1

General Concepts

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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

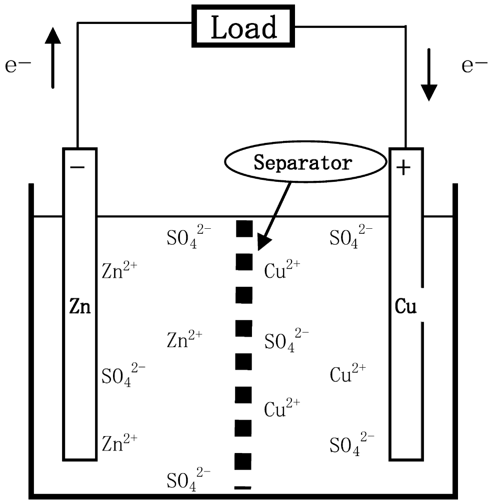

Fig. 1.2 Daniel cell.

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

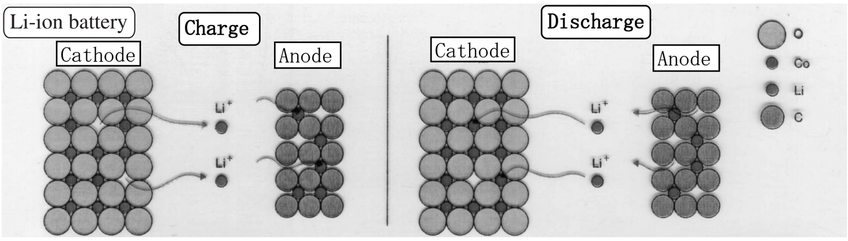

Fig. 1.3 Schematic illustration of the reaction in a lithium-ion battery.

transfer Li^+ ions between cathode and anode with minimal side reactions; (ii) The electrolytes work only as a path for the Li^+ ions; and (iii) The volume of the electrolyte between cathode and anode will not be required.

1.2
Early Development of Lithium-Ion Batteries

The UK Atomic Energy Authority showed in their patent [1] that the intercalation and deintercalation of A_x-ion of the compound $A_xM_yO_2$ reversibly occurs, where A_x is an alkaline metal and M_y is a transition metal. In 1990, Sony used this patent to first produce Li-ion batteries for a cellular phone HP-211. The cell sizes were 14500 and 20500, where 20 refers to the diameter and 50 the length in mm. The chemistry was $LiCoO_2$/soft carbon system, and the capacities of the 14500 and 20500 models were only 350 and 900 mAh, respectively. The production was on a pilot scale. However, the naming of the *lithium-ion rechargeable battery* [2] was a marketing success. It was a controversial issue whether Li existed as ion or metal in the carbon anode. By the measurement using NMR, it was revealed that some part of the Li could exist as ion [3].

The actual mass production of the lithium-ion cell was carried out for a camcorder TR-1 in 1991. The cell size was 18650, which has the same volume as the 20500 cell. The chemistry was $LiCoO_2$/hard-carbon system [4]. Figure 1.4 displays the inside structure of a 18650 cell.

The reasons for Sony's success as the first producer of lithium-ion batteries is explained in the following section.

1.2.1
Ceramics Production Capability

Sony were already one of the biggest Mn–Zn ferrites producers in Japan. They also had considerable experience in the production of $LiCoO_2$.

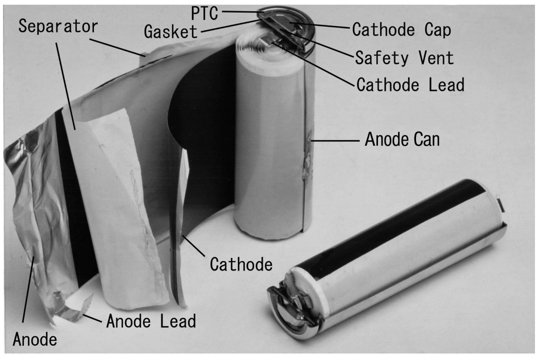

Fig. 1.4 The inside structure of a 18650 lithium-ion cell.

1.2.2
Coating Technology

Sony had been producing magnetic tapes for audio- and videotape recorders. The coating technology for magnetic tapes was very useful and very important in making cathode and anode electrodes, especially in making good slurry and performing intermittent coating.

1.2.3
$LiPF_6$ as a Salt for Electrolytes

$LiPF_6$ is unstable and easily decomposes with heat and moisture. Since the acid HF is produced in the presence of water, numerous arguments opposing the use of $LiPF_6$ were put forth in conferences and seminars. However, it was revealed that a small amount of HF increased the life cycle, because of the formation of a very strong passive layer such as AlF_3 on the surface of an aluminum cathode collector [5]. $LiPF_6$ is also easily soluble in the solvent, making it a good solid electrolyte interface (SEI) on the surface of anode materials.

1.2.4
Graphite Conductor in the Cathode

Synthesized graphite KS-15 was added as a conductor in the cathode. Since the cathode material is an oxide, which is nonconductive, a conductor has to be added. Metallic materials were also considered as conductors, but only carbon was effective for cycle performance because it acts as a reduction material giving a conductive path on the surface of the material.

1.2.5
Using Hard Carbon for the Anode

It is possible to use hard carbon and soft carbon in the form of propylene carbonate (PC) as solvent for the electrolyte. At first, soft carbon was used for the 14500 and 20500 cells, but it was changed to hard carbon in the 18650 cell after considering the float-charge stability – soft carbon is graphitizable carbon, whereas hard carbon is nongraphitizable carbon when it is heated to high temperatures of 2800–3000°C.

