Development of Prototype Micro Fuel Cells for Mobile Electronics

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We have made great progress in developing a new micro fuel cell (μ-FC) technology that enables the use of 30% methanol fuel solution — the highest ever reported for passive systems — and the fabrication of a prototype power unit for mobile phones with the following specifications: a cradle-shaped interconnection for W-CDMA mobile phones, 18 ml of 30% methanol solution to recharge the internal Li-ion battery of the mobile phone to enable 150 minutes of continuous talking and 400 minutes of stand-by. In this study, our attention was focused on evaluating the environmental impact of newly developed μ-FCs to gather data, which is essential in developing environmentally friendly products. In this regard, we first evaluated the effect of greenhouse gasses such as CO_2 exhaust during material production, cell manufacturing, distribution, use, and disposal of μ-FCs on global warming and ozone layer depletion. Then, we assessed the consequent impact on human health and the ecosystem as the society cost according to the LIME method. This evaluation revealed that the society cost of μ-FCs is only 5% that of LR6 (IEC) alkaline dry batteries for a 10 kWh energy supply if the same cartridge is used 10 times.

1. Introduction

1.1 Fuel cells in general

Fuel cells (FCs) are energy generating devices in which energy stored in a fuel in chemical form is converted to electricity through electrochemical reactions rather than combustion. FCs are similar to batteries in terms of energy transformation, but they utilize externally supplied fuel and hence electrical recharging is unnecessary. Although FCs have a fairly long history of nearly 160 years, they had very limited applications in the past due to their poor performance and the availability of other products that used superior technologies. However, with the increasing global environmental concerns in recent years together with the environmentally friendly nature of FCs and recent technological developments that pave the way to outstanding performance in FCs, there has been new interest in this field.

In an FC, the anode and cathode are kept apart by an electrolyte, which is considered to be the heart of an FC. There are several types of electrolytes that produce different types of FCs; they are generally named after the electrolyte, for example, Solid Oxide Fuel Cells (SOFCs), Molten Carbonate Fuel Cells (MCFCs), Phosphoric Acid Fuel Cells (PAFCs), and Polymer Electrolyte Membrane Fuel Cells (PEMFCs).

Among FC systems, PEMFCs have attracted much attention during the last few years as a power source for automobile and portable applications due to special features that include high resistance to mechanical vibrations (no electrolyte leakage), small size because they have a thin electrolyte membrane, and low operational temperatures (mainly from room temperature to 100°C). In the early days of PEMFC technology, H_2 was mainly used as the fuel, and presently several organic materials such as methanol are being used. When methanol is directly used in PEMFCs, the FCs are called Direct Methanol Fuel Cells (DMFCs). PEMFC systems with power capacities of several tens of watts are categorized as μ-FCs. They have received much attention as small-scale power sources for future mobile electronics. According to the latest IEC definition, FC systems that produce a DC output not exceeding 60 V and 240 W are classified as μ-FCs. Among μ-FCs, methanol μ-FCs are considered to be the most suitable for portable applications due to the ease of handling methanol.

1.2 μ-FCs

1.2.1 Background

Since portable electronics such as mobile phones, notebook PCs, and Personal Digital Assistants (PDAs) have evolved to deliver higher performance and new advanced functionalities, they have also come to demand more and more electrical power. For example, there is a strong tendency toward increasing power consumption with the introduction of mobile phones with videophone functions as well as the increase of usage time with the introduction of fixed-charge communication packages. Presently, lithium-ion batteries (LIBs) are commonly used in these mobile electronics, but they have already approached the limits of their capacity, thus making the development of a higher-capacity power source a matter of great urgency. On the other hand, it has been theoretically proved that μ-FC systems can produce two to three times more power per unit weight than conventional LIBs and therefore could meet the power demand of future portable electronics. A comparison of the energy densities of existing battery systems and μ-FCs, together with the power demands of future portable electronics, is shown in **Figure 1**.

