

# Direct methanol fuel-cell combined with a small back-up battery

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## Abstract

A description is given of a fuel-cell power-supply for mobile phones that operates at room temperature and ambient pressure using liquid methanol and ambient air. The unit is a hybrid system in which a direct methanol fuel-cell (DMFC) and a back-up battery are connected in parallel to meet the power requirements of mobile phones. Electrochemical catalysts for the anode and the cathode of the DMFC are synthesized and Nafion-115 is used as the electrolyte. A 2 M methanol solution is filled in the feed reservoir, and the cathode is exposed to ambient air. Eight unit cells, each having 9 cm<sup>2</sup> of active area, are connected in series in order to raise the output voltage to 2.5–3.9 V, which is the typical voltage range for most mobile phones. Also, to simulate the practical application, an electric circuit is included to increase the output voltage of the back-up battery to repeat the charge–discharge cycle. During talk mode, the DMFC supplies 10–50% of the required power and the back-up battery supplies the remainder. In standby mode, the DMFC covers 100% of the required power and charges the back-up battery.

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**Keywords:** DMFC; Mobile phone; Battery; Methanol

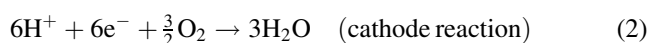
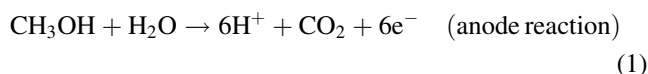
## 1. Introduction

Fuel cells have been attracting world-wide attention because of their prospects as clean and efficient electric power generating systems. Although the first applications were in generating power and potable water for spaceship missions with alkaline fuel cells (AFCs), the first wave of commercialization effort in the real sense started in the 1980s when the phosphoric fuel-cell (PAFC) was developed for stationary power generation. The PAFC eliminated the need for pure hydrogen and pure oxygen demanded by the AFC system. Development of the PAFC to meet market requirements is still in progress, mainly by International Fuel Cells [1].

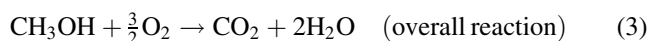
The proton exchange membrane fuel-cell (PEMFC) was introduced in the early 1990s and used a highly selective CO oxidation catalyst [2]. PEMFC has several critical advantages over other types of fuel cells. These include rapid start-up, compactness, and mass production capability. Once the only technical obstacle, namely, that CO has to be as low as 10 ppm in the anode gas, was overcome by the catalyst, PEMFC expanded its potential application to fuel-cell vehicles [3–5]. Accordingly, the present intensive development

of PEMFC system is being driven mainly by the world-leading automotive companies.

The third phase of fuel-cell evolution has come from a desire to apply the fuel-cell to very small power-supply units such as those required for mobile phones, notebooks, and other advanced mobile electronic devices. All of the above-mentioned types of fuel-cell require hydrogen as the fuel. Conventional methods to supply hydrogen, such as compressed hydrogen, metal hydride, or reformation of liquid hydrocarbons have not been generally accepted as a viable practical solution because of their low specific energy and safety concerns. At present, the direct methanol fuel-cell (DMFC) which uses liquid methanol without a reformer is considered as the most promising type of fuel-cell for small power-supply units. The electrochemical reactions of DMFC are described by the following equation:



Adding reactions (1) and (2) we get



Unlike other types of fuel cells, the DMFC can be operated at ambient temperature and pressure. The specific

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energy of liquid methanol is about  $3000 \text{ Wh kg}^{-1}$ , and hence, the DMFC can, theoretically, provide about 15 times longer use than conventional lithium-ion batteries whose state-of-the-art specific energy is about  $200 \text{ Wh kg}^{-1}$ . Moreover, recharge is as simple as just refilling the methanol or changing the methanol cartridge.

Currently, the battery market for portable electronic devices is growing by more than 20% annually and such a high growth rate is expected to continue for at least several years. The rapid advancement of wireless data communication and electronic circuit design technologies has resulted in a great diversity of the functions of personal portable electronic devices. Accordingly, the performance capability of conventional lithium-ion battery is unlikely to keep pace with the expanded power requirements. Thus, the DMFC is considered as a strong candidate for the next generation of power units for wireless data communicating devices. During the past few years, a growing number of researches on DMFCs have been conducted for the power-supply of portable electronics [6,7].

