

# Development Trend of Rechargeable Nickel-Metal Hydride Battery for Replacement of Dry Cell

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## Abstract

This paper presents overview of the development of the nickel-metal hydride (Ni-MH) battery to replace dry cells. The new development concept for breaking away from the higher-capacity competition has led to create ultra-fast 15-minute charging Ni-MH battery and ultra-low self-discharge Ni-MH battery. As a recent trend, Ni-MH battery has appeared on the market as environment friendly secondary battery which takes the place of disposable dry cell. Inherently safe and durable Ni-MH battery will win much greater acceptance in a cyclical society.

*Key words*: Ni-MH battery; Dry cell replacement; Self-discharge; Fast charge; Rare earth-Mg-Ni alloy

## 1 Introduction

Some years have passed since people began saying that the 21st century is the environmental and new-energy era, and in terms of real-world events the imbalance and disruption of energy supply and demand, which have arisen in conjunction with the Iraq War and rapid economic growth in China, have triggered awareness even among the general populace that energy problems are their own problems, too, as seen in skyrocketing gasoline prices around the world. In addition, although the current situation is one of pollution and inefficient heavy energy consumption owing to the economic growth particularly in China, there is an emerging orientation toward a cyclical society with recycling instead of discarding

even at the level of individuals, and this is also manifested in trend in the personal consumption market.

This is a trend of note also to those who develop new products, and they have adopted a product strategy which emphasizes "environmental friendliness", "energy conservation", and "recycling". As a recent similar trend in the battery industry, Ni-MH battery that is compatible with disposal dry cell as well as Ni-Cd battery has appeared on the market with a new image as "environment-friendly" secondary cells. This article focuses mainly on the technical aspects of rechargeable Ni-MH battery for dry cell replacement.

## 2 Background of dry cell replacement

As a rule, primary and secondary batteries have not previously intruded into each other's territory, but recently the latter battery has been put on the mar-

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ket as the former one replacement. It appears that behind this is the widening group of products such as digital cameras, MP3 players, and PDAs in which both type batteries can be used as well as changes in the environmental consciousness of individual consumers.

In response to high-drain loads the development of primary battery has proceeded from manganese dry cell to alkaline dry cells including nickel type cell, but a limit has been reached in terms of both performance and cost, and they are still single-use disposable batteries.

Sales of Ni-MH battery has slumped due to the rapid growth of lithium ion battery (LIB) since 2000, and although they have begun to experience some growth in high-power applications such as HEVs, there has been a great need for the development of new product based on a new concept, in particular something other than "higher capacity", which has been the focus in the commercial sale and resale areas.

For these reasons attention is focused on the development of Ni-MH battery using a totally new concept whose appeal involves taking advantage of the compatibility with various types of dry cells from the points of view of same shape and voltage that is lacking in lithium ion batteries, adding the ability to recharge and use repeatedly, which is an intrinsic distinctive characteristic of secondary battery, and the convenience is equal to that of dry cells (instant use anytime). As indicated in Table 1, the main advantage of dry cells except cost is its capacity retention characteristic which is much higher than that of a conventional type Ni-MH battery. In other words, the disadvantage of Ni-MH battery is its relatively high

self-discharge rate.

Citing dry cell substitutability, we started with the sale of ultra-fast 15-minute charging Ni-MH battery with Rayovac in 2002, and ultra-low self-discharge type one was commercialized and put on the market with Matsushita Battery Industry early in 2006.

