | 3.0 | 50 | 140 | '89 Tadiran |
| Li/VO$x$ | 3.2 | 200 | 300 | '90 HydroQuebec |

areas as a capacitor PAS-PAS or Li-doped PAHs-PAS hybrid battery, in which PAHs (polycyclic aromatic hydrocarbons) is the reformed structure from PAS.[4,5] Some other lithium alloys also are being developed for use as active materials for LIB and will be considered later in this book.

## 3   History of LIB and Patents on Lithium-Ion Cells

Since lithium metal constituted a safety problem, attention shifted to the use of a lithium-intercalation material as an anode. H. Ikeda of Sanyo was the first to patent an intercalation material in an organic solvent such as graphite in his June 1981 Japanese Patent No. 1769661.[6] One year before the Ikeda patent on graphite, Goodenough filed his $LiCoO_2$ patent for an intercalation cathode material.[7] S. Basu of Bell Laboratories filed U.S. Patent 4,423,125, in 1982, based on his finding of lithium intercalation in graphite at room temperature.[8] Previously, Basu had found lithium intercalation into graphite in molten salt electrolytes at high temperatures (U.S. Patent 4,304,8259). I. Kuribayashi and A. Yoshino developed a new cell design using an intercalation carbon anode and a $LiCoO_2$ cathode and filed patents worldwide.1 Using a pilot plant developed for rechargeable $Li-MnO_2$ cells, Sony Energytec Inc. began to produce commercial cells (called the Li-Ion Battery) based on the Asahi patents in 1991.2 They also introduced electronic circuitry to control the charge-discharge, the use of a current interrupt device to interrupt current flow on buildup of excessive internal cell pressure, and the use of a "shut-down" polymer separator.

The name "lithium-ion" now is accepted by the battery community worldwide, although there is no lithium metal in the cell. However, very often lithium-metal deposition occurs during charging with the graphite anode and it may cause the many troubles on the LIB. Both electrodes operate by intercalation of lithium ions into the structure of the active materials. AT Battery Co., a joint venture of Toshiba Battery Co. and Asahi Chemical Co., was the second to commercialize the technology using Asahi patent portfolio. Table 2 shows the prominent patents in the lithium-ion battery field.

## 4   Electrolyte Additives: A Means for Increasing the Energy Density and Safety of the LIB

Figure 1 depicts the increase in capacity of the cylindrical 18,650 cell (18 mm in diameter and 65.0 mm long) from 1992 to 2006. The early LIBs had a capacity of 800 mAh and an end-of-charge voltage of 4.1 V. The initial cells used hard-carbon anode materials which had a capacity of about 200 mAh/g, and the $LiCoO_2$ had a capacity of nearly 130 mAh/g due to 4.1 V charging voltage. The early lithium-ion cells used a propylene carbonate-based electrolyte. However, energy density of LIB

**Table 2** Patents related lithium-ion batteries

| Patents | Patents No. and application date | Name | Company |
|---|---|---|---|
| Transition metal oxides as cathode, LiCoO$_2$ | US 4,302,518 (1980/3/31) | J.B. Goodenough | United Kingdom Atomic Energy Authority |
| Graphite/Li in nonaqueous solvents | Japan 1769661 (1981/6/18) | H. Ikeda, K. Narukawa, H. Nakashima | Sanyo |
| Graphite/Li in nonaqueous solvents | US 4,423,125 (1982/9/13) | S. Basu | Bell Telephone Laboratories, Inc. |
| Grapahite/Li in molten salt | US 4,304,825 (1980/11/21) | S. Basu | Bell Telephone Laboratories, Inc. |
| Graphitized mesophase carbon | Japan 2,943,287 (Sept. 1990) | Kawagoe, Ogino | Bridgistone |
| Li-Ion battery (battery based on carbonaus material) | Japan 1989293 (1985/5/10) | A. Yoshino, K. Jitsuchika, T. Nakajima | Asahi Chemical Ind. |
| Cabonous/Li nonaqueous | US 4,959,281 (1989/8/29) | N. Nishi | Sony Co. |
| Additives for Gr vinylene carbonate | Japan 3059832 (1992/7/27) | M. Fujimoto, M. Takahashi, A. Nishio | Sanyo |
| Additives for Gr vinylene carbonate | US 5,626,981(May 6, 1997) | A. Simon, J-P. Boeuve | Saft |
| Additives of propane sulton | US 6,033,809 (1997/8/22) | S. Hamamoto, A. Hidaka, K. Abe | Ube |
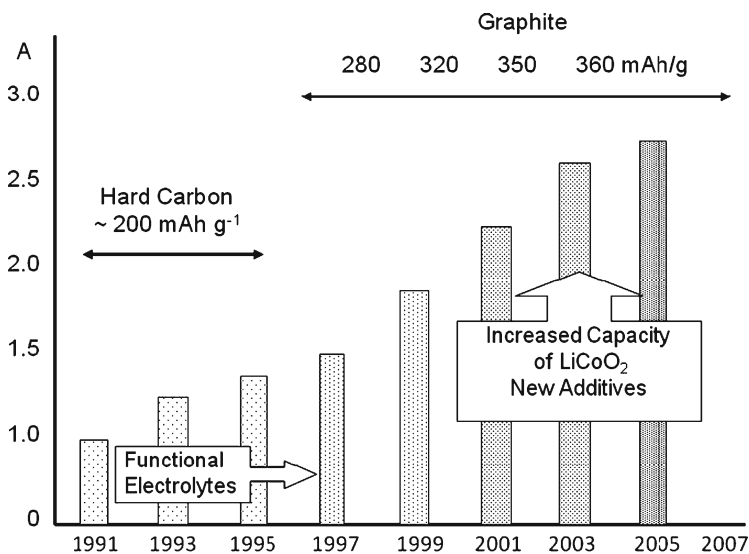


