

# All-solid-state supercapacitor using a Nafion<sup>®</sup> polymer membrane and its hybridization with a direct methanol fuel cell

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## Abstract

An all-solid-state supercapacitor is fabricated and optimized using a Nafion<sup>®</sup> membrane and an ionomer. The device shows good capacitance (ca. 200 F g<sup>-1</sup>) as demonstrated by cyclic voltammograms (CVs) and charge–discharge curves. The supercapacitor exhibits a relatively stable capacitance during 10,000 cycles of operation. A hybrid system comprising a direct methanol fuel cell (DMFC) and an all-solid-state supercapacitor has been designed and tested. It is confirmed that the power discharged by the supercapacitor is transferred effectively to the DMFC. The power of the hybrid is immediately improved by 30% compared with that of a DMFC alone operating at 25 °C. The possibilities of using this system for high energy and high instantaneous power devices and integrated fabrication processes are discussed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Direct methanol fuel cell; All-solid-state supercapacitor; RuO<sub>2</sub>; Nafion<sup>®</sup> membrane; Hybrid power source

## 1. Introduction

Following the development of proton-conducting polymer membranes such as Nafion<sup>®</sup>, solid-state electrolyte membrane fuel cells have been studied intensively. In particular, the direct methanol fuel cell (DMFC), which uses Nafion<sup>®</sup> as a solid electrolyte, has received considerable attention because of its numerous advantages, which include high specific energy, ease of handling a liquid, and operating temperatures [1–3]. Due to the low pulse power density of the DMFC, however, significant limitations exist for applications that require an instantaneous high power source. On the other hand, a supercapacitor has advantages that include high specific power and a rapid charging time, but these are coupled with a low specific energy [4,5]. Therefore, a new power source or system could be developed by combining the advantages of the high specific energy of the DMFC and the high specific power of a supercapacitor. Nevertheless, only a few efforts and some preliminary results have been reported relative to the hybridization of DMFC and supercapacitors [6,7].

All-solid-state supercapacitors may also be advantageous for hybridization or integration with a DMFC. To date, supercapacitors have generally used H<sub>2</sub>SO<sub>4</sub> and NaOH as

the liquid electrolytes. Recently, Osaka et al. [8] reported a supercapacitor based on a Li-conducting gel electrolyte. A Li-ion-based supercapacitor is, however, difficult to seal and protect from atmospheric water molecules. Accordingly, a proton-conducting polymer membrane such as Nafion<sup>®</sup> would be suitable for hybridization with a DMFC in an aqueous atmosphere [9]. The Nafion<sup>®</sup>-supercapacitor could, however, suffer from stability, potential windows, and variations in conductivity according to humidity. Therefore, the reliability of an all-solid-state supercapacitor needs to be confirmed.

In this paper, we report the fabrication of an all-solid-state supercapacitor, which uses a Nafion<sup>®</sup> membrane, for hybridization with a DMFC. The capacitance of the supercapacitor was optimized by the amount of Nafion<sup>®</sup> ionomer used in the RuO<sub>2</sub> electrode. In order to verify the reliability and properties of the all-solid-state supercapacitor, cyclic voltammetry and charge–discharge tests were performed. The potential for its application as a high energy and power device was investigated by preliminary hybridization tests.

## 2. Experimental

The structure of an all-solid-state supercapacitor was fabricated using a Nafion<sup>®</sup> polymer membrane. The pastes of RuO<sub>2</sub> particle (Aldrich) and a Nafion<sup>®</sup> ionomer (Aldrich)