### 3 Two approaches to dry cell replacement

To claim that Ni-MH battery is capable for the dry cell replacement, the battery absolutely must have the convenience to be used immediately at any time that is the biggest characteristic of dry cell. The two technical approaches are inevitable to attain the characteristic, as shown in Fig. 1. One is shortening charging time, and the other is reducing self-discharge. These are two sides of the same coin, and there is a

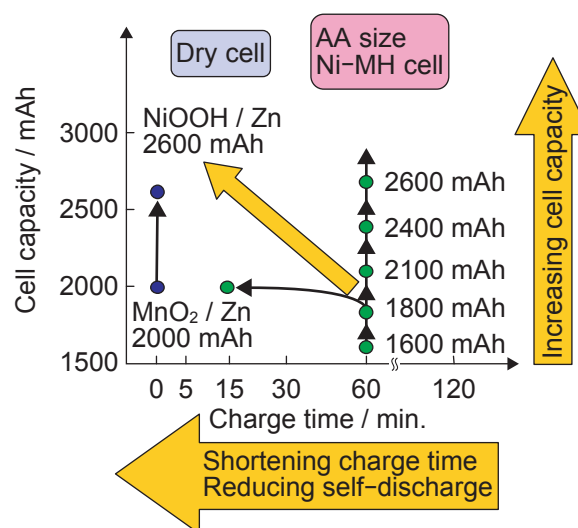


Fig. 1 Two approaches to dry cell replacement by Ni-MH battery.

Table 1 The advantage and disadvantage inherent in Ni-MH battery for dry cell replacement.

AA size cell	Alkaline dry cell	Nickel type dry cell	Ni-MH (Conventional type)	Lithium ion battery
Compatibility with dry cells (Operation voltage / V)	— (1.5)	— (1.5)	Appropriate (1.2)	Inappropriate (3.5)
Capacity / mAh	ca. 2000	ca. 2000	ca. 1600-2600	ca. 800
High rate discharge	Poor	Good	Very good	Very good
Charge by large current (Fast charging)	Impossible	Impossible	Good	Very good
Capacity retention (Self-discharge)	Very good	Very good	Poor	Very good
Cycle life / cycles	1*	1*	ca. 500	ca. 300

\* Only one time use

conflict between solving the technical challenges. In terms of battery capacity, an AA size dry cell provides 2000 – 2500 mAh, and the same size Ni-MH battery has, thanks to competition to increase capacity, attained the same level.

#### 4 Improving fast-charge performance (Creating batteries for ultra-fast 15-minute charging)

When dry cell is spent, one has only to replace it with new cell purchased beforehand (no recharge time is needed), but secondary battery is used by recharging it in a charger. The key to making it as convenient as dry cell is therefore how to shorten charging time, but developers faced a technical barrier in that system with external control (such as  $\Delta V$  or  $\Delta T$  cutoff) using the usual battery parameters (battery voltage and temperature). The limit is a 1- to 2-C rate charge (30- to 60-minute charge), so that charging at large currents greater than that brings about a rapid temperature increase and the detection of  $\Delta V$  itself cannot be done, making stable charging control impossible. The charging control is more difficult especially with high-capacity type Ni-MH battery due to its design.

As one challenge, we developed together with Rayovac an ultra-fast 15-minute charging Ni-MH battery based on an "old but new" concept for the first time in the world, and put it on the North American market in 2002. Technical characteristics of this battery are charging control by the battery itself and its design (a new material technology) which makes this possible.<sup>1,2)</sup> The direct parameter which tells whether charging is complete is the battery's own internal pressure, but when using commercially available batteries, the internal pressure cannot be simply measured externally as voltage and temperature can, and therefore until now it could not be used as a charging control parameter even if so desired.

However, this problem was solved by building the internal pressure control function into the battery itself. Specifically, a pressure-operated switch mechanism was built into the positive electrode head. Fig. 2 shows the principle of the charging control by using

a cell pressure-operated switch vent. When internal cell pressure reaches the prescribed value at the end of charging, the built-in switch is activated and closes the current path. Because each individual battery controls charging with its own internal pressure, this simplifies the charger itself, and makes constant-voltage charging possible. Although this idea for a pressure switch control mechanism is nothing new, its actual use in dry cell-like battery and the marketing are new.

Of course essential for bringing this about is technology to increase large-current charging efficiency, and especially important are limiting the rise in battery temperature when a large current is flowing (such as by decreasing internal battery resistance) and limiting the decline in charging efficiency which it brings about, but this article will discuss only heavy rare earth additive technology, which relates also to the ultra-low self-discharge battery described below.