From the user's perspective, μ-FCs have an advantage in that they offer a cheap and easy means to power electronic devices immediately by simple refueling, enabling almost continuous use when traveling with no need to access a power outlet. Another prominent feature of μ-FCs is that although they are like primary batteries, for example, dry batteries, they produce a smaller volume of solid waste and therefore cause less environmental impact than conventional alkaline dry batteries, which are a low-cost power source for mobile equipment and are sometimes used to recharge the LIBs of mobile equipment such as mobile phones when it is urgently needed. Moreover, methanol can be derived from plants and other biomass materials, and at the same time, carbon dioxide exhaust from FCs is re-absorbed by plants. This means that methanol can be part of the carbon cycle and therefore μ-FCs can be considered a carbon-neutral energy device (**Figure 2**).

1.2.2 Market trends

During the last couple of years, there has been a steady increase of FC applications, in particular in portable equipment, where a 75% growth was seen just in 2004 (**Figure 3**).1) Also, as shown in **Figure 4**,2) there will be a rapid expansion of FCs in portable applications beyond 2006. Regarding the technology types, the FC systems manufactured last year were 55%

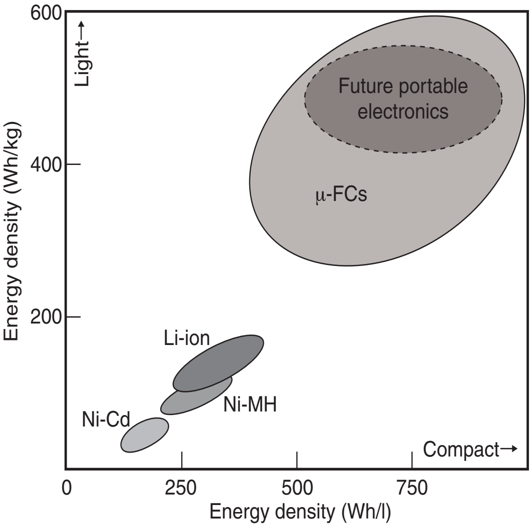


Figure 1
Energy density comparison of battery systems.

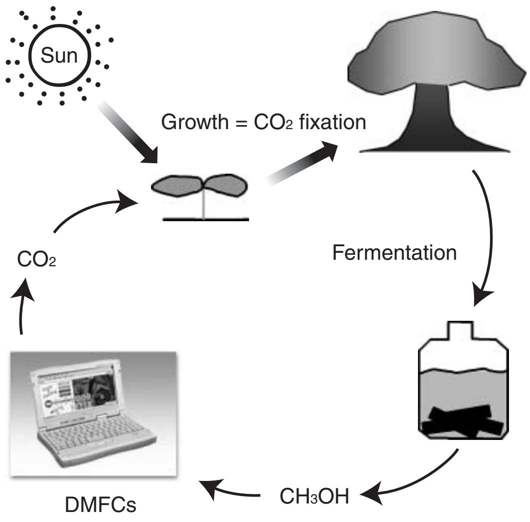
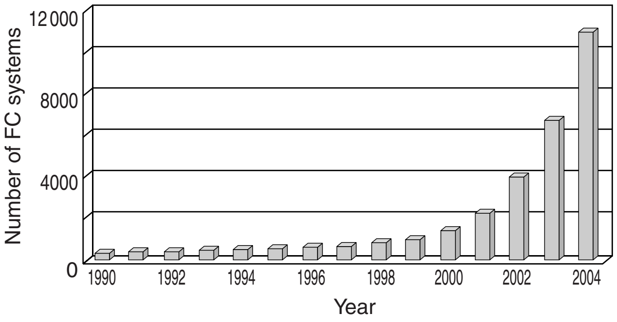
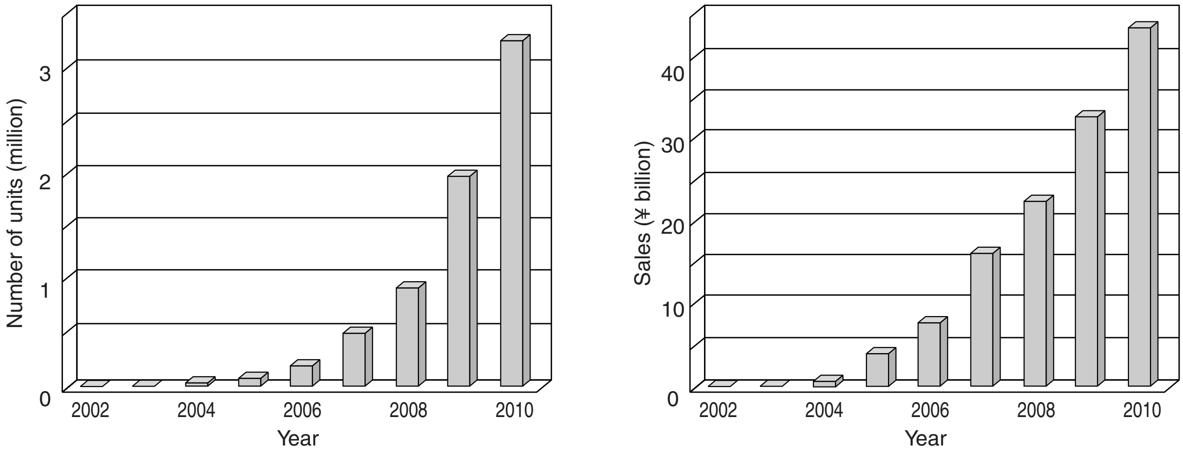