Although the DMFC has a high specific energy, there are technical hurdles to overcome before it can be introduced commercially, how activity of the anode catalyst for methanol oxidation and methanol cross-over in the electrolyte are the two major obstacles that limit the performance of DMFCs. Combinatorial electrochemistry has been applied to screen better anode catalysts [8], and modifications of proton-conducting membranes have been tried to eliminate the methanol cross-over [9,10]. Also, there are several studies on the design of DMFC to alleviate these technical difficulties [11]. Although there have been quite a few advancements, the performance of DMFCs is still short of the technical targets for commercial applications.

This study focuses on practical aspects of DMFC and suggests a new hybrid design concept which uses a small back-up battery. Most wireless electronic devices frequently switch between standby mode and operation mode and the power requirement varies from 10 to 100% of the full power according to the mode change. Hence, it is more practical to use the battery-DMFC hybrid instead of a DMFC alone to provide 100% of required power. The methanol cross-over problem is beyond the scope of this study. The performance of the battery-DMFC hybrid is tested for mobile phones and the results indicate that it is superior to conventional secondary batteries.

## 2. Experimental

Electrochemical catalysts for the anode and the cathode of the DMFC were made from platinum and ruthenium. The method of preparation was as follows. First,  $\text{Na}_6\text{Pt}(\text{SO}_3)_4$  was synthesized from  $\text{H}_2\text{PtCl}_6$  and  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_6\text{Ru}(\text{SO}_3)_4$  from  $\text{RuCl}_2$  and  $\text{Na}_2\text{CO}_3$ . Then, the  $\text{Na}_6\text{Pt}(\text{SO}_3)_4$  and  $\text{Na}_6\text{Ru}(\text{SO}_3)_4$  were dissolved in 1 M  $\text{H}_2\text{SO}_4$  solution together with Ketjen-Black 600-TD (Akzo Chemie). After

reduction of the solution with 1 wt.% formic acid, the suspended particles were filtered and dried in oven for 2 h. The resulting catalysts were 60% Pt/C and 40% Pt-Ru/C for the cathode and the anode, respectively.

The catalyst was mixed with Nafion solution (Aldrich), PTFE, and isopropyl alcohol and rigorously stirred until it became a smooth paste. The paste of the cathode catalyst was coated on hydrophobically treated carbon paper, and that of the anode catalyst on non-treated carbon paper. The hydrophobic treatment was done by a Teflon solution. The catalyst-coated carbon papers were then dried in oven for more than 20 h. The dried anode and cathode catalyst layers were hot-pressed at  $100^\circ\text{C}$  and  $100 \text{ kgf cm}^{-2}$  for 1 min on each side of a Nafion<sup>®</sup> membrane (Dupont) to complete the membrane electrode assembly (MEA). The carbon paper was a Kureha product and the area of the MEA was  $9 \text{ cm}^2$ . The amount of catalyst in each of the anode and the cathode was  $8 \text{ mg cm}^{-2}$ .

Once the MEA was fabricated, it was combined with current-collectors on both sides of the electrodes to form the unit cell. Each current-collector was 0.2 mm grid-shaped SUS304L foil and was coated with gold. Gold coating was necessary to reduce the contact resistance and hence to increase the specific power of the DMFC cell. Mechanical contact of the current-collectors to the MEA was achieved by adding a novel polymer on the contacting surfaces and hot-pressing them together. The performance of the unit cell was evaluated with a potentiostat (Galvanostat 273A) and a battery cycler (Bitrode) as shown in Fig. 1. The 'fuel' was 2 M methanol solution and was stored in a small container ( $\sim 20 \text{ cm}^3$ ) on top of the anode. The cathode was simply exposed to ambient air so that natural convection of the atmospheric air supplied the oxygen to the cell. For operation over an extended period of time, the feed was continuously recycled from a large reservoir to eliminate any effects of methanol concentration change and temperature variances.

