

Development of Materials for Mobile-use Lithium-ion Batteries and Fuel Cells

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OVERVIEW: As regards the expansion of “ubiquitous networks,” as the functionality of mobile information devices improves, the power source of such devices must also be improved. At present, to boost the performance of the lithium-ion battery commonly used today, new technical innovations regarding anode and cathode materials are necessary. In accordance with these needs, Hitachi is engaged in development and commercialization of next-generation lithium-ion- and lead-acid-battery systems as well as boosting the capacity of the flat-type lithium-ion battery used in mobile phones. Furthermore, aiming to develop a next-generation power source for mobile information terminals, we are speeding up the development of direct methanol fuel cell while developing new innovative materials that will underpin these new batteries.

INTRODUCTION

IN regards to the growth of “ubiquitous networks” for supporting the information society of the 21st century, evolution of mobile-use batteries for powering mobile hand-held terminals is indispensable—and growing more so all the time. These days, as the power source for mobile hand-held terminals, lightweight lithium-ion batteries are popular, and their capacity has been improved by about 10% per year. Applying our successful achievements over many years, Hitachi, Ltd., Shin-Kobe Electric Machinery Co., Ltd., and Hitachi Vehicle Energy, Ltd. have continued to develop and commercialize next-generation lithium-ion- and lead-acid-battery systems. As for the field of batteries for mobile terminals, Hitachi Maxell, Ltd. is practically

applying flat-type lithium-ion batteries in mobile phones and presently engaged in boosting the capacity of these batteries. Furthermore, aiming to develop the power source for the next generation of mobile hand-held terminals, Hitachi—working in collaboration with other Hitachi Group companies—is speeding up the development of the direct methanol fuel cell. In the meantime, regarding the materials that underpin these devices, Hitachi including Hitachi Chemical Co., Ltd., Hitachi Cable, Ltd., and Hitachi Metals, Ltd. are coming up with technical innovations based on achievements gained while developing from materials for lithium-ion and direct methanol fuel cells (see Fig. 1).

The rest of this paper first gives a taste of the

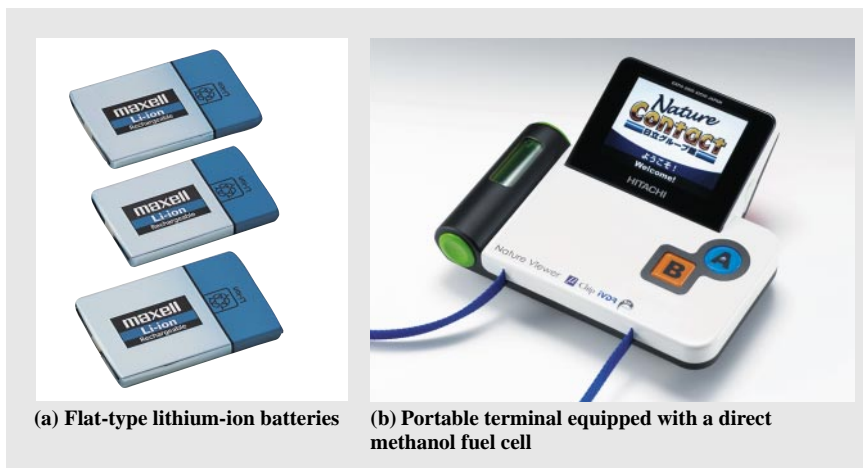


Fig. 1—(a) Flat-type Lithium-ion Battery for Mobile Phones Commercialized by Hitachi Maxell, Ltd.; (b) Portable Terminal Equipped with a Direct Methanol Fuel Cell Jointly Developed by Hitachi Group Companies. As regards the power source for mobile phone, development of next-generation batteries that have long usage times is being strongly demanded. Accordingly, Hitachi is driving the development of next-generation of materials that are vital for the development of high-performance batteries.

battery-material technologies being developed at Hitachi Group companies, and then describes a direct methanol fuel cell we have developed as a next-generation power source.

