Edited by Kazunori Ozawa

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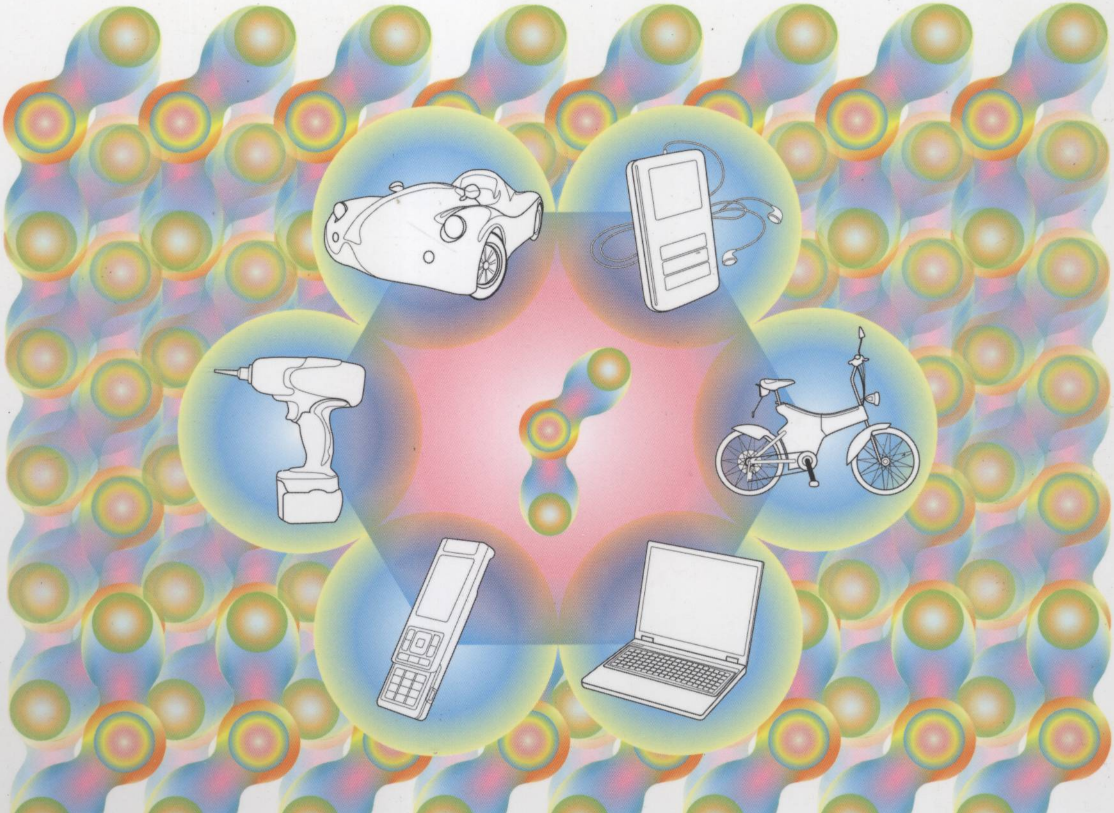
Lithium Ion Rechargeable Batteries

Materials, Technology, and New Applications



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Preface

Lithium ion battery has become the basis of the huge market for cellular phones and lap top computers, and these mobile communication market continues to grow at a rapid rate, supported by the demand all over the world. Even so, intensive efforts are still under way to further improve the technology. The main target of the effort is not only the automobile industry by achieving higher energy and higher power, but also the energy storage market supplementing environmentally friendly power source such as solar energy and wind turbine.

Though the lithium ion technology is so wide this book can include only a few topics, I believe the readers can find an indicator to do the research.

Chapter one covers the basic concepts of electrochemical devices and lithium ion battery.

From Chapter two to Chapter four cathode materials are described, and Chapter two especially proposes new application such as an accumulator.

The basic thoughts of the materials are mentioned in Chapter five and Chapter six. These two Chapters are so new , then they may give a big impact to the readers.

Chapter seven and Chapter eight focus on the solid electrolyte interface, so called SEI which is important to develop high performance lithium ion batteries.

Solid state batteries are discussed in Chapter nine and Chapter ten. These batteries may show the big business chance in the future.

Las but not least, Chapter eleven explain advanced lithium ion batteries for high performance environmental vehicles.

The substantial contribution of each of the authors to this book is gratefully acknowledged, as well as their cooperation in preparing their manuscripts in the style and format selected. I also wish to express my appreciation to the companies, associations who supported the contributing authors and willingly provided their technical information and data permitted its use in this book.