**Fig. 1** Capacity increase resulting from changes in materials and charging protocol

improved rapidly and increased on average by 10% per year and has approached 2.6 Ah in 2005.

Responding to pressure from device manufacturers, the cell capacity improved through engineering and the introduction of graphite anodes, improved $LiCoO_2$-based cathode materials, and the introduction of electrolyte additives. The solvent–solute relationships and the control of impurities became very important. Ethylene carbonate replaced propylene carbonate as a principal electrolyte component in the middle 1990s in order to suppress solvent decomposition. Researchers found that increasing the degree of graphitization increased the capacity. But, a high degree of graphitization of carbon increased solvent decomposition. LIB manufacturers could not quickly overcome this obstacle and the early cells employed artificial blends of graphite such as graphitized mesophase carbon of 280 mAh/g (first-generation MCMB 6-28 with a low degree of graphitization) which is still in use. The presence of trace amount water impurities in cell yield HF via hydrolysis of lithium hexafluorophosphate ($LiPF_6$) electrolyte and is particularly harmful for cathode components.

In 1998, Ube Industries Ltd. introduced a high-purity "functional electrolyte" which contained special additives that reacted during the first charge to form a protective solid electrolyte interphase [novel type of solid electrolyte interface (SEI)] surface film.[10,11] This film covers the "active spots" on the graphite materials to prevent electrolyte decomposition. As a result, the degree of graphitization of the anode carbon materials in use first increased up to 320 mAh $g^{-1}$ [graphitized mesophase carbon fiber (MCF) or second generation MCMB-6–28] and now approaches closely the theoretical value of 372 mAh.$g^{-1}$ (for example, the massive artificial battery (MAG), which has a narrow canal in its structure to adsorb electrolyte additives). Another electrolyte additive – cyclohexylbenzene (CHB) – generates hydrogen gas at higher voltages to prevent overcharge in case of electronic control circuitry failure. In such a case gas generation activates the current interrupt device and safety vent to prevent serious safety issues.

In 2003, the capacity of the 18,650 cell reached 2.4 Ah. This corresponds to an energy density of over 200 Wh/kg or 500 Wh/l, respectively. These values were reached in part by increasing the cell-operating voltage higher than 4.2 V due to the availability of improved graphite anode materials, electrolyte additives, and a stabilized $LiCoO_2$. In order to suppress the decomposition of the cell electrolyte at the active sites on the surface of $LiCoO_2$, Ube Co. Ltd. has developed a new generation of additives that eliminated electrolyte decomposition on the active sites of the cathode.[12,13] The concept was based on the formation of a conductive membrane to cover the particles of positive active material just as the SEI formation protects the anode. The commonly used anode additives are 1,3-propanesulton,[14] vinylene carbonate,[15] plus two or three types of additives for anode, cathode additive and the main overcharge protection additive is cyclohexylbenzene (CHB). Although the varieties and amounts of anodic additives are different depending on the graphite type, one of the popular graphite anodes would be MAG, showing a good affinity to additives. The capacity of the 18,650 cell had reached 2.9 Ah in 2006 by using graphite anode, planar Ni-based cathode, and several different types of additives. Other proprietary additives are included in the cell electrolytes in small amounts.