Figure 2
Carbon cycle including DMFCs as a stage.



Source: FUEL CELL TODAY, December 2004.

Figure 3
Number of FC systems used in applications.



(a) Total number of units

(b) Total sales value

Source: Yano Research Institute, Press release-Advanced Fuel Systems Market: trends in R&D 2002, August 2002.

Figure 4
Market forecast for FCs in portable applications.

PEMFCs and 43% DMFCs (**Figure 5**),1) and most of these were used in military applications. It is expected that DMFCs will take the market lead from PEMFCs because of technological advances that help improve performance and reduce costs to competitive levels, thus opening new markets for DMFCs over the next couple of years.

Although the current market for DMFCs is limited, robust R&D work is being conducted worldwide by a large number of consumer electronics manufacturers to commercialize power units for mobile electronics, and some of these manufactures have already announced commercialization plans for methanol μ-FC systems for notebook PCs, 3G mobile phones, PDAs, and military equipment within the next few years.

1.2.3 Cell structure and basic principals

The basic cell is composed of seven layers: a proton exchange membrane at the center, anode and cathode layers on either side of the membrane, two gas diffusion layers (GDLs), and two sealing gaskets. These seven layers are sandwiched between two electrical collectors and the outer housings to integrate the cell system (**Figure 6**). In this system, when reactants are continuously fed to the anode (methanol) and cathode (O_2), the cell produces DC current from electrochemical reactions as follows:

$$\text{Anode: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

$$\text{Cathode: } 6H^+ + 6e^- + 3/2O_2 \rightarrow 3H_2O \quad (2)$$

$$\text{Overall reaction } CH_3OH + 3/2O_2 \rightarrow 3H_2O + CO_2 \quad (3)$$

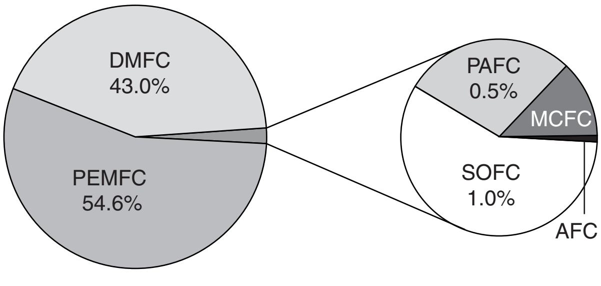
During current generation, the methanol is electrochemically oxidized in the presence of a Pt/Ru anode catalyst to produce free electrons and protons. The electrons travel through the external circuit to the cathode, and the protons migrate through the membrane to the cathode, where they combine with oxygen in the presence of a Pt catalyst to produce water.