Ni-MH battery is composed of a nickel positive electrode (NiOOH), a polymeric separator (hydrophilic polypropylene non-woven cloth), electrolyte solution (mainly KOH solution) and a negative metal-hydride electrode (hydrogen storage alloys) in a sealed case. The sharp drop in Ni-MH battery charging efficiency at high temperature is due to the decline in oxygen overpotential of the nickel positive electrode, and it is a well-known fact that adding oxides of lanthanoid heavy rare earths such as Er, Tm, Yb, and Lu effectively prevents this (See Fig. 3). It is also effective for charge acceptance when charging with a large cur-

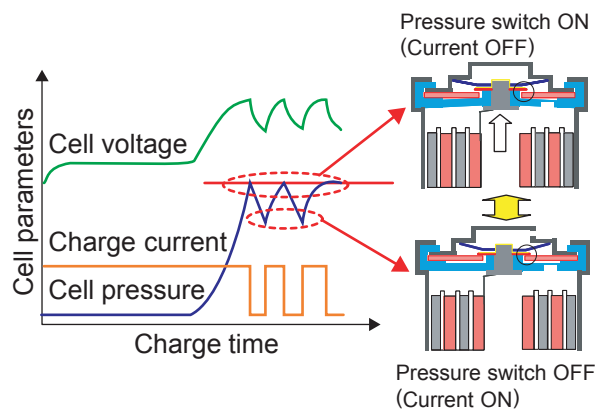


Fig. 2 Schematic model of cell pressure-operated switch control.