However, charging the cells to higher cutoff voltage highlights safety concerns of any lithium-based power source. Growing an appropriate SEI film, particularly at higher cutoff voltage, becomes essential for both the safety and the battery performance. The process of special SEI film formation by the additives and growth is called the "conditioning process" in the LIB community. This is one of the most important manufacturing operations to suppress the electrolyte decomposition and to maintain safety.

Electrode conditioning, especially containing the well-designed additives, is typically achieved in the following manner. First, several charge-discharge cycles are performed to decompose the additives at rather a low rate (about 1/4 C rate). These cycles initiate the protective film layer formation. After the completion of these initial (conditioning) cycles, the cells are kept in their charged state at room or elevated temperature for several days in order to complete the protective film growing process.

Figure 2 shows the same electrode with SEI on its surface grown in the absence and in the presence of additive (VA). It is clearly seen that SEI film formed on the graphite surface is not a homogeneous formation. A large number of minute spots are observed instead. They form due to the VA addition to the electrolyte. The adequately formed SEI film has a crucial role for improvement of performance and of safety of the LIB in operation.

On the other hand, intercalation of $Li^+$ into graphite in propylene carbonate (PC)-based electrolytes is possible even in the absence of additives, but only at the expense of a reduced PC ratio, as shown in Fig. 3. However, in this case a voltage plateau at around 0.6–0.8 V appears. The initial coulomb efficiency drops drastically and metallic lithium deposition seems to occur. Such behavior can be explained by the large number of the active sites present on the electrode. These active sites are the net result of the variable electric potential over the anode surface. Such nonhomogeneous voltage distribution facilitates the deposition of metallic lithium at the charged state, because there are many points under potential approaching 0 V vs. $Li/Li^+$ during the course of $Li^+$ intercalation.

Figure 4 clearly illustrates that the charge distribution on the graphite surface is not homogeneous. Some parts of the electrode surface resemble exfoliated-expanded graphite. The $Li^+$ cannot intercalate into the exfoliated graphite. On the other hand it is a good electric conductor on which lithium or another metal ion deposition may take place.

Figure 4 would represent a typical example of the LIB graphite anode in several tens of cycles. Some graphite would be damaged or exfoliated and would not accept $Li^+$ intercalation, but it would facilitate lithium-metal deposition instead. Conditioning process aims to establish a stable and robust SEI film in order to avoid this scenario.

Graphite has competition reactions especially at low temperature; one is a lithium intercalation into its structure and the other is the lithium deposition on it, which means the rather low intercalation reaction kinetics. Another important and interesting result revealing the importance of the electrolyte additives is shown Fig. 5, representing a graphite anode after the completion of six cycles under the
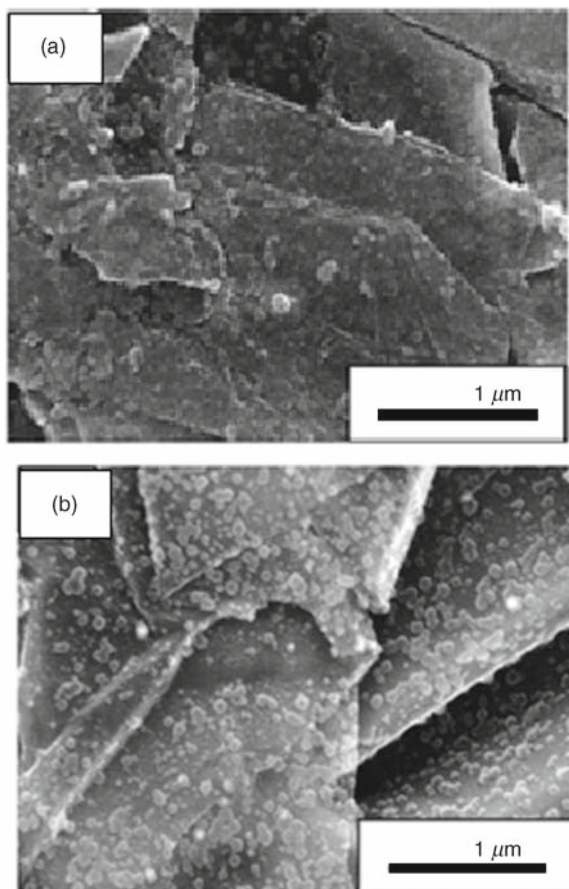
**Fig. 2** Scanning electron micrograph (SEM) of natural graphite after charging (a) in the absence of VA, and (b) in the presence of 1% VA
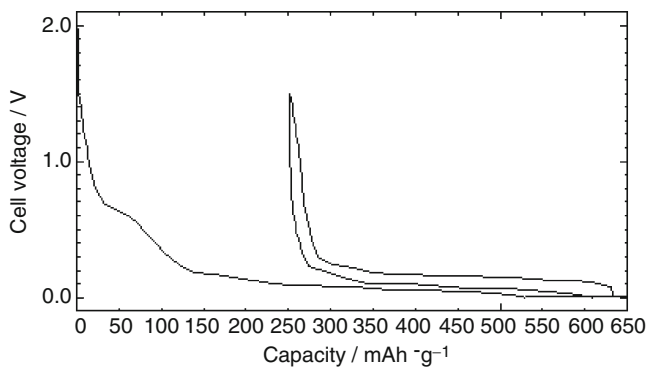


