

Lithium-Ion Batteries

Masaki Yoshio • Ralph J. Brodd • Akiya Kozawa
Editors

Lithium-Ion Batteries

Science and Technologies

 Springer

Editors

Prof. Em. Masaki Yoshio
Advanced Research Center, Saga University
1341 Yoga-machi, 840-0047, Japan
yoshio@cc.saga-u.ac.jp

Ralph J. Brodd
Broddarp of Nevada, Inc.,
2161 Fountain Springs Dr.
Henderson, NV 89074, USA
ralph.brodd@earthlink.net

Akiya Kozawa
ITE Aichi Office, 2-15-19 Kamejima
Nakamura-ku, Nagoya 453-0013
Japan

ISBN: 978-0-387-34444-7 e-ISBN: 978-0-387-34445-4
DOI: 10.1007/978-0-387-34445-4

Library of Congress Control Number: 2008940833

© Springer Science+Business Media, LLC 2009

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, LLC, 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks, and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed on acid-free paper

springer.com

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 Leichtmetall der negativen Elektrode aus Be, Mg, Ca, B, Al, Sc, C, Si, As oder aus einer überwiegend aus diesen Leichtmetallen aufgebauten Leichtmetalllegierung 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 NiO_2 layers during charge-discharge reactions. By analogy with this phenomenon, a bright idea occurred to us that LiMO_2 ($M = \text{Ni, Co, etc.}$) 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.

References

1. M. Iguchi, *Br. Polymer J.*, 5 (1973) 195
2. Y. Nishi, M. Uryu, *New Mater. New Process.*, 3 (1985) 102
3. M. Iguchi, T. Suehito, Y. Watanabe, Y. Nishi, M. Uryu, *J. Mater. Sci.*, 17 (1982) 1632
4. Y. Nishi, M. Uryu, S. Yamanaka, K. Watanabe, K. Kitamura, M. Iguchi, N. Mitsuhashi, *J. Mater. Sci.*, 25 (1990) 2997
5. F. Heinz, German Patent, DE 2834485 C2, filed in 1978
6. A. G. MacDiarmid, A. Heeger, P. J. Nigrey, U.S. Patent 4,442,125, filed in 1980
7. R. Yazami, Ph. Touzain, Abstract No. 23, International Meeting on Lithium Batteries, 1982
8. S. Basu, U.S. Patent 4,423,125, filed in 1982
9. F. P. McCullough, Jr., U.S. Patent, filed in 1984
10. T. Nagaura and T. Aida, Japanese Patent S62-11460, filed in 1980
11. J. B. Goodenough, M. Miaushima, P. J. Wiseman, British Patent, filed in 1979
12. Y. Nishi, *Chem. Rec.*, 1 (2001) 406
13. Y. Nishi, Lithium Ion Batteries, M. Wakihara, O. Yamamoto, Eds., Kodansha/Wiley-VCH, Tokyo (Japan), 1998, p. 181
14. Y. Nishi, Advances in Lithium-Ion Batteries, W. A. van Schalkwijk, B. Scrosati, Eds., Kluwer/Plenum, New York, 2002, p. 233

Contents

Contributors	xiii
Introduction	xvii
1 Synopsis of the Lithium-Ion Battery Markets	1
Ralph J. Brodd	
2 A Review of Positive Electrode Materials for Lithium-Ion Batteries	9
Masaki Yoshio and Hideyuki Noguchi	
3 Carbon Anode Materials	49
Zempachi Ogumi and Hongyu Wang	
4 Role Assigned Electrolytes: Additives	75
Makoto Ue	
5 Carbon-Conductive Additives for Lithium-Ion Batteries	117
Michael E. Spahr	
6 Applications of PVdF-Related Materials for Lithium-Ion Batteries	155
Aisaku Nagai	
7 SBR Binder (for Negative Electrode) and ACM Binder (for Positive Electrode)	163
Haruhisa Yamamoto and Hidekazu Mori	
8 Production Processes for Fabrication of Lithium-Ion Batteries	181
Kazuo Tagawa and Ralph J. Brodd	
9 Polyanionic Cathode-Active Materials	195
Shigeto Okada and Jun-ichi Yamaki	