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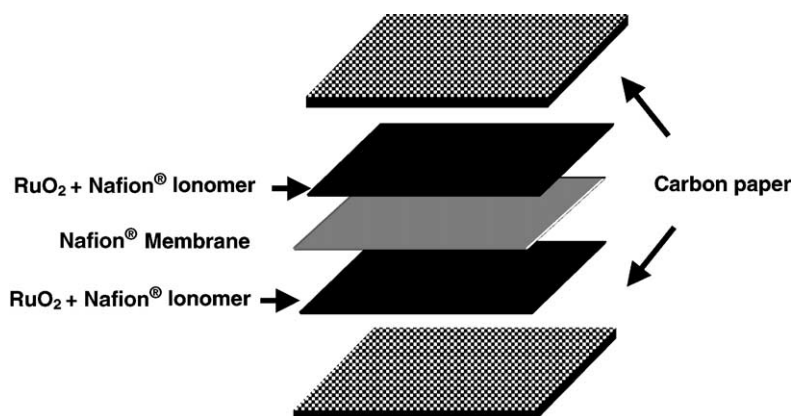


Fig. 1. Structure of all-solid-state supercapacitor using Nafion<sup>®</sup> solid polymer electrolyte membrane. The membrane is Nafion<sup>®</sup> 117 and carbon paper serves as the current collector.

were applied to carbon fiber paper (Torray Inc.) by the brush method with the same loading on each electrode. A Nafion<sup>®</sup> solid polymer membrane served as the solid electrolyte and was obtained after treatment with H<sub>2</sub>O<sub>2</sub>, deionized water, and then a sulfuric acid solution at boiling temperature for over 1 h. These electrodes and the membrane were hot-pressed to prevent ohmic resistance and to form good contact between the inorganic electrodes and the polymer membranes.

The membrane–electrode assembly (MEA) in the DMFC consisted of catalyst electrodes and the Nafion<sup>®</sup> membrane. The catalyst pastes were prepared with mixtures of catalysts, namely, Pt at the cathode and Pt–Ru at the anode, and a Nafion<sup>®</sup> ionomer solution. The pastes were applied by

means of a brush method to carbon fiber paper for the anode and cathode. The loading on both electrodes was 5 mg cm<sup>-2</sup>. A Nafion<sup>®</sup> membrane for use as a proton-conducting path was obtained by the method described before. The hot-pressing step for the MEA was carried out at 110 °C and 800 psi for 3 min. The MEA was fixed by a carbon plate with a channel as a path for methanol solution and oxygen.

Charge–discharge curves were obtained using a WMPG 3000 cyclor (Wonatech) in order to confirm the capacitor characteristics of the supercapacitor. The constant-current mode was utilized and the voltage range was 0–1 V. Cyclic voltammogram (CV) of the supercapacitor was obtained using an AUTOLAB from Eco Chemie. A unit cell test of the

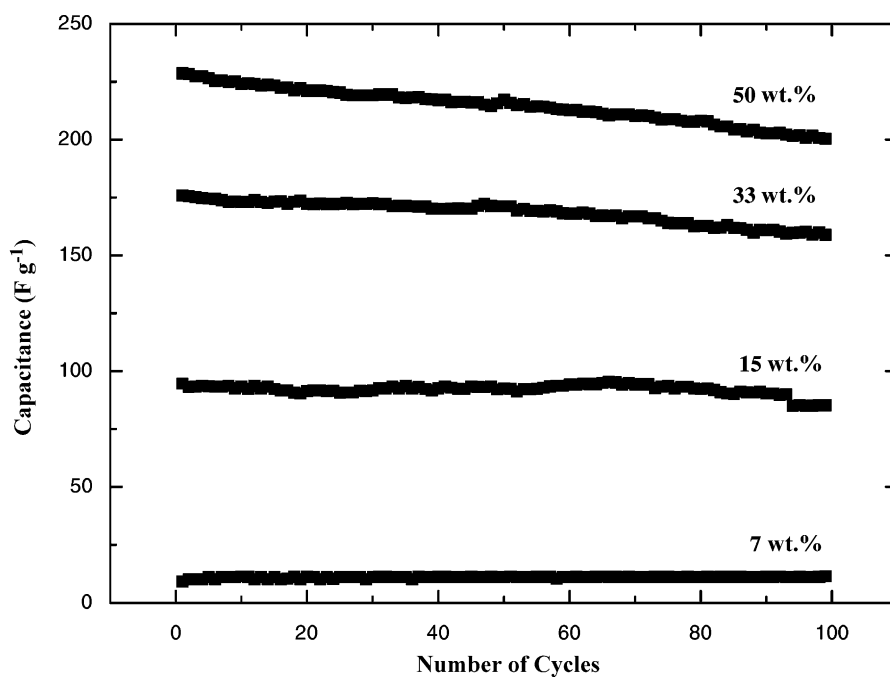


Fig. 2. Comparison of capacitance as function of amount (wt.%) of Nafion<sup>®</sup> ionomer in supercapacitor pastes. The pastes are mixtures of RuO<sub>2</sub> and Nafion<sup>®</sup> ionomer using isopropyl alcohol as solvent.