1.2.6
Nonwoven Shut-down Separator

Nonwoven polyethylene (PE) separators made by Tonen could be used for the 18650 cell. This separator melted at ~140°C and gave good safety results by shutting down the rush current in the case of abuse.

1.2.7
Ni-Plated Fe Can

Since the acid HF is produced inside the cell, a can should be made with stainless steel. However, the conductivity of stainless steel is so low that it is not suitable for the can, which requests low electroresistance. Ni-plated Fe can was then used for producing cylindrical cells.

After Sony's commercialization, various modifications have been made to develop advanced Li^+ ion batteries with higher energy density, retaining their good safety characteristics. These efforts achieved energy density of $200\,W\,h\,kg^{-1}$ and $500\,W\,h\,l^{-1}$, values of which would be close to those postulated earlier.

The shapes of cells have been widely expanded from cylindrical to prismatic and laminated. The applications of cells have also widely expanded from cellular phones and camcorders to laptop computers, power tools, and light electric vehicles.

Not only $LiCoO_2$ but also $LiMn_2O_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiNiAlO_2$, etc. have been developed as cathode materials.

It has become possible to use graphite for the anode by controlling the SEI layer. However, $LiPF_6$ is interestingly still preferred as a salt in the electrolyte, and components of the solvent are usually still cyclic carbonates such as PC, ethylene carbonate (EC), and linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl–methyl carbonates (EMC), and/or their combinations. Lithium-ion batteries are considered to be good in electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid vehicles. In tune with the increased and diverse applications, a strong demand for higher power density (kilowatts per kilograms) and higher energy density (kilowatt hours per kilogram) will become the target of the further research and development activities.

1.3
Toward a Realistic Goal

One of our final goals is a high-energy and high-power battery that can replace the lead/acid battery of automobiles satisfying EU RoHS (EU Directive: Restrictions on Hazardous Substances) instructions. To realize lead-free accumulators (engine starters), it is important to study the materials from their basic properties. Lithium insertion materials without the destruction core structures, called *topotactic reactions*, are classified into three categories:

1. Layer structure: $LiCoO_2$, $LiNiO_2$, $LiNi_{1/2}Mn_{1/2}O_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, $LiAl_{0.05}Co_{0.15}Ni_{0.8}O_2$, etc. [6];
2. Spinel-frame work structure: $LiMn_2O_4$, $Li[Ni_{1/2}Mn_{3/2}]O_4$, LiV_2O_4, $Li[Li_{1/3}Ti_{5/3}]O_4$, etc. [7, 8];
3. Olivine structure: $LiFePO_4$, $LiMnPO_4$, $LiCoPO_4$, etc. [9].

Table 1.1 Redox Potential.

Electrode reaction	E^0 (V)	Electrode reaction	E^0 (V)
$Li^+ + e \rightleftarrows Li$	−3.01	$Co^{2+} + 2e \rightleftarrows Co$	−0.27
$K^+ + e \rightleftarrows K$	−2.92	$Ni^{2+} + 2e \rightleftarrows Ni$	−0.23
$Ba^{2+} + 2e \rightleftarrows Ba$	−2.92	$Sn^{2+} + 2e \rightleftarrows Sn$	−0.14
$Sr^{2+} + 2e \rightleftarrows Sr$	−2.89	$Pb^{2+} + 2e \rightleftarrows Pb$	−0.13
$Na^+ + e \rightleftarrows Na$	−2.71	$H^+ + e \rightleftarrows 1/2H_2$	0.00
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.38	$Cu^{2+} + 2e \rightleftarrows Cu$	0.34
$Ti^{2+} + 2e \rightleftarrows Ti$	−1.75	$Cu^+ + e \rightleftarrows Cu$	0.52
$Al^{3+} + 3e \rightleftarrows Al$	−1.66	$Ag^+ + e \rightleftarrows Ag$	0.80
$Mn^{2+} + 2e \rightleftarrows Mn$	1.05	$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.23
$Zn^{2+} + 2e \rightleftarrows Zn$	−0.76	$Cl_2 + 2e \rightleftarrows 2Cl^-$	1.36
$Fe^{2+} + 2e \rightleftarrows Fe$	−0.44	$F_2 + 2e \rightleftarrows 2F^-$	2.87

$LiMn_2O_4$ is a very attractive material as a cathode, but is reported to have a poor cycle performance. Measurement of the entropy of lithiation may indicate a solution [10], which is described in Chapter 5. Olivine structure, also called *chrysoberyl structure*, has a space group system of Pnma and shows excellent stability, but very low electric conductivity.

As for an accumulator of a consumer car, the battery has to have very high energy that resists overdischarging during parking. For the higher energy density, the species that have the biggest redox potential should be considered. The term *redox* is obtained from a contraction of the words *reduction* and *oxidation*. Table 1.1 shows the standard potentials of electrode reaction at room temperature. Lithium has the maximum potential on the negative side, and fluorine has the maximum on the positive side. These suggest our future target.

It is also necessary to consider the fact that the key elements of lithium-ion batteries are facing the crisis of exhaustion. Co metal used for the cathode has been in great shortage for quite some time. Element resources in the earth were estimated as the Clarke number, which was presented about 80 years ago. These values are not fully accepted, but they suggest our standpoint.

Focusing on the transition metals, they are ranked as follows in weight:

$$Fe > Ti > Mn > Cr > V > Ni > Cu > \cdots$$

Lithium-ion batteries are still one of the most promising storage devices. To realize the ideal battery, further development efforts are continuing all over the world.

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