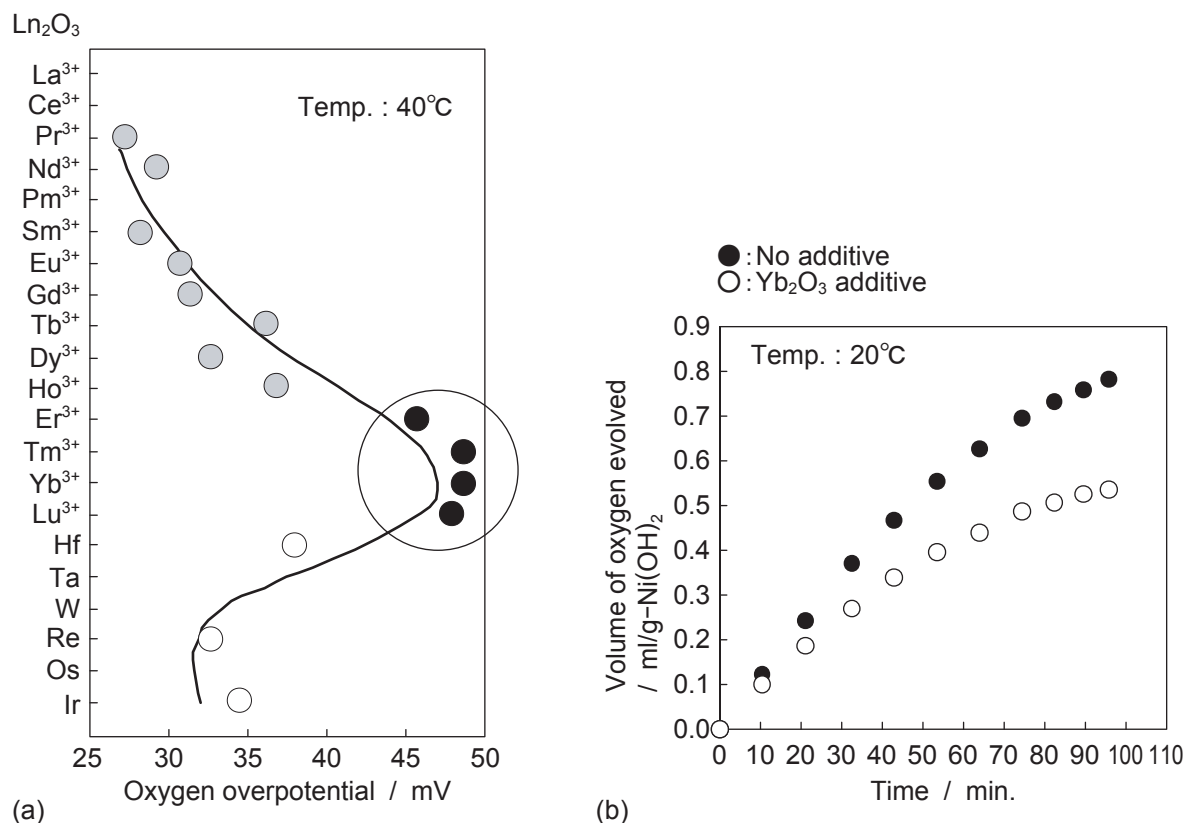


Fig. 3 Effect of heavy rare earth oxides on oxygen overpotential (a) and self-discharge reaction with water (b) of nickel hydroxide positive electrodes.

rent, making capacity of at least 90% possible even in a 10- or 15-minute ultra-fast charge.

## 5 Improving capacity retention (Creating an ultra-low self-discharge battery)

Dry cells (primary batteries) are of course characterized by high capacity retention. In sealed Ni-MH battery, the hydrogen (H) in the hydrogen storage alloy of negative active material has gas-solid contact directly in the form of hydrogen gas with the positive active material NiOOH. For this reason Ni-MH battery is grouped into larger self-discharge batteries, compared with Ni-Cd and lithium ion battery. This reduction in self-discharge had been a technical challenge from the outset.

An effective approach to reduce the self-discharge in Ni-MH battery is to inhibit: (1) reduction reaction of NiOOH by hydrogen described above; (2) reduction reaction of NiOOH by water accompanied with oxygen evolution; or (3) shuttle reactions of impurity

ions from the separator and both active materials. Subsequent improvements in both positive and negative active material components (impurity ions removal, lower hydrogen equilibrium pressure, surface treatment of AB<sub>5</sub> alloys, etc.) and advancements in separator materials (nitrogen removal, addition of an ion trap function, etc.) have currently raised the level at least up to that of Ni-Cd battery. However, high-capacity type batteries still tend to have large self-discharge that is inevitable due to the battery design.

Another technological interest to the positive electrode is the improvement of charging efficiency by adding oxides of Er, Yb, and other heavy rare earth elements as noted above. Their addition also suppresses the self-discharge of positive active material accompanied with oxygen evolution from water ( $2\text{NiOOH} + \text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + 1/2\text{O}_2$ ), as shown in Fig. 3. It means that these additives are also effective against battery self-discharge. Further, if the negative electrode uses some kinds of Mn-free rare earth-Mg-Ni alloys, which will be discussed below,

there is an improvement especially in high-temperature capacity retention. Optimizing these constituent materials made a reality of Ni-MH battery with stable capacity retention over a broad temperature range.

Application of these existing and new technologies for suppressing self-discharge<sup>3-7)</sup> has enabled us to develop the extremely low self-discharge Ni-MH battery for replacing dry cells. Two types of newly developed cell are depicted in Fig. 4. Comparative results of capacity retention characteristics for these cells and dry cells are shown in Fig. 5. Even after six months to a year after charging, they still maintain ca. 80% of their capacity, and are available for instant use just as dry cell is. Fig. 6 shows the test results in shot numbers of the practical use in digital cameras mounted with the developed Ni-MH battery and alkaline dry cells. Shot numbers were remarkably increased by using Ni-MH battery compared with alkaline dry cells after full charging, because of relative large current in digital camera's use. This advantage of the ultra-low self-discharge type Ni-MH battery over alkaline dry cells was kept even when stored in a charged state for one year.

Therefore as with dry cell, even if the battery in a device is spent, one can replace it with battery purchased beforehand, which will have plenty of capacity left even if stored for a long time, and available for instant use. Users can recharge spent battery and keep it on hand, and chargers are to be inexpensive because there is no need any more for fast charging.