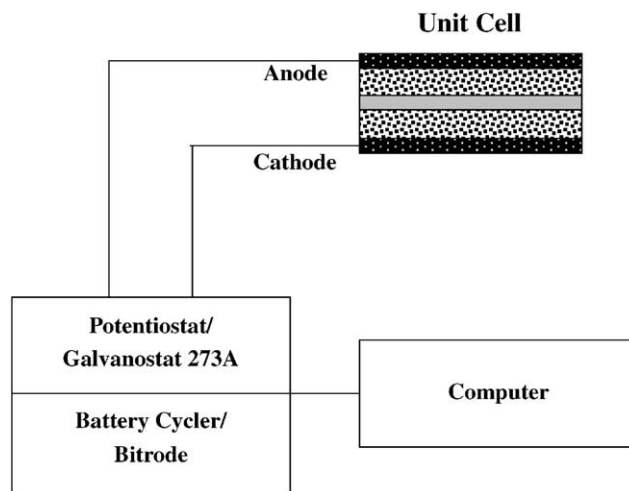


Fig. 1. Experimental set-up for measuring performance of DMFC unit cells.



Fig. 2. Photograph of DMFC sub-module of four unit cells connected in series.

Four of the above unit cells composed a sub-module, and two sub-modules formed a complete power module. The eight unit cells were electrically connected in series in order to meet the voltage requirement of mobile phones. A photograph of the sub-module is shown in Fig. 2, the cross-sectional view of the sub-module, is given in Fig. 3. The 2 M methanol solution was held between the two monopolar plates of a sub-module. The cathode was exposed to ambient air. Replenishment of the feed solution was made through a hole on top of the module. The hole was covered with a specially designed ventilation polymer made by SK Corporation so that CO<sub>2</sub> generated as a byproduct could be removed easily but the methanol solution did not escape from the reservoir.

The configuration of the hybrid system is shown schematically in Fig. 4; the DMFC power module is connected in parallel with a back-up battery. The battery was a prismatic lithium-ion unit cell (model: SK BAT300S) which was taken from a battery pack for a IM-1100 mobile phone (SK Teletec). The maximum electricity storage of the back-up battery was 750 mWh and the volume and the weight were 5.5 cm<sup>3</sup> and 17 g, respectively. In order to protect the battery

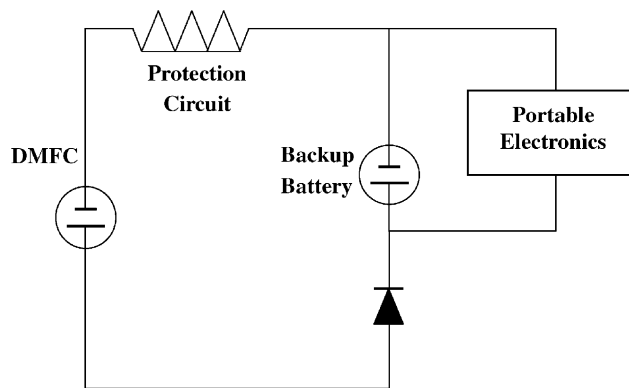


Fig. 4. Schematic representation of hybrid DMFC.

from over-charge and over-discharge, possibly caused by a sharp increase in temperature, a specially designed miniature protection circuit was included in the system.

### 3. Results and discussion

Polarization curves for DMFC unit cells with different amounts of catalyst are shown in Fig. 5. The optimum amount of catalyst appears to be about 8 mg cm<sup>-2</sup>. This suggests that the methanol oxidation reaction is highly dependent on the amount of catalyst, but that excess catalyst blocks the supply of the feed as well as the removal of the by-product CO<sub>2</sub> from the reaction zone. Most of previous studies [12–14] has used 1–5 mg cm<sup>-2</sup> of catalyst on each electrode. Minimizing the use of the precious metal is an important cost consideration in vehicular applications since these require electrodes of large surface area to meet the power requirements. For portable electronics, however, the maximum power requirement is less than 0.1% of those for vehicles, so that the amount of platinum does not significantly affect the cost of the DMFC power-supply. It is recommended to use an amount of catalyst that is sufficient to enhance the performance of the DMFC. The optimum