10 Overcharge Behavior of MetalOxide-Coated Cathode Materials	207
Jaephil Cho, Byungwoo Park, and Yang-kook Sun	
11 Development of Metal Alloy Anodes	241
Nikolay Dimov	
12 HEV Application	267
Tatsuo Horiba	
13 Flame-Retardant Additives for Lithium-Ion Batteries	275
Masashi Otsuki and Takao Ogino	
14 High-Energy Capacitor Based on Graphite Cathode and Activated Carbon Anode.....	291
Masaki Yoshio, Hitoshi Nakamura, and Hongyu Wang	
15 Development of LiCoO_2 Used for Rechargeable Lithium-Ion Battery	299
Hidekazu Awano	
16 Cathode Materials: LiNiO_2 and Related Compounds.....	315
Kazuhiko Kikuya, Masami Ueda, and Hiroshi Yamamoto	
17 Manganese-Containing Cathode Active Materials for Lithium-Ion Batteries	323
Koichi Numata	
18 Trends in Carbon Material as an Anode in Lithium-Ion Battery	329
Tatsuya Nishida	
19 Functional Electrolytes Specially Designed for Lithium-Ion Batteries	343
Hideya Yoshitake	
20 Lithium-Ion Battery Separators.....	367
Zhengming (John) Zhang and Premanand Ramadass	
21 Polymer Electrolyte and Polymer Battery.....	413
Toshiyuki Osawa and Michiyuki Kono	
22 A Novel Hard-Carbon Optimized to Large Size Lithium-Ion Secondary Batteries.....	427
Aisaku Nagai, Kazuhiko Shimizu, Mariko Maeda, and Kazuma Gotoh	

23	LiMn₂O₄ as a Large Capacity Positive Material for Lithium-Ion Batteries	435
	Masaki Okada and Masaki Yoshio	
	Index	445

Contributors

Hidekazu Awano

Nippon Chemical Industrial Co., Ltd., 9-11-1, Kameido, Koto-ku,
Tokyo 136-8515, Japan, hidekazu.awano@nippon-chem.co.jp

Ralph J. Brodd

Broddarp of Nevada, Inc., 2161 Fountain Springs Dr., Henderson, NV 89074,
USA, ralph.brodd@earthlink.net

Jaephil Cho

Department of Applied Chemistry, Hanyang University,
Ansan 426-791, South Korea, jpcho@hanyang.ac.kr

Nikolay Dimov

Department of Applied Chemistry, Saga University, 1 Honjo, Saga 840-8502,
Japan, nikjapan@yahoo.com

Kazuma Gotoh

Department of Chemistry, Faculty of Science, Okayama University,
Okayama 700-8530, Japan

Tatsuo Horiba

Shin-Kobe Electric Machinery Co., Ltd., 2200 Oka, Fukaya, Saitama 369-0297,
Japan, t.horiba@shinkobe-denki.co.jp

Kazuhiko Kikuya

Toda Material Corp. Kyushu, 1-26 Hibiki-machi, Wakamatsu, Kitakyushu,
Kazuhiko_Kikuya@todakogyo.co.jp

Michiyuki Kono

R&D Division, Dai-Ichi Kogyo Seiyaku Co., Ltd., 55, Nishi-Shichijo,
Higashikubo-Cho, Shimogyo-Ku, Kyoto 600-8873, Japan,
m-kono@dks-web.co.jp

Akiya Kozawa

ITE Aichi Office, 2-15-19 Kamejima, Nakamura-ku, Nagoya 453-0013, Japan

Mariko Maeda

Research Center, Kureha Corporation, 16, Ochiai, Nishiki, Iwaki, Fukushima 974-8232, Japan

Hidekazu Mori

ZEON Co., Yako 1-2-1, Kawasaki 210-9507, Japan, h.mori@zeon.co.jp

Aisaku Nagai

Research & Technology Division, Kureha Corporation, 3-3-2, Nihonbashi-Hamacho, Chuo-ku, Tokyo 103-8552, Japan, a-nagai@kureha.co.jp

Yoshio Nishi

1-7-302 Wakabadai, Asahi-ku, Yokohama 241-0801, Japan, west24440@mmm-keio.net

Tatsuya Nishida

Hitachi Chemical Co. Ltd., Japan, 13-1, Higashi-Cho 4-chome, Hitachi City 317-8555, Japan, t-nishida@hitachi-chem.co.jp

Hideyuki Noguchi

Department of Applied Chemistry, Saga University, 1 Honjyo, Saga 840-8502, Japan

Koichi Numata

Mitsui Mining & Smelting Co, Ltd., Corporate R&D Center, 1333-2 Haraichi, Ageo, Saitama 362-0021, Japan, k_numata@mitsui-kinzoku.co.jp

Takao Ogino

Research and Development Division, Bridgestone Corporation, 3-1-1 Ogawa-higashi, Kodaira 187-8531 Tokyo, Japan

Zempachi Ogumi

Department of Energy & Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan, ogumi@scl.kyoto-u.ac.jp