DMFCs operate isothermally, and therefore the free energy difference of the overall reaction should in principle be converted to electrical energy. However, the kinetic constraints of the electrode reactions and the resistive components of the cell prevent total conversion to electrical energy. This means that the working voltage of the cell falls with increasing current. Therefore, careful control of these factors is indispensable in order to achieve high performance in DMFCs.

1.2.4 Objectives of present study

Passive DMFC systems that do not use fuel pumps or circulatory fans are the most suitable choice for μ-FCs because they help keep the package compact and light. In order to obtain high efficiency and long operation times without such functions as water circulation and fuel dilution, DMFCs must be able to directly operate with highly concentrated methanol solutions. However, highly concentrated methanol would cross over the polymer electrolyte membrane and reach the cathode, where it would burn and consequently poison the cathode. If methanol burns without current generation, the energy conversion efficiency would decrease drastically, making it difficult to realize high performance.

To date, DMFCs have mainly employed sulfonated fluoropolymers for the solid electrolyte membranes; however, these membranes are too readily permeated by methanol molecules, so only very diluted solutions can be used with these polymers. Therefore, in order to use concentrated methanol solutions, electrolyte membranes with a low methanol crossover (MCO) and high proton conductivity should be developed.



Source: FUEL CELL TODAY, December 2004

Figure 5
Distribution of new FC systems manufactured in 2004.

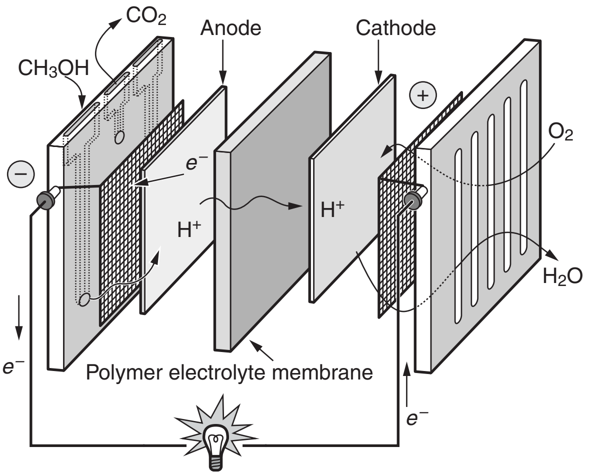


Figure 6
Internal structure of μ-FC system.

Another growing concern about DMFCs is the compositions of the catalyst layers. It should be noted that in order to get a high power density in a DMFC with a particular electrolyte membrane, certain electrode properties, for example, Pt particle size, Pt/Ru ratio, metal/carbon ratio, metal/ionomer ratio, electrical conductivity, proton conductivity, and layer porosity, must be optimized. Furthermore, in passive systems there is particular need to improve the mass transfer between the active sites of the electrodes.

Taking into consideration the above technical challenges, we carried out the following: 1) performed molecular design and polymer synthesis to develop a polymer electrolyte membrane with a low MCO and high proton conductivity; 2) developed high-density Pt nanoparticles and optimized the anode and cathode constituents to maximize the power density using the new polymer; 3) fabricated compact and lightweight passive type planer methanol μ-FC units for mobile phones with the new materials by optimizing the cell structure; and 4) studied the feasibility of future products.

Moreover, we compared the effects of CO_2 exhaust during raw material production, cell manufacturing, distribution, and use of μ-FCs and R6 (IEC) dry batteries on global warming and ozone layer depletion and then assessed the consequent impacts on human health and the ecosystem.