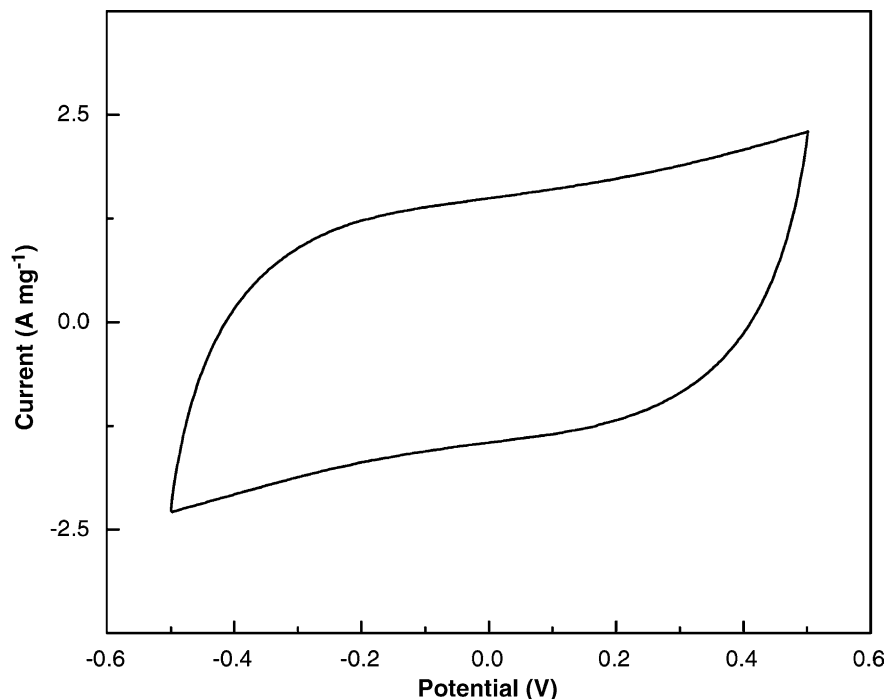


Fig. 3. Cyclic voltammogram for all-solid-state supercapacitor containing 33 wt.% Nafion<sup>®</sup> at scan rate of 20 mV s<sup>-1</sup>.

DMFC was performed with an electrical load by measuring the cell potential under constant current. A 2.0 M methanol solution, as the fuel, was supplied by a liquid micropump (Masterflex) at 1 cm<sup>3</sup> min<sup>-1</sup>, and O<sub>2</sub> was regulated by a flow-meter (500 cm<sup>3</sup> min<sup>-1</sup>, dry O<sub>2</sub>).

### 3. Results and discussion

The structure of the supercapacitor is shown in Fig. 1. The substrate, the current collector, is carbon fiber paper. As a separator and solid electrolyte, Nafion<sup>®</sup>, an excellent