January, 2009 *Kazunori Ozawa*

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1

General Concepts

Kenzo Matsuki and Kazunori Ozawa

1.1
Brief Outline of Batteries

The first practical battery is the generally known *Volta cell* (also called the *Galvanic cell*). Its invention, over two centuries ago, spawned the invention of a variety of batteries based principally on the Volta cell. However, interestingly, during the last century, only three batteries, namely, the MnO_2 primary battery and the secondary batteries of lead/acid or nickel have been in use. Knowing why such batteries continue to be used would give us some important pointers toward the development of new technology in this line. These old batteries are close to reaching their technical limit. Recently, however, new concepts have been used in the development of lithium-ion secondary batteries with higher ability.

A battery generally provides two functions – the ability to supply power over a duration of time and the ability to store power. These are defined by two operations, charge/discharge (progress of the reaction) and storage/stop (termination of the reaction), that is, a battery is a device that provides two functions, namely, energy storage and energy conversion (from chemical to electrical, and vice versa). As shown in Figure 1.1, the field of energy conversion is a multiphase system that is composed of positive/negative terminals and positive/negative active materials and electrolyte; the ions and electrons transfer through their interfaces. The interfaces reflect the nature of each phase. In addition, the state of these interfaces changes over time with the operation of the battery. The cell voltage is supported by an electric double layer with a remarkably high electric field between the electrodes and the electrolytic solution in which the electrode reactions take place. It should be emphasized that battery technology is essentially the same as the technology that controls these interfaces.

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Phase (I)		**Phase (II)**		**Phase (III)**		**Phase (IV)**		**Phase (V)**
e–	$\rightleftarrows$	e– ion	$\rightleftarrows$	ion	$\rightleftarrows$	e– ion	$\rightleftarrows$	e–
Electronic conductor		Metal electrode		Ionic conductor		Solid matrix		Electronic conductor
Negative terminal		Negative(anode) active material		Electrolyte		Positive(cathode) active material		Positive terminal

Fig. 1.1 Multilayer system composed of five phases and four interfaces.

1.1.1
Galvanic Cell System – Aqueous Electrolyte System

To understand the cell structure and its reaction, the well-known Daniel cell is schematically shown in Figure 1.2.

The two half cells of $Zn|Zn^{2+}$ and $Cu|Cu^{2+}$ are combined and a separator is placed between them so that they are not miscible with each other. The formula that shows the principle and the structure of the Daniel cell is as follows:

$$(-)\ Zn|Zn^{2+}, SO_4{}^{2-}||Cu^{2+}, SO_4{}^{2-}|Cu\ (+)$$

where the symbols | and || show the interface of different phases and the liquid–liquid junction (separator), respectively.

The cathode (positive electrode) active material of the Daniel cell is the Cu^{2+} ion in the electrolyte, while the Zn anode (negative electrode) dissolves to form the Zn^{2+} ion. The drop in voltage of the cell occurs because of self-discharge of

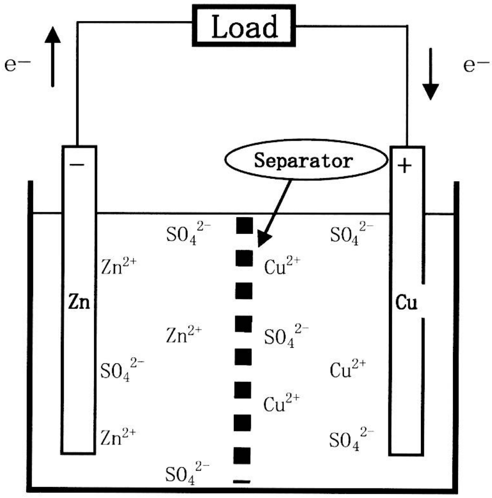

Fig. 1.2 Daniel cell.

the active materials. Generally, a self-discharge tends to occur when the dissolved chemical species such as Cu^{2+} ion are used as the cathode-active material. This is one of the reasons that the Daniel cell was not used for practical purposes.

Cathode- and anode-active materials in the Leclanche cell are MnO_2 (solid) and Zn metal, respectively. These electrode reactions are as follows:

$$\text{Cathode:}\quad 2MnO_2 + 2H^+ + 2e \longrightarrow 2MnOOH$$

$$\text{Anode:}\quad Zn + 2NH_4{}^+ \longrightarrow Zn(NH_3)_2{}^{2+} + 2H^+ + 2e$$

When the discharge reaction takes place, the Zn anode dissolves to form a complex ion. Since MnO_2 has a depolarizing ability that reduces the potential drop produced, the Leclanche type battery has been improved progressively to produce several kinds of batteries for commercial use, such as the manganese dry cell, the $ZnCl_2$ cell, and the alkaline MnO_2 cell.