**Fig. 3** The voltage profile of graphite vs. Li/Li$^+$ in 1-M LiPF$_6$ PC:MEC (ethylmethyl carbonate) = 1:4
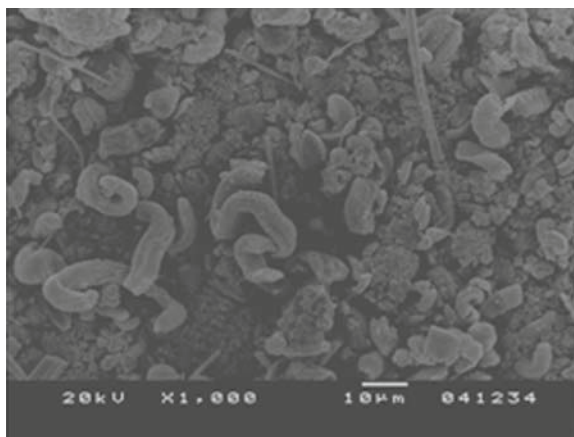
**Fig. 4** SEM image of the graphite electrode cycled vs. Li/Li$^+$ in 1-M LiPF$_6$ PC:MEC = 1:4



**Fig. 5** Appearance of the graphite electrode cycled/equilibrated (**a**) in the absence of electrolyte additives and (**b**) in the presence of 0.5 wt% propane sulton, at 0°C vs. Li/Li$^+$. Cell configuration: Li//1-M LiPF$_6$-EC/DMC(1:2 by vol.)//graphite. Each cycle the cell was equilibrated at 0.005 V for 10 h at 0°C

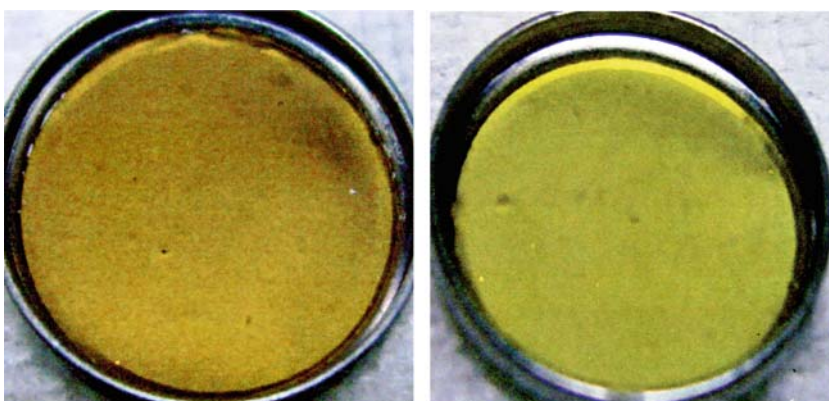following conditions: voltage window 0.005–2.500 V, current density 0.4 mA cm$^{-2}$ at 0°C. Cell configuration in this case was Li//1-M LiPF6-EC/DMC (1:2 by vol.)// graphite. Each cycle the cells were equilibrated at 0.005 V vs. Li/Li$^+$ for 10 h. The color of the electrode shown in Fig. 5 a is not golden, which is the first-stage color of lithiated graphite (LiC$_6$), because equilibrating the cell at low temperature induces Lilithium-metal deposition, especially in the absence of additives.