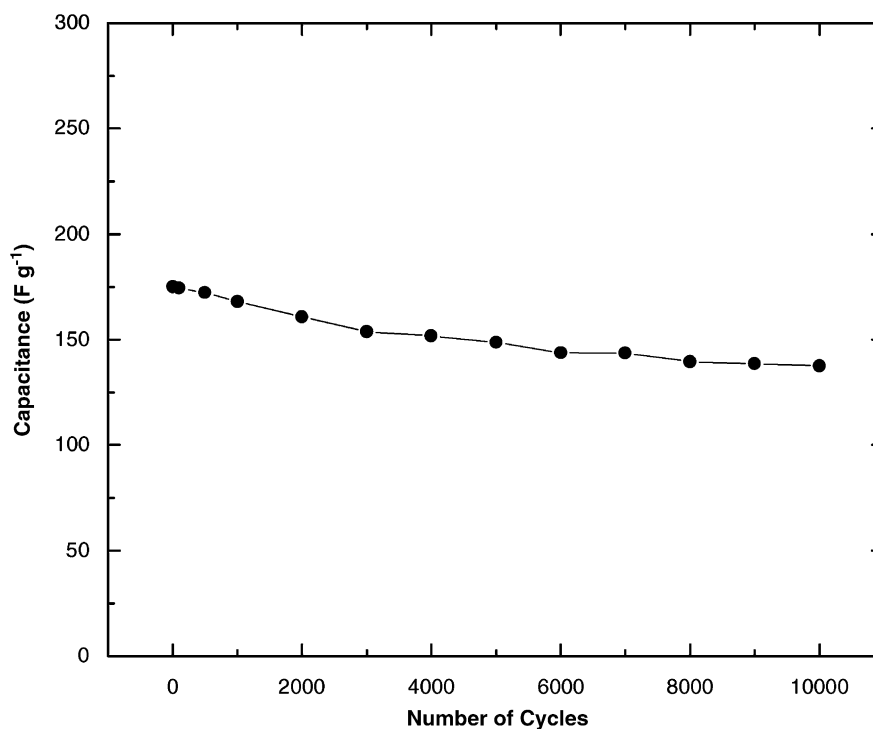


Fig. 4. Capacitance of all-solid-state supercapacitor containing 33 wt.% Nafion<sup>®</sup> ionomer at constant current of 12.5 mA cm<sup>-2</sup> during 10,000 cycles.

proton-conducting membrane, is used. The electrodes of the supercapacitor consist of amorphous ruthenium hydroxide and the Nafion<sup>®</sup> ionomer. Such a structure is very similar to that of a conventional MEA in a polymer electrolyte membrane fuel cell (PEMFC) using a Nafion<sup>®</sup> membrane. The conventional MEA structure of a PEMFC is a sandwich-like structure which comprises a polymer membrane inserted between the anode and cathode which use metal catalysts such as a platinum or platinum–ruthenium alloy instead of capacitor materials.

The capacitances of the Nafion<sup>®</sup>-supercapacitors were compared in terms of the amount of Nafion<sup>®</sup> ionomer in the electrode pastes, as shown in Fig. 2. Nafion<sup>®</sup> ionomer was

added to the paste to enable interface formation between the capacitor material and the solid electrolyte. In fact, catalyst pastes for the DMFC electrodes contain Nafion<sup>®</sup> ionomer for achieving an effective interface between the catalyst and solid electrolyte. Optimum values of the Nafion<sup>®</sup> ionomer at the anode and cathode have been reported [10]. A Nafion<sup>®</sup>-based supercapacitor is believed to provide a higher proton conductivity than a supercapacitor without a Nafion<sup>®</sup> ionomer. The supercapacitor with 50 wt.% Nafion<sup>®</sup> ionomer shows the best capacitance, viz. 200–230 F g<sup>-1</sup> (Fig. 2). Due to the degradation and instability of 50 wt.% Nafion<sup>®</sup>, however, a 33 wt.% Nafion<sup>®</sup> ionomer was determined to be the most promising from the point of view of capacitance