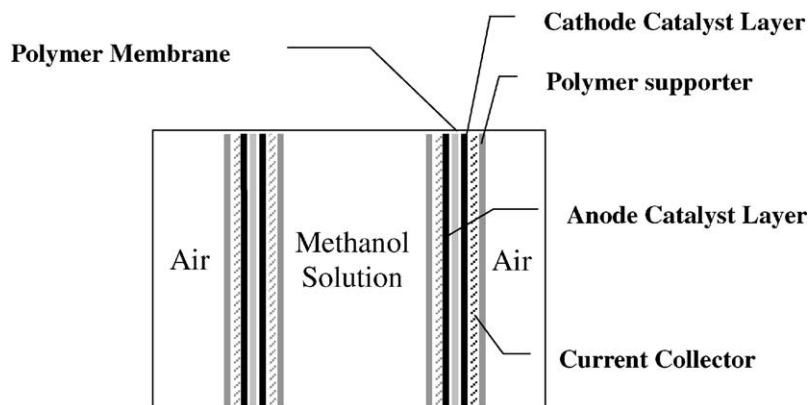


Fig. 3. Cross-sectional view of sub-module.

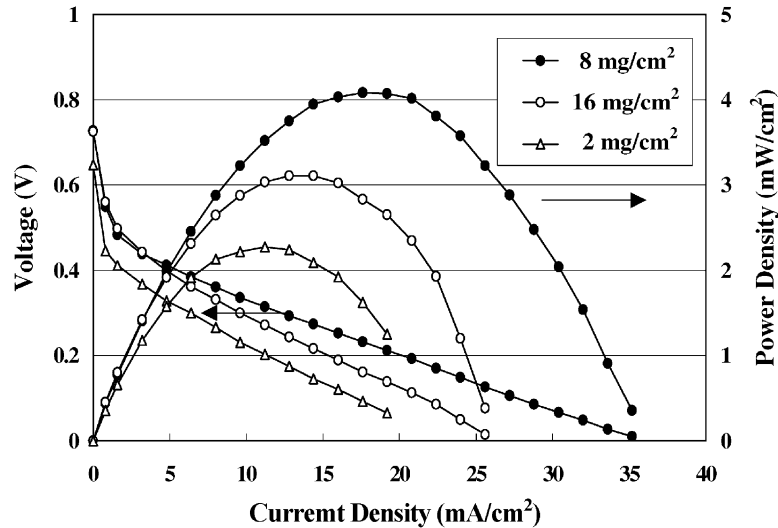


Fig. 5. Effect of amount of catalyst at room temperature and ambient pressure.

amount of catalyst will depend on the fabrication procedure, and in this work was  $8 \text{ mg cm}^{-2}$ .

The power density,  $4 \text{ mW cm}^{-2}$  is quite small compared with those reported by others. It should be noted that whereas this study operates the DMFC at ambient conditions, most of the published studies were based on DMFC operation at elevated temperatures ( $60\text{--}120^\circ\text{C}$ ), with forced circulation of feed, and sometimes by blowing pressurized air into the cathode. In general, these do not represent the actual operating conditions of portable electronics. There are only a few reports [6,15] that describe the performance of DMFCs at the ambient conditions with power densities in the range  $8\text{--}10 \text{ mW cm}^{-2}$ . As shown in Fig. 6, the power density increases significantly as the temperature is raised from  $20$  to  $60^\circ\text{C}$ , but since this study relates to the conditions of the actual utilization of a DMFC, the design of the

power module is based on the performance at ambient temperature.

In order to determine the long-term operation capability of the DMFC power module, a unit cell was run continuously for about a week. A constant current of  $150 \text{ mA}$  ( $\sim 17 \text{ mA cm}^{-2}$ ) was been extracted during the operation. The voltage of the module is shown Fig. 7. The temperature surrounding the unit was always between  $25$  and  $28^\circ\text{C}$ . The feed,  $2 \text{ M}$  methanol solution, was initially filled in the reservoir, but after  $24 \text{ h}$  of operation, fresh feed was continuously supplied on the purpose of eliminating the effect of the change of methanol concentration in the feed. There appears to be gradual decrease in cell voltage as the operation continues. This is probably caused by methanol cross-over lowering activity of the cathode catalyst. Incidentally, there was a power failure of  $\sim 66 \text{ h}$  and the current extracted