When using an appropriate additive, for example, propane sulton (PS), the appearance of the same type of electrode under the same conditions is shown in

Fig. 5b. It has the typical golden color of $LiC_6$.[16] This means that the additive has decomposed during the equilibration cycles and has deposited at the active sites of graphite, preventing the formation of metallic lithium. We believe that electrolyte additives improve the performance of the graphite electrodes by changing the kinetics of elemental lithium deposition. Because the electrolyte additives make the usage of highly crystalline graphite anodes possible and at the same time suppress the coexistence of elemental Li along with the lithiated graphite, they are considered to be a key material in the LIB industry.

Other recent developments include the incorporation of a fire retardant, which retards the combustion of the solvent, and a new additive to improve the wetting of the separator. It is difficult to use these additives in the gel-type electrolytes employed in lithium-ion polymer cells. This may be one reason for the lower market share experienced by lithium-ion polymer cells.

The capacity of the 18,650 cell appears to have reached its practical limit of 2.9 Ah based on the present graphite and planar nickel-based cathode in 2007. Further improvement in capacity is expected to be realized from the development of a silicon alloy type anode with a capacity of 700 mAh/g or more and the planar lithium-nickel-cobalt-aluminum and nickel-manganese-cobalt cathode materials with capacities approaching 250 mAh/g. New electrolytes and/or additives also are under development.

As society advances, a variety of new technologies, machines, and systems have been developed and more efficient industrial operations have been adopted. The concern for global warming and a clean environment along with the development of advanced electric and hybrid vehicles may be served well by advanced LIB. This situation has resulted in increased demand for high-performance batteries and power generation and storage. At the same time, demand has increased for a cleaner environment and a more efficient energy production coupled with low power consumption systems. In this context, the LIB has made and will continue to make significant contributions and advances.

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# Chapter 1
# Synopsis of the Lithium-Ion Battery Markets

**Ralph J. Brodd**

## 1.1 Introduction

Research and development of the lithium-ion (Li-Ion) battery system began in the early 1980s at Asahi Chemicals[1] and was first commercialized in 1990 by Sony Corp. for the Kyocera cellular phone in the 14,500 and 20,500 cell sizes.[2] The following year Sony introduced the 18,650 cell in its camcorder. (The nomenclature for cells size: the first two numbers indicate the cell diameter in millimeters and the last three are the cell length in tenths of millimeters.) Since its introduction, the Li-Ion market has grown to about $4 billion in 2005.

The higher volumetric and gravimetric energy storage capability are key characteristics of the Li-Ion battery system compared to the conventional sealed nickel–cadmium (Ni–Cd), nickel-metal hydride (Ni-MH), and valve-regulated lead acid (VRLA) battery systems (Fig. 1.1). For a given cell size, larger values of Wh/l and Wh/kg translate into smaller and lighter cells. These characteristics became the enabling technology for the proliferation of portable battery-powered electronic devices, especially notebook computers and mobile phone applications.

Safety of the system has been a watchword for Li-Ion batteries. They have the ability to self-destruct if abused. Manufacturers are careful to ensure that the cells are safe in normal operations. In addition, cell designs incorporate features such as devices that shut off current flow when an abuse condition arises. The United Nations[3] as well as the transportation agency in each country have requirements for testing to ensure a safe product for shipping.
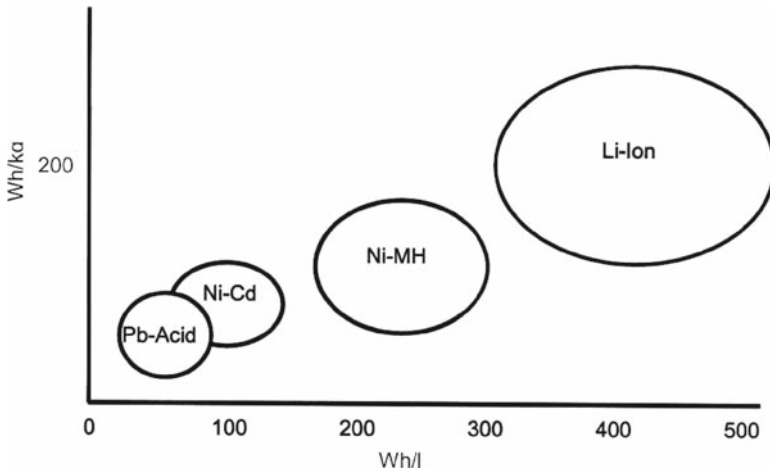
Table 1.1 shows the advantages and disadvantages of the Li-Ion and Li-Ion polymer rechargeable batteries.