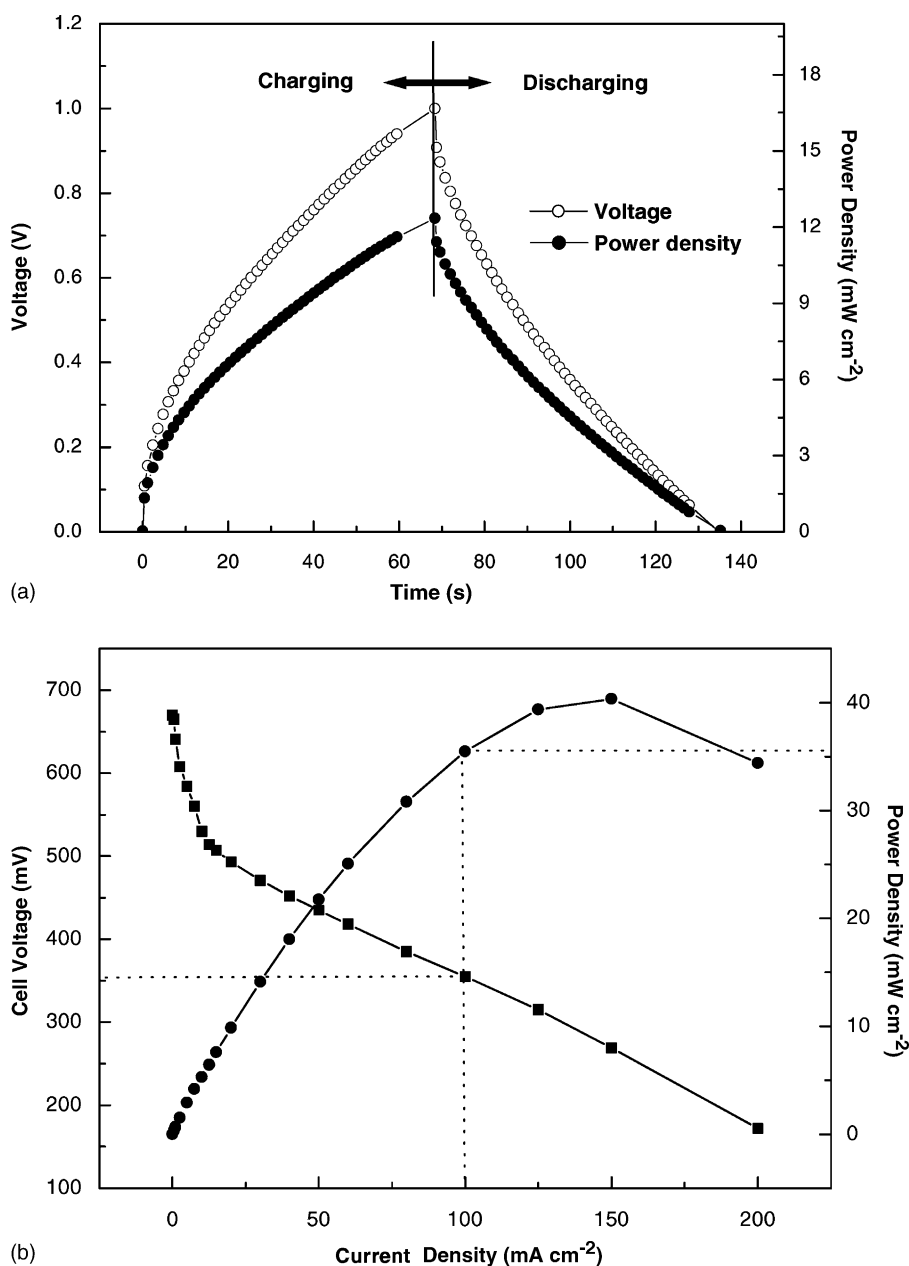


Fig. 5. (a) Charge and discharge curve of supercapacitor at 12.5 mA cm<sup>-2</sup>; (b) polarization curve of DMFC at 25 °C; 2 M methanol solution at anode is supplied at rate of 1 cm<sup>3</sup> min<sup>-1</sup> and a stream of dry oxygen is present at cathode at 500 cm<sup>3</sup> min<sup>-1</sup> (both electrodes operated at atmospheric conditions).

and stability. A very small amount of Nafion<sup>®</sup> ionomer, namely, 7 wt.%, did not improve the capacitance of the supercapacitor electrode.