2. Experiments

2.1 Materials

Pt and Pt/Ru nanoparticles were prepared by the chemical reduction method. Carbon-supported catalysts with Pt/Ru ratios from 1 to 1.5 Ru parts per 1 part of Pt and 40 to 60wt% on Ketjen black (highly conductive carbon) were prepared. They were mixed with Nafion (ionomer) binder in propanol with catalyst/Nafion ratios in the range from 1/0.5 to 1/1.

The newly synthesized sulfonated aromatic hydrocarbon polymer was dissolved in dimethylacetamide (30 wt%) and applied to a glass plate using a doctor blade with a gap size of 500 μm. The solvent was distilled off at 50°C, 120°C, and 170°C, each time for one hour, to form a membrane. The membrane was then immersed in 1 mol/l sulfuric acid for 24 hours and washed with de-ionized water until the acid was undetectable.

2.2 Measurements

2.2.1 Methanol crossover

The MCO values were determined by keeping a 10 wt% aqueous methanol solution and de-ionized water separated from each other by the electrolyte membrane (140 μm thick) in a stainless steel vessel at 30°C and then measuring the amount of methanol that seeped into the de-ionized water by gas chromatography/mass spectroscopy (GC/MS) at regular time intervals.

2.2.2 Proton conductivity

The test sample was placed between two platinum electrodes that were 1 cm apart. The surface resistance of the test sample was measured by an alternating current impedance method (frequency: 100 Hz to 100 kHz) using a 4-point probe at room temperature and a voltage of 0.3 V. The proton conductivity was calculated from the surface resistance.

2.3 Membrane electrode assembly (MEA) and test-cell fabrication

An anode (Pt/Ru catalyst)/new membrane/cathode (Pt catalyst) sandwich structure was prepared by hot-press bonding at 170°C. A thin adhesive layer was used to improve the adhesion between the catalyst layers and polymer membrane. Test fuel cells with an active area of 9 cm^2 were prepared with the above MEAs. Methanol (20 to 30 vol%) was injected into the test cells, and the power output was estimated by applying a fixed voltage between electrodes.

2.4 Prototype fuel cell unit design

A fully passive prototype μ-FC module with a planar cell structure was fabricated for mobile phones (**Figure 7**). This module measures 152 mm × 57 mm × 16 mm, has a volume of 180 cc, and weighs 190 g. A fuel cartridge was designed that could be fixed to the FC module, and the fuel can be transferred to the module with no pressure applied (**Figure 8**). This cartridge has a volume of 40 cc and a fuel capacity of 18 cc. The mobile phone was fixed to the μ-FC module through a cradle type interconnection.

2.5 Environmental impact evaluation

In this study, Life Cycle Assessments for μ-FCs and LR6 (IEC) alkaline dry batteries were conducted for 10 kW power generation. The environmental impact was estimated by Life Cycle Impact Assessment Method Based on Endpoint Modeling (LIME),[3] taking into account the material production, fuel cell manufacturing, distribution, usage, and disposal. In the case of μ-FCs, we made assessments for 1, 5, and 10 uses of the same cartridge.

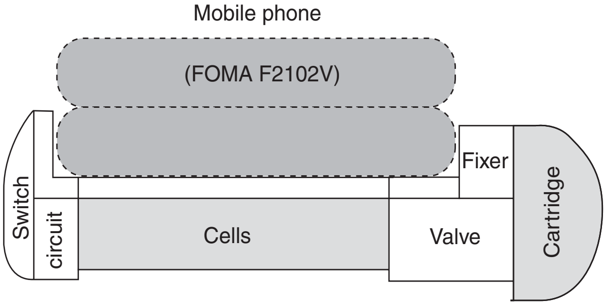


Figure 7
Cross-sectional structure of prototype μ-FC system for mobile phones.

3. Results and discussion

3.1 New membrane

The basic properties of the membrane together with those of Nafion 117 are summarized in **Table 1**. The proton conductivity of the new membrane was found to be nearly equal to that of Nafion 117, while the methanol permeation rate was found to be 3/10 that of Nafion 117. It should be noted that the new polymer membrane drastically reduced the methanol permeation while maintaining proton conductivity at the high level of Nafion 117. These properties allow us to use concentrated methanol solutions (30 vol%), which was previously impractical in passive DMFCs.