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**Fig. 1.1** Energy density (Wh/l) and specific energy (Wh/kg) for the major small-sealed rechargeable battery systems

**Table 1.1** Advantages and disadvantages of Li-ion and Li-ion polymer rechargeable cells

| Advantages | Disadvantages |
|---|---|
| • Chemistry with the highest energy (Wh/g) and lightest weight (Wh/kg) | • Relatively expensive |
| • No memory effect | • Lightest weight |
| • Good cycle life | • Requires protection circuitry for safety and to prevent overcharge and overdischarge |
| • High energy efficiency | • Nominal 3-h charge |
| • Good high-rate capability | • Not tolerant of overcharge and overdischarge |
| | • Thermal runaway concerns |
| Added advantages and disadvantages of Li-Ion polymer/laminate cells | |
| • Flexible footprint | • Limited high rate capability |
| • Plasticized electrolyte | • More expensive |
| • Internal bonding of anode | • Poor low-temperature performance |
| • Cathode and separator | |

## 1.2 Present Market for Li-Ion Cells

Lithium ion cells serve the small-sealed rechargeable battery market and compete mainly with the Ni–Cd and Ni-MH cells for the various applications. The Li-Ion cells are available in cylindrical and prismatic format as well as flat plate constructions. The cylindrical and prismatic constructions use a spiral-wrap cell core where the cell case maintains pressure to hold and maintain compression on the anode, separator, and cathode. The lighter-weight polymer constructions utilize the adhesive nature of a polymer/laminate-based electrolyte to bond the anode to the cathode.

As a result, it does not need outside pressure to hold the electrodes in contact with each other. A light-weight polymer-aluminum laminate pouch can substitute for a heavier metal cell enclosure. All three constructions employ the same chemistries.

The sales of Li-Ion cells are shown in Table 1.2.[4] The Li-Ion market is very competitive. The data for the competing Ni–Cd and Ni-MH cells are included for comparison purposes. The market growth for Li-Ion is spectacular and driven by the proliferation of portable electronic devices such as notebook computers and cellular phone applications. In 15 years between 1991 and 2006 the sales and production of Li-Ion batteries experienced double-digit growth. The slower growth period, around 2000, occurred when cell production in China and Korea began to ramp up and may not have been included in the database.

In 1995, an 18,650 cell sold for $8, while in 2006 the same size cell with 2.6 Ah sold for about $4. Over this period the energy density of the cell more than doubled, while the price fell by 50%. The cell producers accomplished the performance improvements through engineering improvements in cell design, new carbon materials for the anode, and automated high-speed production to reduce the cost. The Li-Ion market is expected to continue growing as new technology is introduced and new applications develop.

The major cell manufacturers are listed in Table 1.3. The Japanese manufacturers (Sanyo, Sony, and Matsushita) have a clear lead but the Chinese manufacturers (BYD, Lishen) and Korean manufacturers (Samsung and LG Chemical) are challenging. There are no major Li-Ion manufacturers in the United States (or in Europe), even

**Table 1.2** Worldwide Sales (Million of Dollars)[4]

| Cell type | Year | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
|  | 1991 | 1992 | 1994 | 1996 | 1998 | 2000 | 2002 | 2004 | 2005 | 2006[a] |
| Ni–Cd | 1,535 | 1,823 | 2,060 | 1,695 | 1,394 | 1,204 | 935 | 1,006 | 935 | 939 |
| Ni-MH | 39 | 100 | 746 | 863 | 848 | 1,245 | 667 | 767 | 726 | 891 |
| Li-Ion | 1 | 10 | 152 | 1,292 | 1,900 | 2,805 | 2,458 | 4,019 | 3,899 | 3,790 |
| Lam Li-Ion | 0 | 0 | 0 | 0 | 2 | 187 | 299 | 487 | 547 | 657 |