LITHIUM-ION BATTERIES

Principle and Problems Regarding Lithium-ion Batteries

The principle of lithium-ion batteries is that lithium ions are exchanged through a porous separator—which is installed between the cathode and anode. In this way, the electrical energy thus generated can be charged or discharged (see Fig. 2). In the case of the current 4-V lithium-ion battery marketed as a power source for mobile devices, the main components are a cathode comprising laminated LiCoO_2 , an anode made of graphite (carbon), and an organic solvent that acts as the medium for lithium-ion transport. In the case of a lithium-ion battery as the main power source, to attain long-term driving of mobile devices, high durability and stability—in conjunction with increased capacity—are also important requirements. Accordingly, in meeting these requirements, the main challenge is continuously innovating new materials. At present, by applying a new cathode structure of laminated manganese and a new anode made of graphite, we expect the improvement in battery performance to continue.

Manganese-nickel-laminated Superstructure Electrode and Electrical Characteristics

As an alternative to LiCoO_2 used as the standard cathode in lithium-ion batteries, materials such as LiMn_2O_4 (with a spinal structure) and laminated $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ (with nickel as the main component) have been proposed. These materials, however, have not yet been able to provide satisfactory battery performance in terms of capacity, durability, and stability.

In recent years, as a cathode material providing high capacity with high durability and stability, laminated MnNi, namely, $\text{Li}(\text{Co}_{\frac{1}{3}}\text{Ni}_{\frac{1}{3}}\text{Mn}_{\frac{1}{3}})\text{O}_2$, has been drawing attention. It has been reported that this material has a superstructure composed of trivalent cobalt, bivalent nickel, and quadrivalent manganese⁽¹⁾ (see Fig. 3). To evaluate the applicability of this material to batteries, which metal ions contribute to the charge and discharge reactions was analyzed by *ex-situ* X-ray absorption spectroscopy. The results of this analysis demonstrated that the main valence change comes about at the nickel ions, thereby creating the charge and discharge

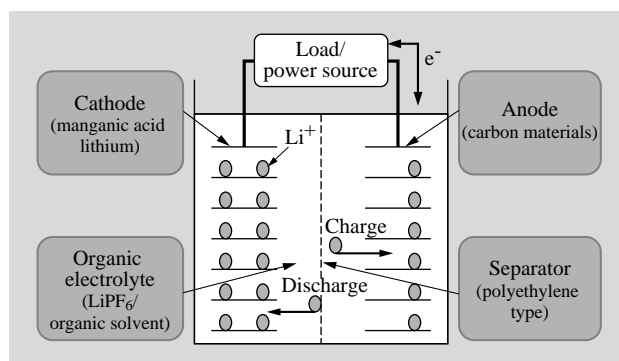


Fig. 2—Principle of Lithium-ion Battery.

In the case of a lithium-ion battery, with an organic electrolyte as a medium, lithium ions in the crystals of the positive electrode are exchanged across a separator (comprising fine pores of several microns) to the negative electrode, thereby generating a high voltage close to 4 V.

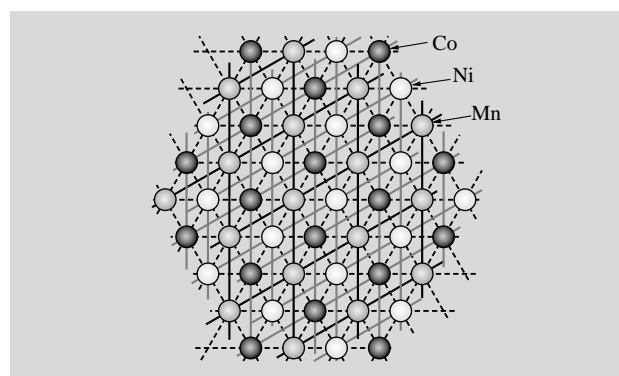


Fig. 3—Triangular Lattice Arrangement of Manganese, Nickel, and Cobalt on Metal Sheet with $\text{Li}(\text{Co}_{\frac{1}{3}}\text{Ni}_{\frac{1}{3}}\text{Mn}_{\frac{1}{3}})\text{O}_2$ Configuration Like Rock Salt.