A CV of an all-solid-state supercapacitor at a scan rate of  $20 \text{ mV s}^{-1}$  is shown in Fig. 3. The capacitance of the supercapacitor, as shown by the CV, corresponds to that obtained from the charge–discharge curve. It has been reported [11] that amorphous ruthenium hydroxide has a high capacity of  $720 \text{ F g}^{-1}$  in acid solution. By comparison, the all-solid-state supercapacitor displays a small capacitance. Nevertheless, such a solid-state supercapacitor, without liquid electrolytes such as  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ , might well have more applications and advantages. Finally, the stability of the Nafion<sup>®</sup>-supercapacitor has been confirmed, as indicated in Fig. 4 which shows capacitance versus number of

cycles. Compared with an initial capacitance of  $\sim 200 \text{ F g}^{-1}$ , the capacitance after 10,000 cycles is reduced to  $150 \text{ F g}^{-1}$ , i.e. by only about 30% of the original capacitance. This implies that an all-solid-state supercapacitor with a Nafion<sup>®</sup> membrane can be operated with acceptable stability under capacitor operating conditions.

A supercapacitor stores and generates electrical energy and power by charging and discharging electricity as shown in Fig. 5a. In general, due to the low ionic conductivity of solid electrolytes, all-solid-state supercapacitors have a low capacitance and current–resistance ( $IR$ ) drop, compared with supercapacitors with liquid electrolytes. An all-solid-state supercapacitor using a Nafion<sup>®</sup> membrane shows, however, a relatively low  $IR$  drop. The excellent capacitance of the supercapacitor is the result of the high ion ( $\text{H}^+$ )

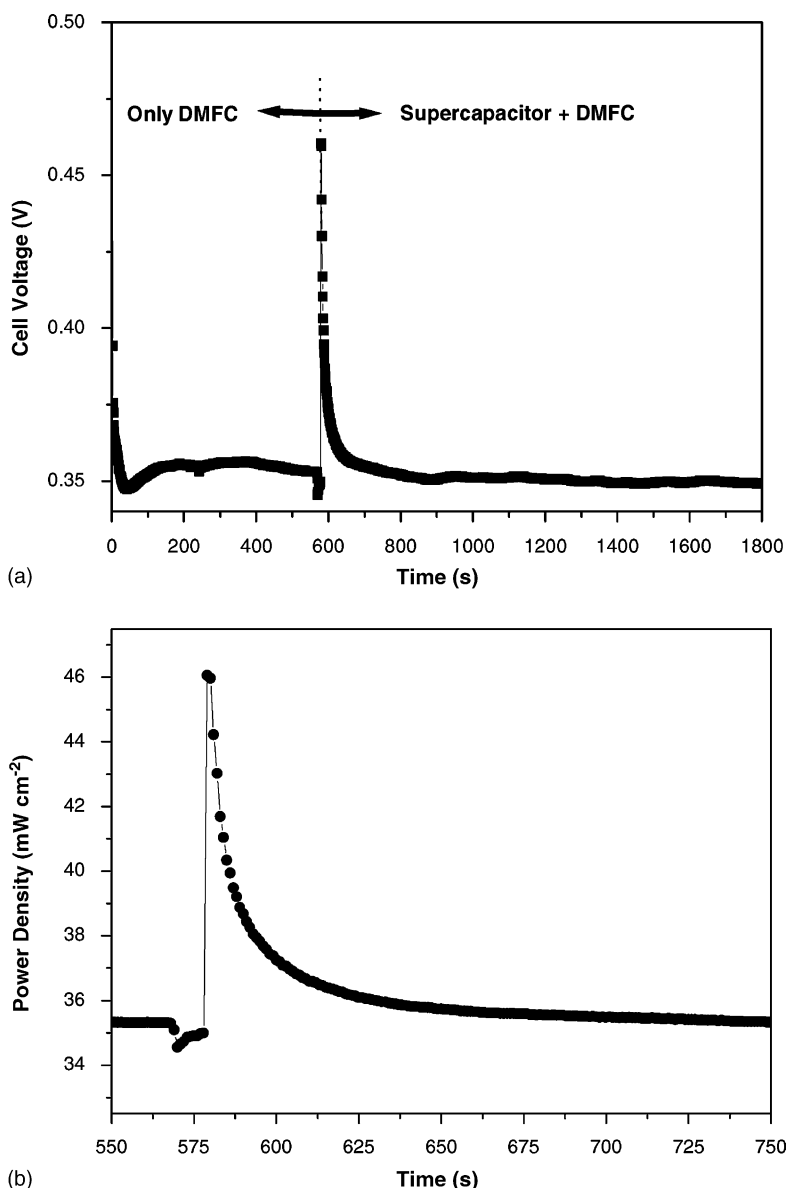


Fig. 6. (a) Cell voltage and (b) power density before/after hybridization of DMFC with supercapacitor.