[a] Estimated

**Table 1.3** 2005 Worldwide cell demand (Millions of Cells)[4]

| Application | Cell type | | | | |
|---|---|---|---|---|---|
|  | Ni-Cd | Ni-MH | Cy Li-Ion | Pr Li-Ion | Lam Li-Ion |
| Cellular |  | 50 |  | 898.16 | 125.85 |
| Notebook |  | 22 | 422.68 | 16.34 | 2.50 |
| Movie | 2 | 4 | 67.98 | 11.91 |  |
| Digital still camera |  | 56 | 18.88 | 48.17 | 0.94 |
| Power tools | 575 | 53 | 20.14 | 0.08 |  |
| Audio | 80 | 35 | 6.99 | 31.02 | 45.63 |
| Games |  |  |  | 26.82 | 14.4 |
| Consumer | 45 | 300 |  |  |  |
| Cordless phones | 190 | 83 |  |  |  |
| Others | 330 | 178 | 22.854 | 28.98 | 14.42 |

though they constitute large markets for devices powered by Li-Ion batteries.[5] Activity in the United States is limited to several companies that supply the niche medical and military markets.

## 1.3   Market Characteristics

The unit cell production for 2005 by product application is given in Table 1.4. Cellular phone applications dominate the unit cell production. The thin, rectangular polymer/laminate cell construction has found favor in the cellular phone market and now accounts for about 13%, with the rest being the prismatic cell sizes. Notebook computers are second followed by cameras.

The period from its introduction in 1991–2002 was a time for establishing the fundamental base for materials and manufacturing processing. During this period, the processing of the materials, cell designs, and production equipment reached a high level of sophistication. The fundamental underpinning of the technology provided a sound basis for future expansion during the next decade. Problems were identified and methods to solve the problems were developed. From a cell engineering viewpoint, the maximum capacity of an 18,650 cell would be 2.5–2.6 Ah with the materials that were available in 2002. Increase in cell capacity and energy storage while maintaining safety would require new materials.

Starting in 2003, a shift in the market applications began to occur, as depicted in Fig. 1.2.[6] In one segment basically the drive to increase capacity and performance for the competitive notebook and cellular phone applications continues. This requires the development and introduction of higher capacity, higher performance anode and cathode materials. Several new high-capacity, safer compositions such as $LiMn_{0.3}Co_{0.3}Ni_{0.5}O_2$ and $LiMn_{0.5}Ni_{0.5}O_2$ cathodes were developed and are in the process of being put into production. In the same line, new anode materials have been developed, based on nanostructured lithium alloy anodes. These materials can drive the 18,650 cell capacity over 2.6 Ah and could approach 3.0 Ah in the future.

**Table 1.4**   Major Li-ion cell manufacturers, 2005[4]

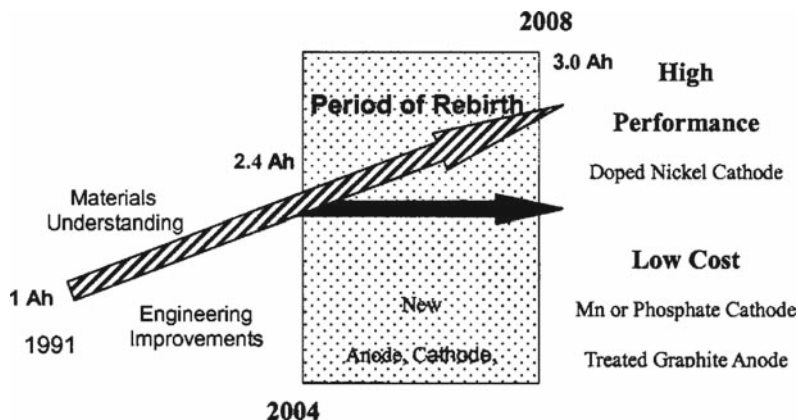| Manufacturers | Percentage of total |
| --- | --- |
| Sanyo | 27.50 |
| Sony | 13.30 |
| Samsung | 10.88 |
| Matsushita | 10.07 |
| BYD | 7.53 |
| LG Chemical | 6.45 |
| Lishen | 4.52 |
| NEC | 3.60 |
| Maxell | 3.26 |
| Others | 12.89 |

**Fig. 1.2**  A split develops in the Li-ion market

The other segment consists of applications that do not require a significant increase in energy storage capability but emphasize lower cost and higher power for new applications such as automotive and power tools. These applications also require new cathode and anode materials to meet the market demands for low cost with high-rate performance. An example of a new material is the $LiFePO_4$ cathode materials introduced in the market in 2003 by Valence Technology and followed by A123, which emphasized power tool applications.[7–9]

## 1.4   Consumer Electronics

Cellular telephones and notebook computer applications drove the market and will continue to dominate cell usage. The Bluetooth and 3G mobile phones should expand the market coupled with expansion as people shift to higher performance devices. The market for portable cellular phone and notebook computers is reaching saturation in the United States and Europe where it is expected to grow in parallel with the gross national product. Large growth areas for cellular phones and notebook computers are in Asia, especially the Chinese and Indian markets.