Now that Ni-MH battery can replace dry cell, the ultra-low self-discharge approach is, paradoxically speaking, the same as the zero charging time, i.e., ultra-fast charging approach.

### 6 Improving battery capacity (Creating large-capacity batteries)

Ni-MH battery's capacity is limited by the nickel positive electrode. Capacity leveled off after a substantial boost achieved by using developed high-density spherical nickel hydroxide particles that serve as the positive active material for pasted type nickel electrodes, but during the last few years battery



Fig. 4 Newly developed ultra-low self-discharge type Ni-MH cells.

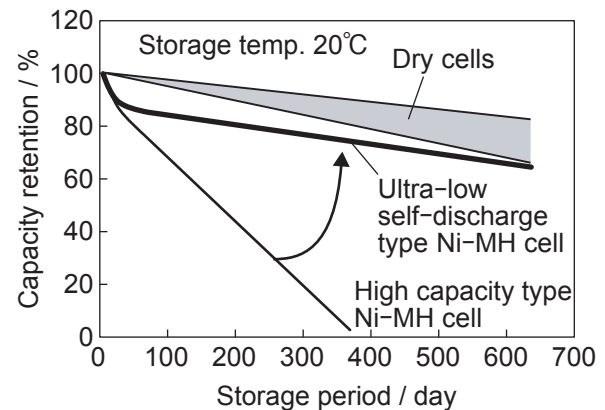


Fig. 5 Improvement of capacity retention in Ni-MH battery compared with dry cells.

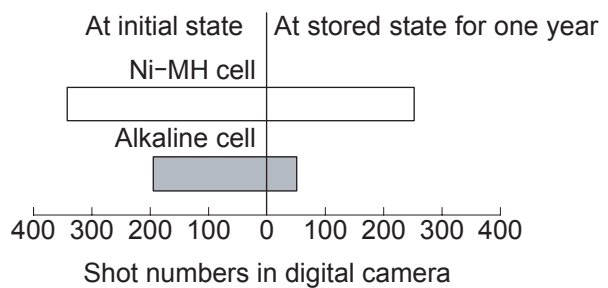


Fig. 6 Test results in shot numbers of digital cameras mounted with ultra-low self-discharge type Ni-MH battery compared with alkaline dry cells.

makers have engaged in fierce, perhaps even strained, competition to squeeze out higher capacity<sup>5,8,9)</sup> as shown in Fig. 7. This has raised capacity in AA cells to 2700 mAh (ca. 400 Wh/l), but in some ways this has sacrificed some of the original characteristics of secondary battery such as cycle life, which has led to

the above-described dry cell-replacement program that serves as the new development concept for breaking away from the higher-capacity program.

On the other hand, competition over raising capacity resulted in development of new high-capacity type

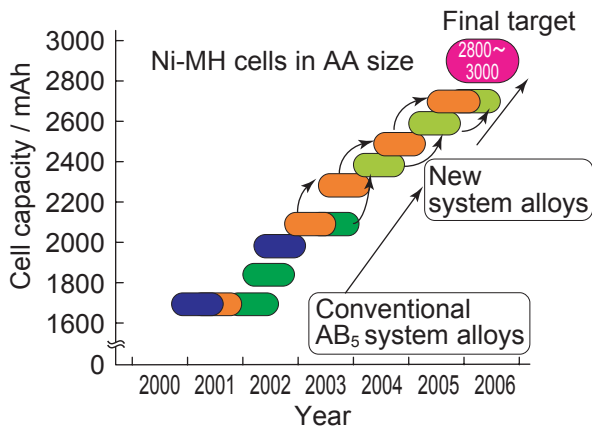


Fig. 7 Competition between battery makers to pursue higher capacity in Ni-MH batteries during the last several years.

alloys other than LaNi<sub>5</sub>-based alloy (AB<sub>5</sub> type) for negative electrodes<sup>10-15)</sup> and in production technology improvements. These achievements were used advantageously in the materials and design of Ni-MH battery that replaces dry cell.