The laminated MnNi cathode material has a superstructure with trivalent cobalt, bivalent nickel, and quadrivalent manganese regularly lined up in the solid phase, thus forming a chemical compound with high structural stability and thermostability.

functions⁽²⁾. Moreover, in the case of this material composition, the binding of manganese and oxygen ions is stable, so the whole structure is also stable. Charging up to a higher electric potential than with a conventional lithium-ion battery is therefore possible. The above-described laminated MnNi structure is, accordingly, expected to be applied as a next-generation cathode. Of a lithium-ion battery utilizing this structure, the discharge curve for a flat “043450”-type battery (4-mm thick, 34-mm wide, 50-mm long) is shown in Fig. 4. Compared to a conventional battery (which can be charged up to 4.2 V), the developed lithium-ion battery with a laminated MnNi cathode can be charged up to 4.4 V; in other words, battery

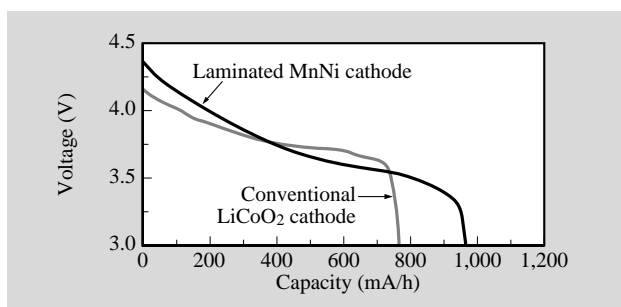


Fig. 4—Discharge Profile of High-voltage Lithium-ion Battery with Laminated MnNi Cathode (voltage range: 3–4.4 V; current density: 0.5 C).

As for a lithium-ion battery with a laminated MnNi cathode, to increase the charge voltage above that used up till now, battery capacity can be increased by about 10%.

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To sum up, it is expected that the MnNi cathode with the above-described superstructure will play a major part in further boosting the capacity of future lithium-ion batteries.

High-capacity Graphite Anode

Since the launch of the lithium-ion battery in 1990, most batteries have used carbon-based anodes. At first, low crystallinity carbon-based materials were used because of their stability⁽³⁾. With recent demands for long operating time and compactness regarding portable electronic terminals, graphite carbon materials—with high energy density produced at higher voltage—have become mainstream. Graphite has a crystal structure built up of many layers of carbon atoms that are regularly lined up on a hexagonal mesh. This structure charges and discharges when lithium ions are inserted between these layers and desorbed. Lithium is inserted into the graphite, and the theoretical capacity of the LiC_6 compound generated between the graphite and lithium layers is 372 Ah/kg, which contributes to battery capacity. This theoretical capacity applies to the case of a perfect crystal; however, with graphite produced industrially, to attain high capacity, how close the crystallinity (i.e. degree of graphitization) gets to the theoretical value is an important point⁽⁴⁾. During the initial development stages, discharge capacity was approximately 300 to 330 Ah/kg, and artificial spherical graphite (called meso-carbon micro beads) was used (since they are easy to apply as an electrode). In the meantime, natural graphite—which has a crystallinity close to the theoretical one—attained a discharge capacity close to the theoretical value of 365 Ah/kg. During discharge

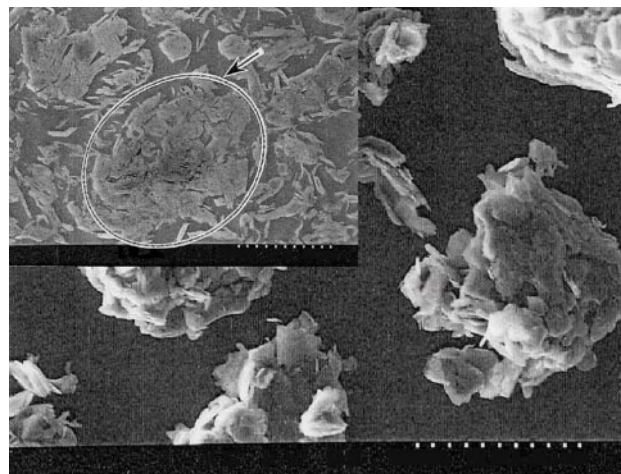


Fig. 5—Grain Structure of Hitachi's Artificial Graphite: Quasi-isotropic Grain Structure.