The electric power generation behaviors of MEAs prepared from the new membrane and Nafion 117 are compared in **Figure 9**. From this figure, it is clear that the new polymer exhibited uniform power generation for about 100 min after the introduction of 1 ml of 30% methanol

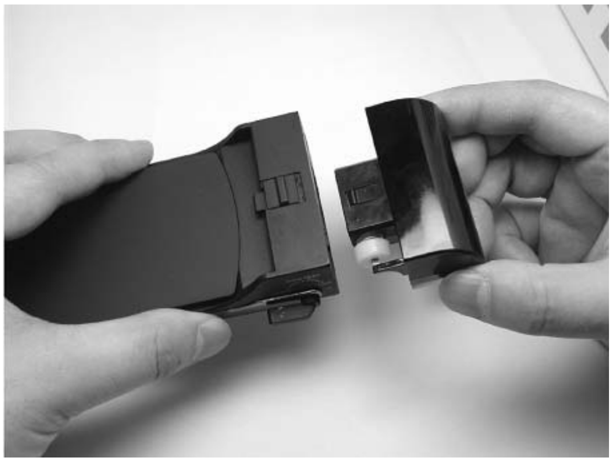


Figure 8
One-touch cartridge attachment.

Table 1
Proton conductivities and MCO rates of membranes.

Membrane	σ (S/cm)	MCO rate (ml/s.cm^2)
FJ membrane (140 μm)	0.092 (0.83)	1.10×10^{-5} (0.3)
Nafion 117 (190 μm)	0.110 (1.00)	3.44×10^{-5} (1.00)

(σ: proton conductivity. σ and MCO rate relative to Nafion 117 are given in parentheses)
FJ: Fujitsu

solution. Whereas, with Nafion 117, a sudden high-power output was observed for a short period and then the cell became dead. Temperature monitoring data of this cell suggests that the sudden power decrease was related to over-heating of the FC due to a high methanol crossover in the Nafion 117.

3.2 Prototype μ-FC units for mobile phones

The newly developed prototype μ-FC module with the attached cartridge and mobile phone connected through a cradle type interconnection is depicted in **Figure 10**. In this prototype, a new material technology consisting of a new polymer electrolyte material and electrode catalyst layers was employed to reduce the MCO. This helped realize the following high-performance specifications: 18 ml of 30% methanol solution to recharge the LIB installed in the mobile phone, 150 minutes of continuous talk time, and 400 minutes of stand-by time. Charging is done at 5.4 V and 700 mA, which is compatible with all DoCoMo 3G mobile phones.

In this system, no pumps or fans are employed for fuel or O_2 supply, which made it possible to realize a highly compact, lightweight module. Another important feature of this design is that the system's physical orientation has no effect on the power output.

3.3 Environmental burdens of μ-FCs

3.3.1 CO_2 release

μ-FCs, which are revitalized by refilling them with fuel, are considered to be like primary batteries, for example, dry batteries, because no electrical charging is employed. Therefore, we evaluated the environmental impact of μ-FCs in comparison with dry batteries. In this evaluation, first, the total amount of CO_2 exhausts were estimated for μ-FCs and LR6 (IEC) alkaline batteries for an energy supply of 10 kWh (**Figure 11**). The power capacities of the μ-FC and LR6 batteries applied in this calculation are 1 Wh/ml methanol and 4.05 Wh/cell, respectively. The total numbers of cartridges and LR6 batteries needed for a 10 kWh energy supply are 1852 and 1469, respectively.

As given in Figure 11 (a), in the case of μ-FCs, there is a drastic reduction in CO_2 exhaust from 115 kg to 26 kg (a 78% decrease) when the same cartridge is used 10 times. On the other hand, the CO_2 exhaust of LR6 batteries was found to be 300 kg, which is very high.