Let's take a brief look at rare earth-Mg-Ni-based alloys with poly-phase intergrowth structures. Conventional AB<sub>5</sub> alloys have actual capacity no higher than ca. 300 mAh/g, which corresponds to 2400 mAh in AA batteries. Further increasing capacity requires high-capacity alloys of at least 350 mAh/g. A candidate is the rare earth-Mg-Ni-based alloys (AB<sub>x</sub> system), and alloys with certain compositions and single-phase structures have been brought into practical use. Moreover, these system alloys offer a variety of possibilities for new poly-phase intergrowth structures, because they can be present in diverse crystal structures which stack n layers AB<sub>5</sub> units/1 layer AB<sub>2</sub> unit as shown in Fig. 8. For example, even a slight change in composition results in a drastic

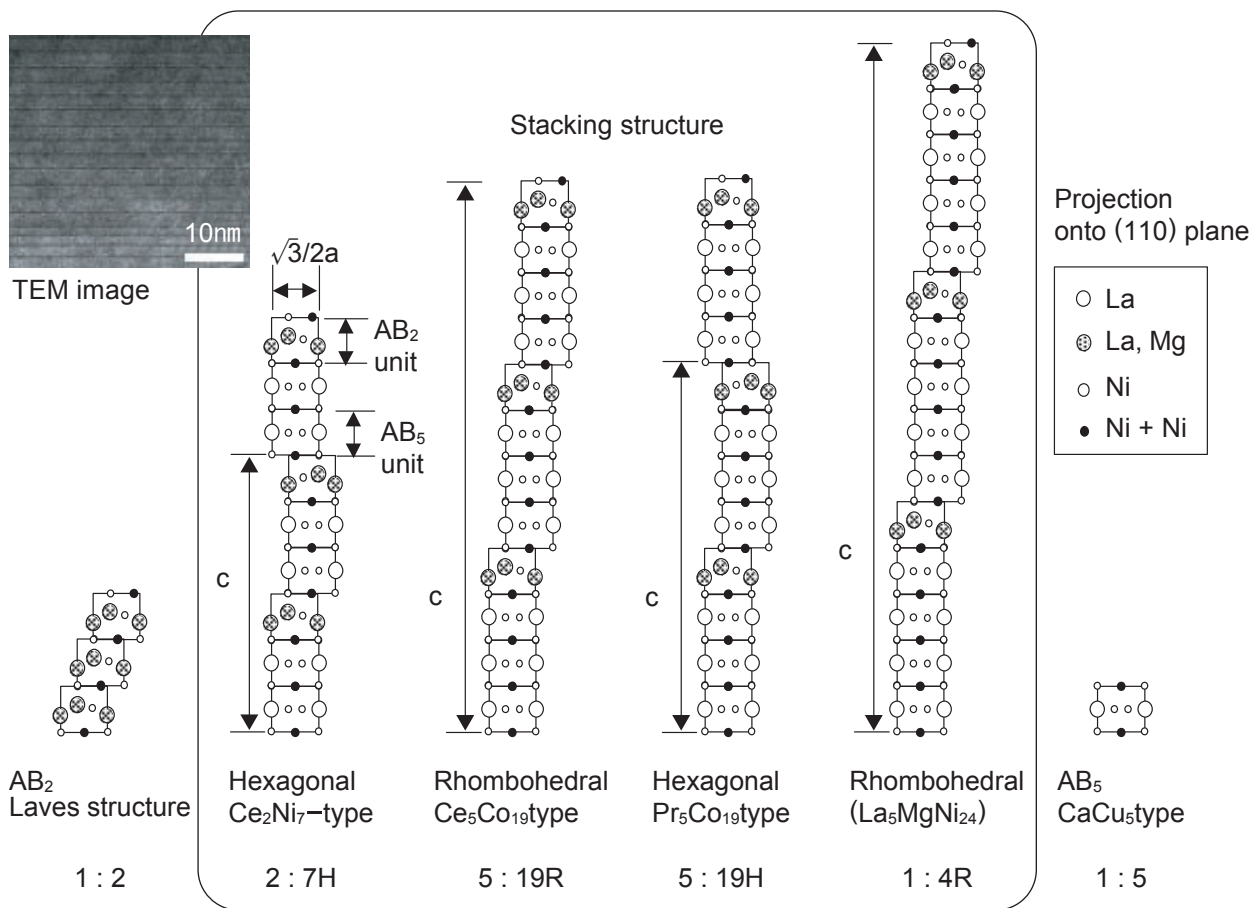


Fig. 8 Crystal structures in rare earth-Mg-Ni alloys.

change in phase abundance, and therefore a change in discharge capacity, which is dependent on both crystal structure and phase abundance. It was found that certain alloys co-existing with several different layer structures in the same grain are suited for high-capacity type Ni-MH battery. An alloy whose main phase is the  $\text{Pr}_5\text{Co}_{19}$  structure phase, a hexagonal system (5 : 19H phase), yielded a large discharge capacity of 350 mAh/g. In Ni-MH battery employing these alloys, they contributed not only to higher capacity, but also to better low-temperature discharge characteristics and improved capacity retention characteristics.

## 7 Improving operating time

Dry cell can be used once, while Ni-MH battery for replacing dry cell can be used 500 to 1000 times, and although their per-use operating time differs according to the portable device, no matter what high-capacity alloys are developed, the energy stored in a battery is limited insofar as it is consumed. For this reason attention is focused on micro fuel cell as dry cell replacement with unlimited service life, and research and development for practical use are in progress. Implementation evaluations are actually underway in notebook computer, mobile phone, and other devices.