Hitachi's artificial graphite has a structure in which compressed graphite crystals within its grains are isotropically lined up. This structure produces high performance characteristics of high capacity and rapid charging.

of a large current, however, it is a problem that capacity decreases; thus, natural-graphite anodes are unsuitable for practical applications. As a consequence, the appearance of graphite anodes with excellent durability and crystallinity equal to that of natural graphite has been much hoped for.

Aiming to produce an anode that satisfies these hopes, Hitachi Chemical Co., Ltd. has developed an artificial graphite (see Fig. 5). In its grain structure, highly graphitized, fine planar grains are randomly located, and a great amount of fine pores are distributed between the grains. As a result of this structure, permeability of an electrolyte between the grains is higher than that in the case of normal graphite grains. This leads to a characteristic high-efficiency insertion and desorption of lithium ions. It can therefore be said that Hitachi's artificial graphite well suited as an anode material in the case of large current discharge—which requires instantaneous movement of lithium ions. Moreover, the planar graphite within its grains has a crystallinity close to a perfect crystal, so the discharge current of 362 Ah/kg is close to the theoretical value for graphite, i.e. 372 Ah/kg. With such a high capacity, Hitachi's artificial graphite (which is capable of handling a large current discharge) is highly rated as an anode material for the lithium-ion batteries used in increasingly power-hungry, high-performance mobile devices. It has, consequently, grabbed a 40% share of the world market for these devices.

As for an graphite anode, it has become

indispensable to surpass the theoretical discharge capacity of 372 Ah/kg. Accordingly, as alternative anodes, metallic materials like silicon and tin are being actively developed. Although the twofold increase in initial charging capacity of these materials compared to graphite looks promising, their durability falls short of that of graphite. Accordingly, though they have found limited applications, it will be some time before their full-blown application. As a consequence, it is considered that the graphite anode era will continue for a few more years yet. This means that as opposed to improving the anode elemental substance alone, the cathode and electrolyte are combined with the anode in the above-described manner, thereby improving the graphite in such a way that increase capacity of the battery.

DIRECT METHANOL FUEL CELL

The direct methanol fuel cell^(5, 6) is expected to become the power source underpinning the “ubiquitous information society.” Its principle is shown in Fig. 6. Protons are generated by a catalytic oxidation reaction of methanol in aqueous solution, and then transported to the opposite electrode via a proton exchange membrane (i.e. an electrolyte membrane). They are combined with oxygen in the air to form water. This generation of water thereby produces electricity that can be drawn off.

Lithium-ion batteries are widely used as the power source of mobile devices. The scope to increase their capacity, however, has reached its saturation point. The energy densities of various kinds of batteries are shown in Fig. 7. Compared to conventional rechargeable batteries like nickel-metal-hydride cells and the previously described lithium-ion cells, direct methanol fuel cells provide a considerably high energy density, and have the potential for exponential increases. Accordingly, the direct methanol fuel cell has attracted much attention as a new power source for mobile devices. The main material of the direct methanol fuel cell is “MEA (membrane-electrode assembly)” consisting of an electrolyte membrane and catalyst electrode.

The key issue for mounting the direct methanol fuel cell in a mobile information terminal is “miniaturization.” That is to say, at Hitachi, by means of a flat arrangement (i.e. laying out the multiple cells in planes), we have developed a thin fuel cell that can be installed on the backside of a mobile terminal (see Fig. 8). Moreover, in regards to methanol supply and air supply/gas discharge, precisely designing the liquid

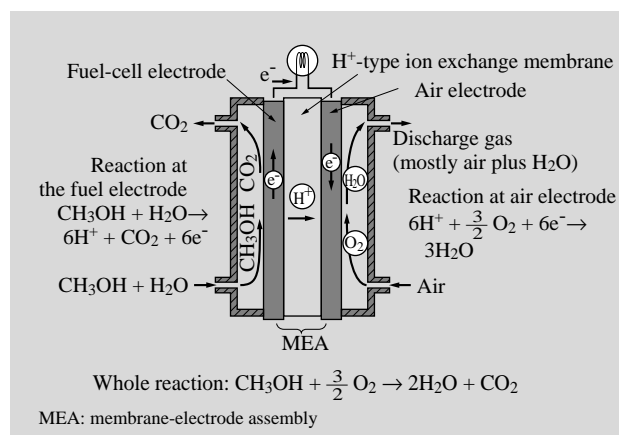


Fig. 6—Operating Principle and Structural Overview of Direct Methanol Fuel Cell.