Movie cameras account for about 25% of cell usage. Often cameras are used intermittently and may sit on the shelf for an extended period before use. The shelf life of the Li-Ion is significantly better than Ni–Cd and Ni-MH cells, the previous battery systems for movie cameras. Digital still cameras are next. They are in the process of transitioning to Li-Ion from alkaline primary and Ni-MH cells. Most primary cells lack the high pulse current required for camera operation. Only the primary Li–$FeS_2$ system gives fully satisfactory performance for digital still camera operation. Notebook computer and cellular phone users have learned to recharge their batteries on a regular basis so that the device gives the expected service. In addition, many mobile phones have a built-in camera and could slow the development of the digital camera market.

## 1.5 Hand Power Tools

The power tool market is dominated by the Ni–Cd system. In terms of cell volumes it is the third largest. However, it is heavy and has a short run time compared to Li-Ion. Previously, Li-Ion cells could not meet the very high rate capability of the Ni–Cd. Recently, Li-Ion cells with excellent high-rate $LiMn_2O_4$ or $LiFePO_4$ cathode materials were introduced for power tool applications. They are about a third smaller and half the weight of the older Ni–Cd. The phosphate cathode cells have a significantly greater safety characteristic as the cells do not go into thermal runaway until heated to over 600°C. The greater safety, coupled with the superior high-rate capability of the nanostructured phosphate materials, make them ideal for this application. This market segment is price-sensitive. Because the Ni-MH has poor low temperature and poorer very high rate performance, it has not made a significant inroad against Ni–Cd. The introduction of Li-Ion–powered tools by DeWalt and Milwaukee Tool offers a growth opportunity for Li-Ion cells.

## 1.6 Uninterruptible Power Sources, Stationary Energy Storage

The uninterruptible power source market is about $ 6–10 billion annually and is growing roughly with the gross national product. This market is dominated by lead acid batteries. The technology is slowly shifting from the flooded to the valve-regulated lead acid technology. The valve-regulated lead acid cells are sealed and do not vent hydrogen and acid vapors on charge or stand, but they are more expensive to produce. The main competition to the lead acid is costly pocket plate Ni–Cd, but it has an exceptionally long life. It is not unusual for Ni–Cd to have an operational life of 15 years or more in this application. Increased emphasis on environmental controls has made lead acid and Ni–Cd vulnerable for penetration by the environmentally acceptable, higher-cost Li-Ion batteries.

   This market is very price-sensitive and the cost of Li-Ion cells will need to reach $0.30/Wh to penetrate this market. The new lower-cost manganese and phosphate cathode materials could reach this cost goal. It should be noted that several large lead acid battery companies in this market recently have entered into agreements with Li-Ion producers to supply cells and batteries for evaluation purposes. This could be an indication that the more traditional lead acid producers are positioning themselves to supply Li-Ion as an alternative for lead batteries.

## 1.7 Transportation

There are many emerging market opportunities for Li-Ion cells in transportation. The motive power market is viewed as the largest future growth opportunity for Li-Ion batteries. Once in place, the transportation market will dwarf the present

portable device market. The Segway Transporter has shifted from Ni-MH to Li-Ion batteries. The Toyota Prius will shift from Ni-MH to Li-Ion in the next model redesign. These, along with the emerging boating motors for freshwater lakes, have set the stage for penetration into this huge market area. Europe is in the process of banning gasoline motors on all lakes. Several U.S. lakes now bar gasoline-powered boats, as well. Boaters must shift to electric drive and batteries to operate on the lakes. These presently use lead acid batteries. The smaller, lighter, Li-Ion battery is already marketed in Europe for this application.

The introduction of the Tesla electric vehicle in 2007 with a 200 + mile range should set the stage for the transition to electric propulsion. The new cathode and anode systems also offer the potential to replace the present lead acid SLI (starting-lighting-ignition) battery on gasoline-powered vehicles.

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