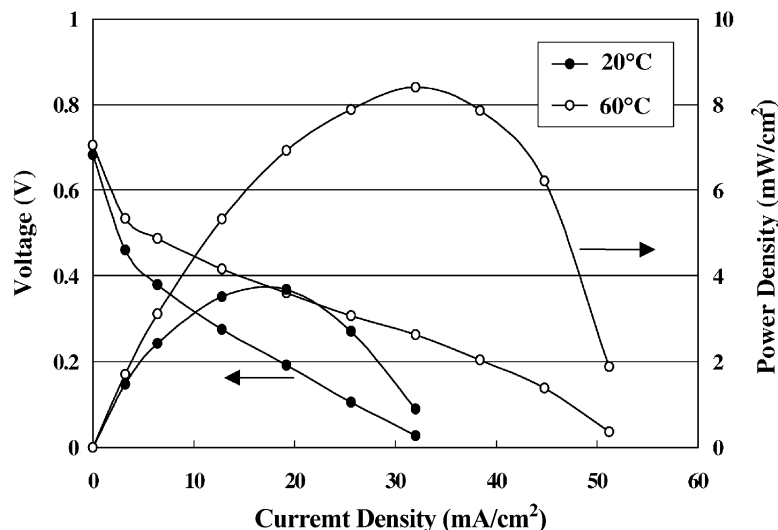


Fig. 6. Effect of operating temperature.

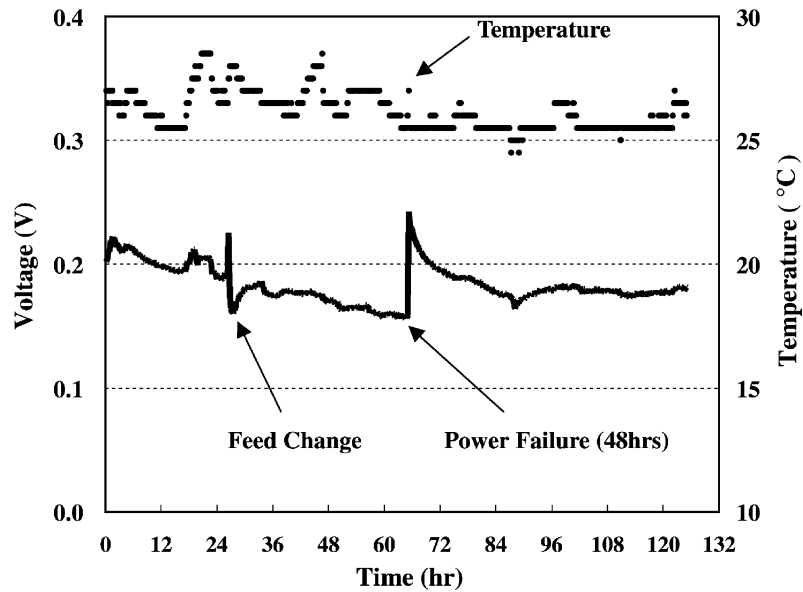


Fig. 7. Long-term operation result of DMFC unit cell.

from the unit was zero for 48 h. When the operation was resumed, the voltage was found to recover to its initial value and then decrease again. This recovery of the voltage is believed to be due to evaporation of methanol at the cathode during the shut-down. Of course, evaporation takes place during operation, but since the amount of the methanol cross-over is proportionally dependent on the current through the polymer membrane [16], the methanol cross-over is larger than the methanol evaporation. Nevertheless, these appears to be an equilibrium which leads to no more drop in voltage during operation, which implies that evaporation and cross-over are balance at this condition. Although such equilibrium helps to block further voltage decrease and enables stable operation of the DMFC, metha-

nol cross-over significantly lowers the energy-storage capacity of the DMFC.

The current–voltage characteristics of the eight-cell module are shown in Fig. 8. When a current of 10 mA is extracted the voltage becomes 3.9 V, and when 50 mA is extracted the voltage becomes slightly above 2.5 V. This means that the DMFC supplies more than enough standby power for most of the mobile phones that consume about 10 mA. The voltage requirement of mobile phones is in generally below 3.9 V. For talk mode, which consumes about 100 mA, 10–50 mA is supplied from the DMFC and the remainder from the back-up battery. As the talk mode continues, the voltage of the back-up battery decreases and the portion of power from the DMFC gradually