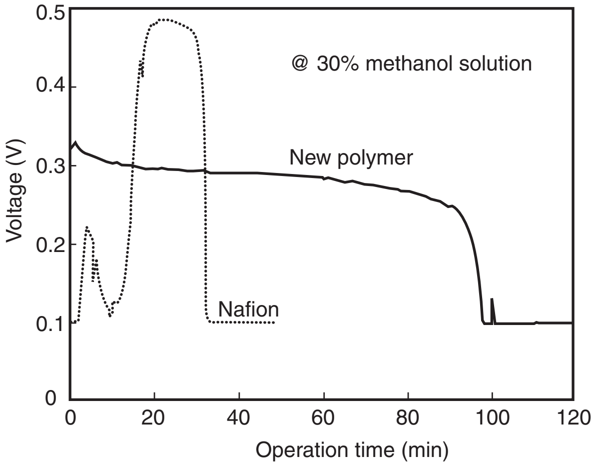
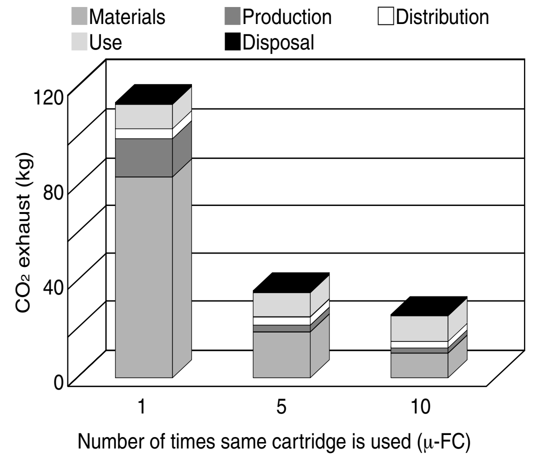
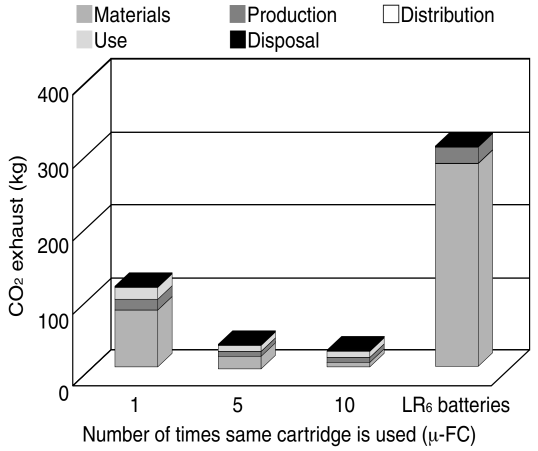


Figure 9
Electric power generation of MEAs with new membrane and Nafion 117 (current density 60 mA/cm²).

Figure 10
Mobile phone mounted on newly developed μ-FC module (cradle type interconnection).



(a) μ-FC system with different number of times same cartridge is used



(b) Comparison of μ-FC system with LR6 dry batteries

Figure 11
CO_2 exhaust of battery systems for 10 kWh power supply.

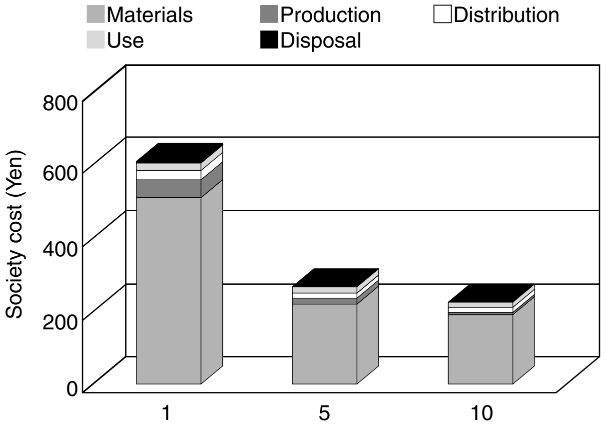
3.3.2 Environmental society cost

In the environmental society cost calculation, major environmental factors such as resource consumption, air pollution, water pollution, and soil pollution are considered. For a particular pollutant, for example, CO_2 exhaust, the effects on global warming and ozone layer depletion were analyzed and the potential impacts on human health and the ecosystem were assessed by taking into account the following according to the LIME method: sustaining human health (A), sustaining photosynthesis (B), resource conservation (C), and bio-diversity conservation (D). The impacts were then converted into a monetary value.