Masaki Okada

Nanyo Research Laboratory, TOSOH Corporation, 4560, Kaisei-cho, Shin-nanyo 746-8501, Japan, okada_m@tosoh.co.jp

Shigeto Okada

Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga Koen, Kasuga-shi, Fukuoka 816-8580, Japan, s-okada@cm.kyushu-u.ac.jp

Toshiyuki Osawa

Kanagawa Industry Technology Center, 705-1, Shimoizumi, Ebina, 243-0435, Japan, tohsawa@kanagawa-iri.go.jp

Masashi Otsuki

Central Research, Bridgestone Corporation, 3-1-1
Ogawa-higashi, Kodaira, Tokyo 187-8531, Japan,
masashi.otsuki@bridgestone.co.jp

Byungwoo Park

School of Materials Science and Engineering and Research Center for Energy
Conversion & Storage, Seoul National University, Seoul, Korea

Premanand Ramadass

Celgard, LLC, 13800 South Lakes Dr., Charlotte, NC 28273, USA

Kazuhiko Shimizu

Research Center, Kureha Corporation, 16, Ochiai, Nishiki, Iwaki,
Fukushima 974-8232, Japan

Michael E. Spahr

TIMCAL Ltd., Strada Industriale, CH-6743 Bodio, Switzerland,
m.spahr@ch.timcal.com

Yang-kook Sun

Department of Chemical Engineering, Hanyang University, Seoul, Korea

Kazuo Tagawa

Hohsen Corporation, 10-4-601 Minami Semba 4-chome, Chuo-ku, Osaka 542-
0081, Japan

Makoto Ue

Mitsubishi Chemical Group, Science and Technology Research Center, Inc.,
Battery Materials Laboratory, 8-3-1 Chuo, Ami, Inashiki, Ibaraki 300-0332,
Japan, 3707052@cc.m-kagaku.co.jp

Masami Ueda

Toda Kogyo Corp., 1-26 Hibiki-machi, Wakamatsu, Kitakyushu, Fukuoka 808-
0021, Japan

Hongyu Wang

Advanced Research center, Saga university,
1341 Yoga-machi, Saga 840-0047, Japan,
wanghongyu@hotmail.com

Jun-ichi Yamaki

Institute for Materials Chemistry and Engineering, Kyushu University, 6-1
Kasuga Koen, Kasuga-shi, Fukuoka 816-8580, Japan,
yamaki@cm.kyushu-u.ac.jp

Haruhisa Yamamoto

ZEON Corporation, Yako 1-2-1, Kawasaki 210-9507, Japan
Hiroshi Yamamoto Toda Kogyo Corp., 1-1-1 Shinoki,
Onoda, 756-0847, Japan

Masaki Yoshio

Advanced Research center, Saga university,
1341 Yoga-machi, Saga 840-0047, Japan,
yoshio@cc.saga-u.ac.jp

Hideya Yoshitake

Specialty Chemicals & Products Company, Ube Industries, Ltd., 1-2-1 Shibaura,
Minato-ku, Tokyo 105-8449, Japan, 27452u@ube-ind.co.jp

Zhengming (John) Zhang

Celgard, LLC, 13800 South Lakes Dr., Charlotte, NC 28273, USA,
johnzhang@celgard.co

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.

Masaki Yoshio
Advanced Research center, Saga University, 1341 Yoga-machi, Saga 840-0047, Japan
E-mail: yoshio@cc.saga-u.ac.jp, GBE03502@nifty.com

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-MnO₂) 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/TiS ₂	2.1	130	280	'78 Exxon
LiAl/TiS ₂				'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/Polypyrrolle	3.0	-	180	'89 Kanebo
Li/Al/Polyacene	3.0	-	-	'91 Kanebo/Seiko
Li/MoS ₂	1.8	52	140	'87 MoLi
Li/CDMO(LixMnO 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.