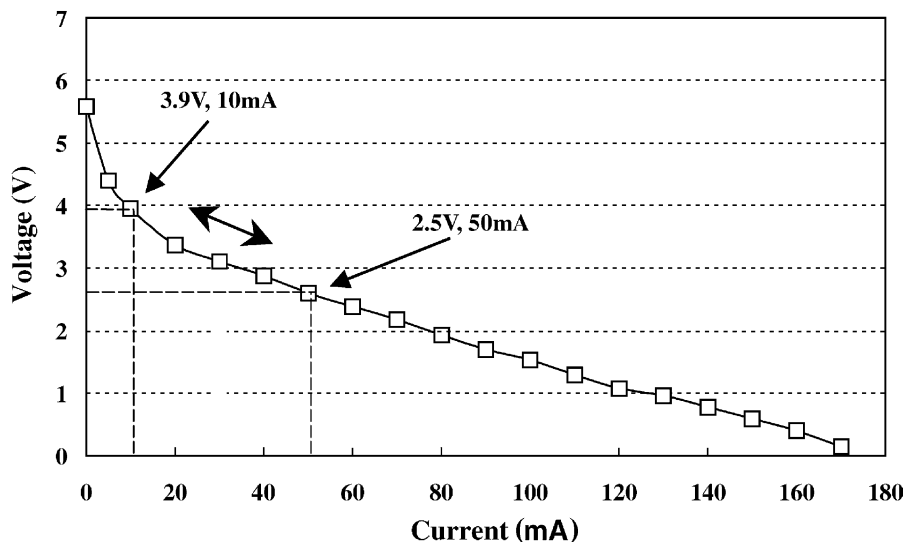


Fig. 8. Polarization curve for complete power module of eight unit cells connected in series (room temperature and ambient pressure).

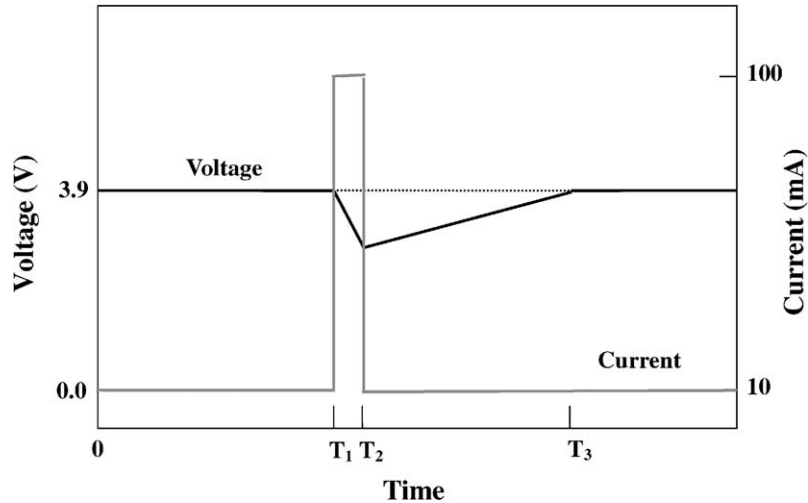


Fig. 9. Expectation of voltage variation during talk and standby modes.

increases. When the phone switches back to standby mode, the DMFC supplies 10 mA for the standby current, and the excess is used to recharge the back-up battery until the voltage is restored to 3.9 V.

The above operation mode for mobile phones is shown in schematically in Fig. 9 in terms of the change in voltage of the back-up battery at load change. The voltage of the back-up battery at full charge is assumed to be 3.9 V. The time between  $T_0$  and  $T_1$  and after  $T_3$  is standby mode during which 10 mA is supplied from the DMFC to the mobile phone. The time between  $T_1$  and  $T_2$  is the talk mode and the voltage drops as talk continues. The time between  $T_2$  and  $T_3$  is the same standby mode as between  $T_0$  and  $T_1$  but the DMFC generates a current of more than 10 mA and the excess current is used to charge the back-up battery.

At the moment, the system does not support an extended period of talk since the voltage gradually decreases and ultimately reaches below the minimum value of 2.5 V. When this happens, the talk has to be stopped and the stand-by mode resumed to recharge the battery. An improved catalyst

with higher power density would increase the maximum talk time. Actual data showing the voltage change from the DMFC module are presented in Fig. 10. Initially, 10 mA is extracted from the battery until the voltage of the lithium-ion back-up battery drops from 3.5 to 2.7 V. At this stage, the current extraction is reduced to 10 mA. Recharge is faster when the voltage of back-up battery is lower. This is due to increased power output at lower voltage, as already shown in Fig. 8. This is highly desirable characteristic of a hybrid DMFC since the charging speed becomes highest when it is most needed. The module made in this study sustains 15 min of talk and restores the voltage to the initial state, viz. 3.5 V, in about 230 min.