In the case of direct methanol fuel cell, at the fuel-cell electrode, methanol is oxidized, and the thus generated hydrogen ions are transported to the air electrode via the electrolyte. At the air electrode, they are combined with oxygen, and the generation of water there produces electricity.

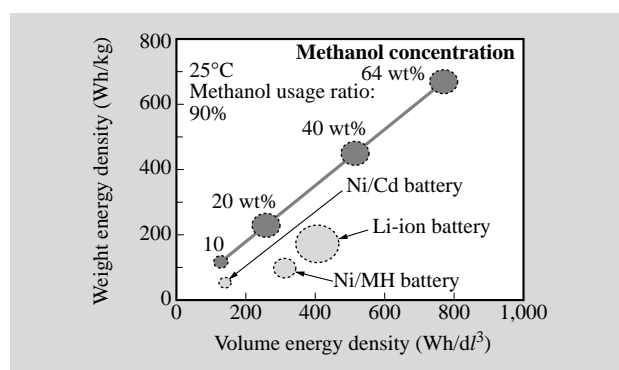


Fig. 7—Energy Density of Direct Methanol Fuel Cell in Comparison with Conventional Cells.

The direct methanol fuel cell is a possible next-generation power source with considerably higher energy density than rechargeable batteries.

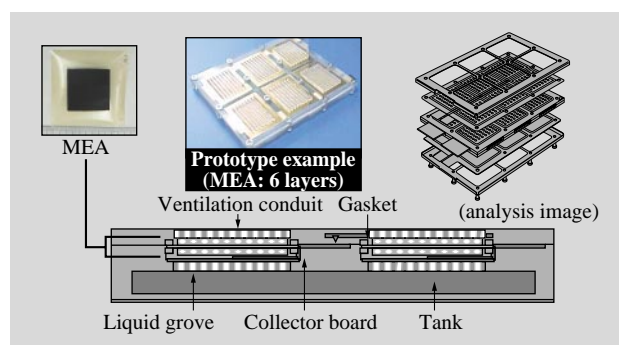


Fig. 8—Example Structure of Direct Methanol Fuel Cell. At Hitachi, in the fuel cell we are developing, the multiple electrodes are laid out in planes, and the battery is structured so that fuel from the tank can be efficiently drawn up.

groves and air-ventilation conduit enables fuel take-up and air supply/exhaust-gas discharge to be done on their accord. An example of a direct methanol fuel cell mounted in a laptop PC is shown in Fig. 9. As regards the methanol supply, in this example, a cartridge-type system enables continuous operation by means of simply replacing the cartridge.

From now onwards, starting with cost reduction, we aim to improve compactness, reliability, and performance of this direct methanol fuel cell in order to bring the battery to full commercial operation as quickly as possible.

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Fig. 9—Example of Mounted Direct Methanol Fuel Cell. External appearance of direct methanol fuel cell mounted on the backside of the display of a laptop PC is shown. As regards refuelling the battery, a cartridge in the top part of the display back face can be simply replaced.

“solution technologies” such as the ones described in this paper.

CONCLUSIONS

This paper first summarized the battery-material technology being developed by Hitachi, and then described a direct methanol fuel cell currently under development as a next-generation power source.

As we greet the era of “ubiquitous networks”—through advances in information technology and mobile-terminal performance—increasing the performance of power sources will be called into question more than ever. Aiming at an era in which “any time, any place” information and energy are freely available, Hitachi—as a “total supplier” of electrical systems—will push forward the development of new

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