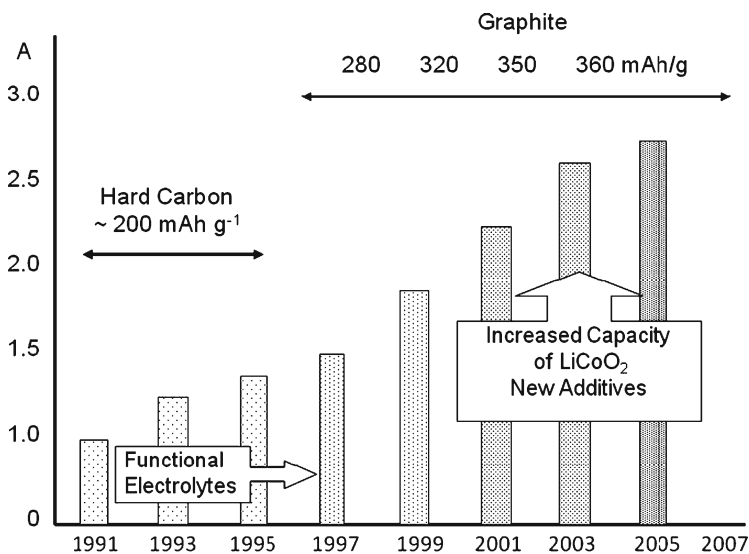
The name “lithium-ion” now is accepted by the battery community worldwide, although there is no lithium metal in the cell. However, very often lithium-metal deposition occurs during charging with the graphite anode and it may cause the many troubles on the LIB. Both electrodes operate by intercalation 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.
Graphite/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	Bridgestone
Li-Ion battery (battery based on carbonous material)	Japan 1989293 (1985/5/10)	A. Yoshino, K. Jitsuchika, T. Nakajima	Asahi Chemical Ind.
Carbonous/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. Boeue	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-propanesultone,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

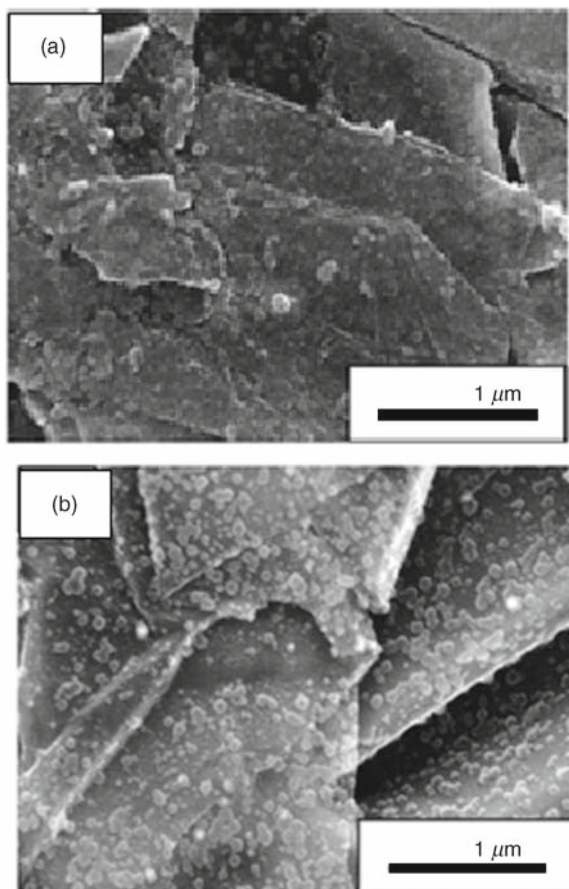


Fig. 2 Scanning electron micrograph (SEM) of natural graphite after charging (a) in the absence of VA, and (b) in the presence of 1% VA

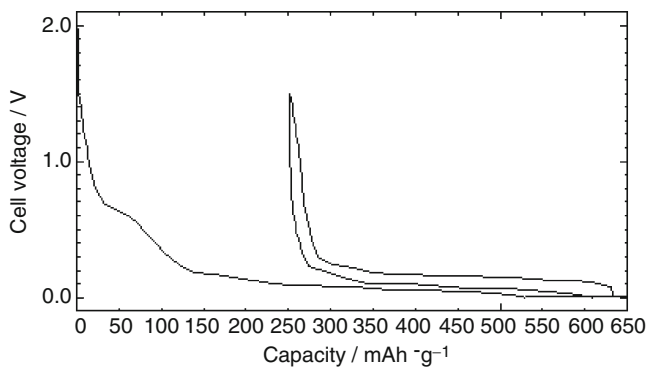


Fig. 3 The voltage profile of graphite vs. Li/Li⁺ in 1-M LiPF₆ PC:MEC (ethylmethyl carbonate) = 1:4

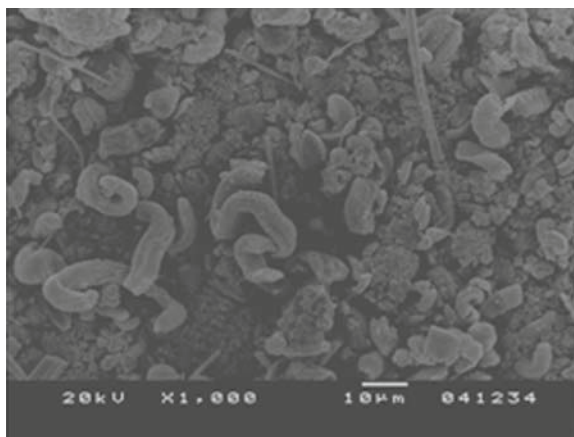


Fig. 4 SEM image of the graphite electrode cycled vs. Li/Li^+ in 1-M LiPF_6 PC:MEC = 1:4