In order for these hybrid DMFC modules to be used commercially, further improvement has to be made. This includes a new fabrication process for a more compact design, a catalyst of higher activity for longer talk time and, most, importantly, removal of methanol cross-over to enable the use of highly concentrated methanol solution. The shape of the DMFC power module which is presently

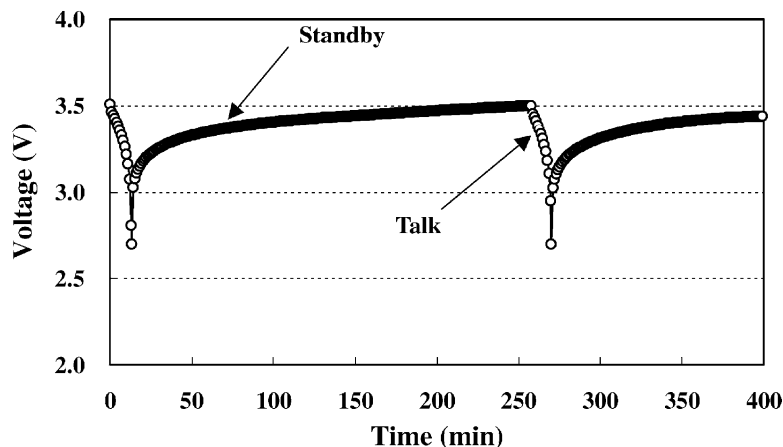


Fig. 10. Voltage variation during talk and standby modes.

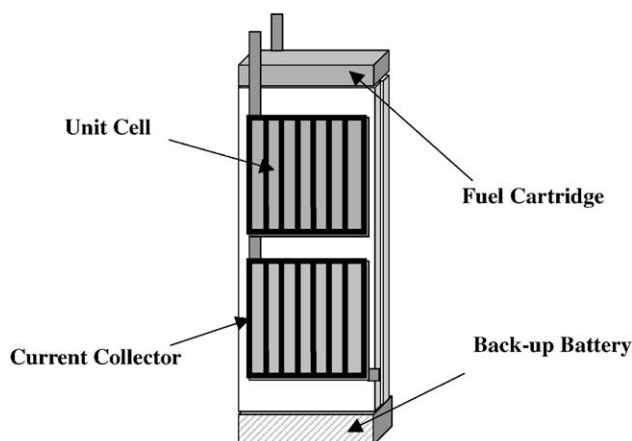


Fig. 11. Conceptual design of complete hybrid DMFC power module.

under development is shown in Fig. 11. The fuel cartridge is installed on top of the hybrid power module. For a reference, the cost of material for fabricating the module is about US\$ 56, and in case of mass production, it is assumed to become as low as US\$ 25. Therefore, if there is no significant rise in cost following performance improvements, the hybrid DMFC is quite competitive against lithium-ion batteries.

#### 4. Conclusions

A hybrid DMFC power-supply has been developed and is composed of a DMFC module and a small lithium-ion back-up battery. The DMFC module is made from eight unit cells and the fabrication of each unit cell includes preparation of anode and cathode catalysts, MEA fabrication, and assembly with current-collectors using a novel polymer. Performance tests have been conducted at the room temperature and under the natural convection of air in order to simulate the operating conditions of portable electronics. The hybrid DMFC has been applied to mobile phones to evaluate the operability as a power-supply. It can supply 100 mA, the full current for the mobile phone during talk mode, in which 10–

50% is provided by the DMFC module and the remainder by the back-up battery. Talk can continue until the voltage of the back-up battery drops to the minimum voltage for the mobile phone. In standby mode, the DMFC module supplies 10 mA to the phone and the excess current recharges the battery. It simulates the actual operating mode of mobile phones during repeated talk and standby. Although this hybrid DMFC power-supply still requires improvements for practical use in portable electronics, this study demonstrates its potential as the next-generation power unit for portable electronic devices.

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