conductivity of the Nafion<sup>®</sup> membrane. On charging at 25 °C with a constant current of 12.5 mA cm<sup>-2</sup> between 0 and 1 V, the supercapacitor delivers a power of 12 mW cm<sup>-2</sup>.

On the other hand, a DMFC, as shown in Fig. 5b produces electrical energy and power by discharging the system without charging as long as fuel and oxidant are supplied. In the polarization curve, a DMFC at high voltage near its open-circuit potential generates a low current density but at low voltage discharges a high current density and a high power density. In general, the power of a DMFC increases with increasing cell temperature (>80 °C). Since, however, a relatively low temperature such as 25 °C would be the practical temperature for applications such as in electric devices, the polarization curve has been measured at 25 °C. The open-circuit potential and maximum power density are 671 mV and 40 mW cm<sup>-2</sup>, respectively.

The DMFC was connected in parallel with an all-solid-state supercapacitor. The DMFC and supercapacitor were linked with an electric load. During a hybridization test, a constant current of 100 mA cm<sup>-2</sup> was applied to the DMFC. As shown in Fig. 5b, a DMFC at current density of 100 mA cm<sup>-2</sup> generates a power density of 35 mW cm<sup>-2</sup>. Ideally, power density should continue as long as fuel and oxidant are available. The supercapacitor was charged and discharged at a constant current of 12.5 mA cm<sup>-2</sup> between 0 and 1 V. In Fig. 5a, charging time and power density are, approximately 70 s and 12 mW cm<sup>-2</sup>, respectively, while the same power density discharged for the same number of seconds. During charging of the supercapacitor, the switch between DMFC and supercapacitor was off in order to store power in the capacitor and to investigate energy transfer of the capacitor into the DMFC. After charging, the switch was on at the same time as supercapacitor discharging.

A comparison of the performance of a DMFC alone and a DMFC hybrid with a supercapacitor is given in Fig. 6. Actually, as indicated in Fig. 6a, at a hybridization DMFC voltage of 0.35 V, the voltage abruptly increases to over 0.45 V after being connected with the supercapacitor. In this experiment, the DMFC was operated under a constant current of 100 mA cm<sup>-2</sup>. Accordingly, the increase of cell voltage led to an enhancement in performance enhancement of the DMFC. The change of power density before/after connecting with supercapacitor is represented in Fig. 6b. The power density of the DMFC alone is about 35 mW cm<sup>-2</sup>, but when connected to the supercapacitor, this value rapidly increases to over 46 mW cm<sup>-2</sup>. After discharging the supercapacitor, the power of the DMFC is recovered and continues at the original value of 35 mW cm<sup>-2</sup>. This indicates that the supercapacitor is discharged when transferring power to the DMFC until the supercapacitor is totally discharged. The power difference for before and after hybridization is 11 mW cm<sup>-2</sup>. The cell power is improved by over 30% compared with that of the DMFC alone at 25 °C. As shown in Fig. 7, the abrupt voltage increase of DMFC by the supercapacitor (hybridization) is similar to an instantaneous change by a higher pulse voltage than the operating conditions (pulse). Such an abrupt change in the pulse peak occurs without any energy transfer, while the increase in voltage of the supercapacitor results from energy transfer from the supercapacitor to the DMFC. In addition, compared with the former case, the abrupt voltage increase of the supercapacitor gradually falls off. Commonly, these changes recover to higher cell voltage, i.e. cell performance is improved after a voltage shock. It is likely that the voltage shock by both supercapacitor and pulse results from a temporary relaxation of the DMFC under the high voltage. Finally, because of the complementary nature and the