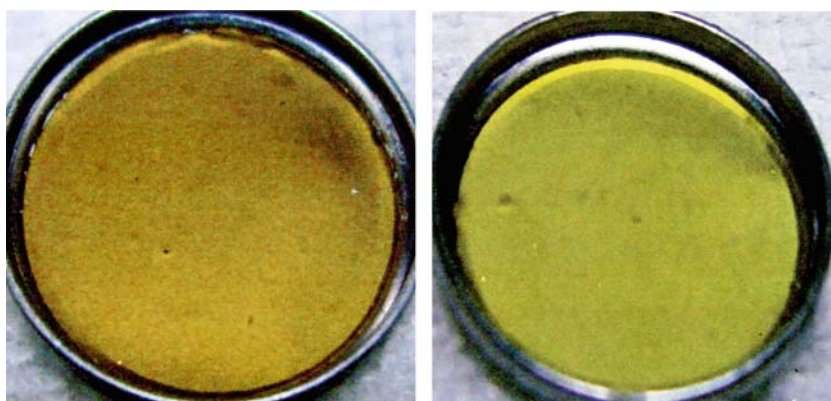


Fig. 5 Appearance of the graphite electrode cycled/equilibrated (a) in the absence of electrolyte additives and (b) in the presence of 0.5 wt% propane sultone, at 0°C vs. Li/Li^+ . Cell configuration: $\text{Li}/1\text{-M LiPF}_6\text{-EC/DMC}(1:2 \text{ by vol.})//\text{graphite}$. Each cycle the cell 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 $\text{Li}/1\text{-M LiPF}_6\text{-EC/DMC}(1:2 \text{ by vol.})//\text{graphite}$. 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 Lithium-metal deposition, especially in the absence of additives.

When using an appropriate additive, for example, propane sultone (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.

References

1. A. Yoshino, K. Jitsuchika, T. Nakashima, Japanese Patent 1989293 (issued 1985/5/10)
2. T. Nagura, K. Tozawa, *Progr. Batteries Solar Cells*, 10 (1991) 218
3. P. Dan, E. Mengeritsky, D. Aurbach, I. Weissman, E. Zinigrad, *J. Power Sources*, 68 (1997) 443
4. S. Yata, Y. Hato, H. Kinoshita, N. Ando, A. Anekawa, T. Hashimoto, M. Yamaguchi, K. Tanaka, T. Yamabe, *Synth. Met.*, 73 (1995) 273
5. S. Wang, S. Yata, J. Nagano, Y. Okano, H. Kinoshita, H. Kikuya, T. Yamabe, *J. Electrochem. Soc.*, 147 (2000) 2498
6. H. Ikeda, K. Narukawa, H. Nakashima, Japanese Patent 1769661 (issued 1981/6/18)
7. J.B. Goodenough, U.S. Patent 4,302,518 (issued 1980/3/31)
8. S. Basu, U.S. Patent 4,423,125 (issued 1982/9/13)
9. S. Basu, U.S. Patent 4,304,825 (issued 1980/11/21)
10. H. Yoshitake, Techno-Frontier Symposium, Makuhari, Japan (1999)

11. H. Yoshitake, *Functional Electrolyte in Lithium Ion Batteries* (in Japanese), M. Yoshio, A. Kozawa, Eds., Nikkan Kougyou Shinbunsha, Japan, 2000, pp. 73–82
12. H. Yoshitake, K. Abe, T. Kitakura, J. B. Gong, Y. S. Lee, H. Nakamura, M. Yoshio, *Chem. Lett.*, 32 (2003) 134
13. K. Abe, H. Yoshitake, T. Kitakura, T. Hattori, H. Wang, Masaki Yoshio, *Electrochim. Acta* 49 (2004) 4613
14. S. Hamamoto, A. Hidaka, K. Abe, U.S. Patent 6,033,809 (issued 1997/8/22)
15. M. Fujimoto, M. Takahashi, A. Nishio, Japanese Patent 3059832 (issued 1992/7/27)
16. Gumjae Park, Hiroyoshi Nakamura, Yunsung Lee and Masaki Yoshio *J. Power Sources*, in press (2009)