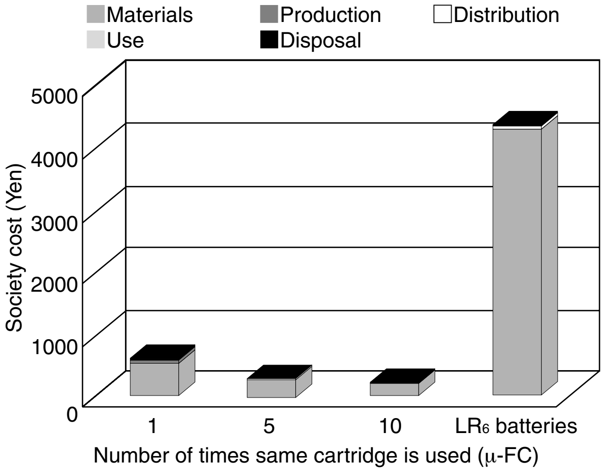
$$\text{Society cost for } CO_2 = A + B + C + D \qquad (4)$$

Likewise, the individual society costs for other elements, which may be in the form of pollution or consumption, are assessed, and their sum is taken as the environmental society cost.

Figure 12 shows the society cost values of the μ-FC system and LR6 battery for an energy supply of 10 kWh. Figure 12 (a) shows that when the same cartridge is used 10 times, the society cost is reduced to 37% of the society cost when cartridges are not reused. The lower society cost



(a) μ-FC system with different number of times same cartridge is used



(b) Comparison of μ-FC system with LR6 dry batteries

Figure 12
Society costs of battery systems for 10 kWh power supply.

reduction compared to the CO_2 reduction can be attributed to the relatively high society cost of materials such as the precious metals that are used in FC module manufacturing. In the case of LR6 batteries, the society cost was found to be very high at 4350 Yen [Figure 12 (b)], which is roughly 20 times that of the μ-FC system with 10 cartridge reuses. We also found that, in addition to the CO_2 exhaust, SO_x release during MnO_2 production and the large volume of solid waste in LR6 batteries also contribute to a higher society cost. From this data it can be said that, particularly from the materials viewpoint, the μ-FC has a drastically lower environmental burden than alkaline dry batteries.

It should be mentioned that in this study, the environmental burdens of μ-FCs was not compared with that of LIBs, the main competitor of μ-FCs, mainly because published data on LIB manufacturing processes was not available. However, with limited available data and with several assumptions, we tentatively calculated that the society cost of LIBs for a 10 kWh energy supply is 15% that of μ-FCs when three Li-18650 LIBs are used. We believe that further technological advances in μ-FCs, for example, power capacity increases per unit fuel volume, cell downsizing, reduced precious metal consumption, and cartridge reuse for several tens of times, may pave the way to reducing the society cost to the level of LIBs.

4. Conclusion

We have developed a new materials technology for μ-FCs that enables the use of 30% methanol fuel solution, which was previously too concentrated for passive systems. A prototype power unit for W-CDMA mobile phones that incorporates this technology was fabricated. This prototype helped realize the following high-performance specifications: 18 ml of 30% methanol solution to recharge the internal LIB of the mobile phone, 150 minutes of continuous talk time, and 400 minutes of stand-by time. We evaluated the environmental burdens of μ-FCs according to the LIME method. The evaluation results indicated that the society cost of μ-FCs is only 5% that of LR6 (IEC) alkaline dry batteries for a 10 kWh energy supply if the same fuel cartridge is used 10 times.

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