In 1859, Plante invented the lead acid storage battery. This battery has been improved over the years and is now industrially mass-produced. The electrode reactions in the lead storage battery are described as follows:

$$\text{Cathode:}\quad PbO_2 + H_2SO_4 + 2H^+ + 2e = PbSO_4 + 2H_2O$$

$$\text{Anode:}\quad Pb + H_2SO_4 = PbSO_4 + 2H^+ + 2e$$

During discharge, a secondary solid phase of $PbSO_4$ is formed on both the anode and the cathode. Moreover, sulfuric acid in the aqueous solution – which is another active species – and water also participate in the charge/discharge reactions. These factors cause some polarizations that lower the cell performance.

Electrode reactions in Ni–Cd cell are as follows:

$$\text{Cathode:}\quad 2NiOOH + 2H_2O + 2e = 2Ni(OH)_2 + 2OH^-$$

$$\text{Anode:}\quad Cd + 2OH^- = Cd(OH)_2 + 2e$$

The cathode reaction involves the insertion of an H^+ ion into the solid NiOOH, which is similar to the cathode reaction of MnO_2 in the manganese battery, while the anode reaction is the formation of a secondary solid phase $Cd(OH)_2$ on the Cd anode. This prevents a smooth reaction as the Cd anode is covered with $Cd(OH)_2$.

The cathode-active material of nickel–metal hydride (Ni–MH) battery is the H species, which is adsorbed by the hydrogen-adsorbing alloy (MH) instead of the Cd anode of the Ni–Cd battery; the cell reaction is very simple because only hydrogen participates in the charge/discharge reaction. The Ni–MH battery has almost same voltage and larger electric capacity when compared with that of the Ni–Cd battery; moreover, it is free from environmental contamination. Therefore, the industrial production of Ni–MH battery has increased rapidly in recent years.

1.1.2
Lithium-Cell System – Nonaqueous Electrolyte System

To realize a battery with high potential of 3 V, batteries using lithium metal as the anode-active material and a powerful oxidizing agent as the cathode-active material were considered to be ideal. One such promising cathode-active material was MnO_2; the development of lithium battery using this commenced in 1962. Fortunately, at that time, substantial amount of basic and application data with MnO_2 was available. About 10 years later, an $Li-MnO_2$ battery with a lithium metal anode was made available by SANYO Inc.; this became the first representative primary lithium battery.

Since then, considerable research and development has taken place in the design and manufacture of rechargeable lithium batteries. Many cathode-active materials such as TiSe, NbSe, MoS_2, and MnO_2 were studied. For example, rechargeable batteries based on a lithium metal anode and a molybdenum sulfide cathode (Li insertion electrode) were developed by MOLI Energy, Inc. in 1985. This battery system was abandoned owing to safety problems. Lithium batteries based on Li metal anodes and commonly used electrolyte systems revealed the thermal runaway of these systems, which can lead to their explosion; this was almost inevitable in abuse cases such as short circuit, overheating, and overcharging. Although the highest energy density available for Li batteries is achieved by a battery system that can use Li metal anode, a solution to safety issues needs to be found.

Active materials with good reversibility for the Li intercalation/deintercalation and low charge/discharge voltage were used as anode materials instead of Li metal. A carbon material was found to meet these requirements, and a rechargeable Li battery based on a carbon anode and $LiCoO_2$ (layered lithium cobalt oxide) cathode was developed, mass-produced, and commercialized by Sony Inc. in 1991; this lithium-ion battery was capable of high performance as well as a high voltage of 4 V. As shown schematically in Figure 1.3, lithium-ion rechargeable batteries are charged and discharged through the transport of Li^+ ions between anode and cathode, with electron exchange as a result of insertion (doping) and extraction (undoping). Both anode and cathode materials are layered compounds, and, as a result, the battery reaction is very simple because only Li^+ ions participate in the charge/discharge reactions.

The features of the Li-ion batteries, compared with the other rechargeable batteries, can be summarized as follows: (i) Charge and discharge reactions

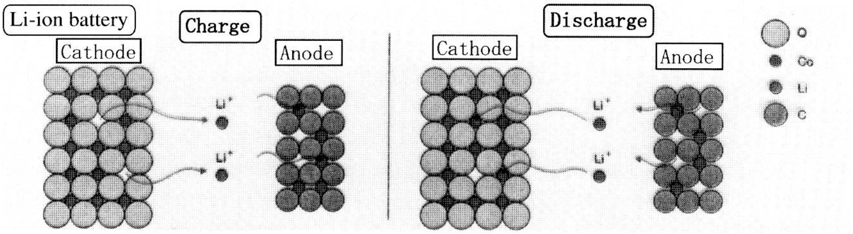

Fig. 1.3 Schematic illustration of the reaction in a lithium-ion battery.