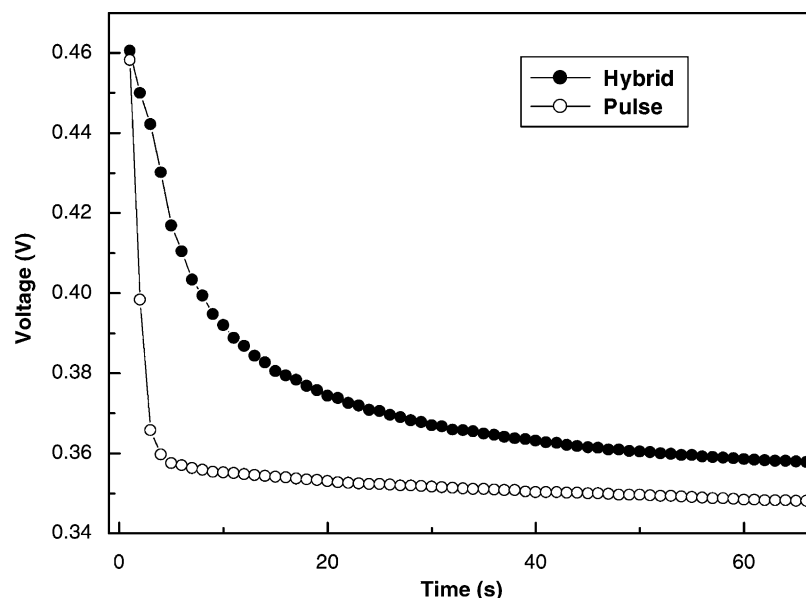


Fig. 7. Comparison of cell voltage with hybridization and pulse.

similarity of the structures of the all-solid-state supercapacitor and the DMFC, the integration of such devices appears to be possible and research on such a process is currently underway.

#### 4. Conclusions

An all-solid-state supercapacitor using a Nafion<sup>®</sup> polymer membrane and an ionomer shows relatively good capacitance ( $\sim 200 \text{ F g}^{-1}$ ) as demonstrated by cyclic voltammetry and charge–discharge tests. This supercapacitor also exhibits a relatively stable capacitance during 10,000 cycles. The role of the Nafion<sup>®</sup> ionomer has been examined in order to optimize the interface between the RuO<sub>2</sub> particles and the solid electrolyte membrane. As a result, a hybrid system comprised of a DMFC with an all-solid-state supercapacitor using Nafion<sup>®</sup> membranes has been designed. It is confirmed that the power density discharged by the supercapacitor is effectively transferred to the DMFC. The DMFC, when connected to the supercapacitor, shows instantaneous high power density and the enhanced power density persists after complete discharging of the supercapacitor. Further work will be required to evaluate such a preliminary device for use in practical applications.

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#### References

- [1] A. Hamnett, *Catal. Today* 38 (1997) 445.
- [2] H.F. Oetjen, V.M. Schmidt, U. Stimming, E. Trila, *J. Electrochem. Soc.* 143 (1996) 3838.
- [3] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, *Science* 280 (1998) 1735.
- [4] B.E. Conway, V. Briss, J. Wojtowicz, *J. Power Sources* 66 (1997) 1.
- [5] S. Trasatti, P. Kurzweil, *Platinum Metals Rev.* 38 (1994) 46.
- [6] L.P. Jarvis, T.B. Atwater, P.J. Cygan, *J. Power Sources* 79 (1999) 60.
- [7] D.J. Tarnowski, H. Lei, C. Peiter, M. Wixom, in: *Proceedings of the 200th Meeting of The Electrochemical Society, Abstracts, San Francisco, 2 September 2001*.
- [8] T. Osaka, X. Liu, M. Nojima, T. Momma, *J. Electrochem. Soc.* 146 (1999) 1724.
- [9] S. Sarangapani, US Patent No. 5,136,474 (1992).
- [10] S.C. Thomas, X. Ren, S. Gottesfeld, *J. Electrochem. Soc.* 146 (1999) 4354.
- [11] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.