In particular there are hydrogen-fueled polymer electrolyte fuel cell (PEFC), which comes in two types: the direct hydrogen type that generates electricity from the direct supply of hydrogen gas, and the reformer type that generates power from a supply of hydrogen obtained by reforming methanol. In both types the hydrogen production methods are key technologies. One example follows.

Recently a new way of producing hydrogen (not including CO, which causes degradation of the PEFC catalyst) from methanol in the temperature range below 100 °C and without any outside supply of electricity was discovered.<sup>16)</sup> This generates gas on the fuel electrode side by supplying methanol to the fuel electrode and air to the air electrode while controlling the flow rate with cell having the same structure as a direct methanol fuel cell (DMFC) in an open-circuit

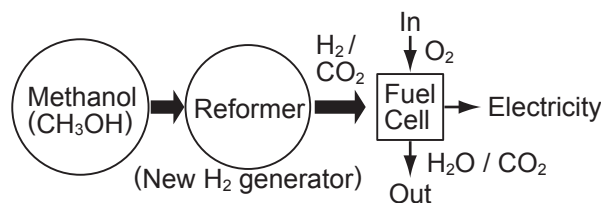


Fig. 9 Application of a new hydrogen generator to reformer type micro fuel cells.

state. Composition of the gas generated is 82% hydrogen gas, 13% carbon dioxide, and nodetectable level of carbon monoxide below 1 ppm, which is suitable as hydrogen fuel for PEFC. There are expectations that the concerned technologies in this area will see practical implementation and lead to the reformer type micro fuel cell shown in Fig. 9 as the ultimate replacement for dry cell.

## 8 Conclusions

This article has presented an overview of the development of Ni-MH battery conducted in accordance with a new concept which departs from the previous higher-capacity program and makes an appeal to the convenience of dry cells in order to expand the applications for Ni-MH battery. Although these batteries are not completely accepted by the market, the perceptions of Japanese consumers are gradually changing to those of Europeans, and the development of new products now involves image and the predilection for authentic things, not just cost as before. In relation to the predilection for authentic products, we feel that with a little more work, inherently safe and durable Ni-MH battery will win much greater acceptance in the market.

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