

Short communication

Compact dynamic hydrogen electrode unit as a reference electrode for PEMFCs

Zyun Siroma, Ryou Kakitsubo, Naoko Fujiwara, Tsutomu Ioroi,
Shin-Ichi Yamazaki, Kazuaki Yasuda*

*Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*

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Abstract

A compact and easy-handling design for the dynamic hydrogen electrode (DHE) was proposed. Before mounting in the cell, a unitized set was made by the hot-pressing of two 2 mm × 5 mm ionomer membranes, between which two PTFE-coated platinum wires were sandwiched. Before the hot-pressing, a small amount of paste composed of platinum black powder and an ionomer solution was dropped at the end of each wires. Prior to use in a PEMFC, a proper current value for the operation was found in an aqueous acid solution. Mounting of the DHE on a membrane electrode assembly (MEA) was done by local hot-pressing. The space for the mounting was only 2 mm in width between the gasket and edge of the gas diffusion electrode. The potential of the DHE fluctuated, but it was in the range of about 5 mV. A PEMFC with both the DHE and conventional RHE was operated, and the *I*–*V* performance of the PEMFC was measured. The potential difference between the conventional RHE and DHE was about 5 mV, which is due to the overpotential of the hydrogen evolution reaction at the DHE. Considering this difference, this DHE is available to monitor single electrode potentials.

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1. Introduction

In fundamental studies of proton exchange membrane fuel cells (PEMFCs), it is necessary to measure the single electrode potentials in order to understand the distribution of the voltage losses. However, there are some difficulties in mounting a reference electrode to the membrane electrode assembly (MEA) due to the geometric restriction. Because the electrolyte membrane is thin and the current density is high, it is hard to eliminate the *iR* drop in the electrolyte membrane. Theoretical and experimental analyses of the effect of the reference electrode position on the *iR* drop amount were investigated [1,2]. Furthermore, due to the long distance between the reference electrode and the working electrodes (gas diffusion electrodes) that may produce a potential drift

caused by the uneven distribution of water or temperature, it is preferred that the reference electrode be positioned as close as the working electrodes, especially in the case of measuring the potential distribution in the electrolyte using several reference electrodes.

For PEMFCs, the reversible hydrogen electrode (RHE) is commonly used as the reference electrode [3,4]. Hydrogen gas for the anode gas is usually shared with the RHE. However, in case the anode gas contains carbon monoxide, a separated channel to feed pure hydrogen gas was used to avoid poisoning [4].

Dynamic hydrogen electrode (DHE) is another kind of reference electrode used for fuel cells. It uses the potential of the hydrogen evolution reaction (HER) [5], and is used as a substitute for the RHE. The potential of the DHE contains a slight overvoltage caused by the reaction, however, is hardly affected by the environment, e.g., presence of some organic species or local hydrogen starvation. Therefore, it can

* Corresponding author. Tel.: +81 72 751 9653; fax: +81 72 751 9629.
E-mail address: k-yasuda@aist.go.jp (K. Yasuda).

be used for the direct methanol fuel cells (DMFCs) [6–10]. Construction of the DHE is complicated and it is not easy to handle it. One reason is that it consists of two electrodes (a hydrogen evolution electrode and a counter electrode), and another is that it needs a constant current source, the value of which depends on the geometric conditions and varies after each placement in the fuel cells. This work proposes a new design for the DHE made by unitizing two electrodes into a compact assembly before mounting on the MEA. Using this design, mounting of the DHE to the MEA became easier, and the geometric conditions of the DHE electrodes remained unchanged.

2. Experimental

2.1. Fabrication of the DHE unit

An acid type Nafion[®] 112 membrane (50 μm thick, EW = 1100, DuPont) pretreated using a common procedure [11] was cut into two 2 mm × 5 mm pieces. Two pieces of PTFE-coated platinum wires (diameters with and without a coating are 0.18 and 0.127 mm, respectively, Nilaco) was prepared. About 1 mm of the PTFE coating at the end of each wire was removed. A catalyst ink mixture containing Pt black (HiSPEC 1000, 27 m² g⁻¹, Johnson Matthey), Nafion[®] solution (5 wt%, Aldrich) and 2-propanol was made. A small amount of the slurry was put on the end of each piece of PTFE-coated Pt wire by dipping, followed by drying in the ambient atmosphere. As shown in Fig. 1, the ends of the two wires were held with a spacing of ca. 1 mm between the two pieces of the Nafion[®] membrane, then hot-pressed at 20 MPa for 1 min at 140 °C. Because no electrochemically active area is exposed on the surface of the unit, there is no need to be careful about electrical isolation.

2.2. Test operation

The fabricated DHE unit was tested using a three-electrode system in a 0.5 mol dm⁻³ sulfuric acid solution deaerated by

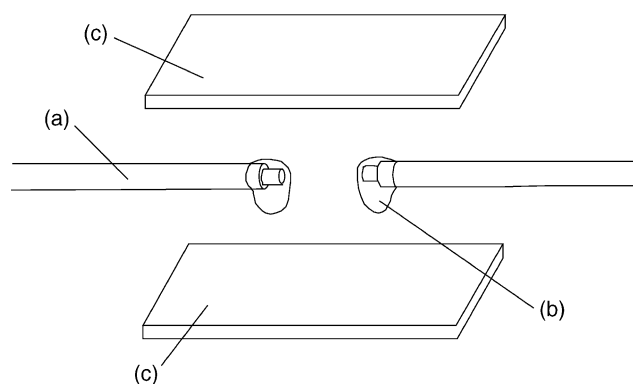


Fig. 1. Schematic diagram of the DHE unit. (a) PTFE-coated platinum wires (Ø0.18 mm), (b) small drops of the ink containing Pt black powder and a Nafion[®] resin, (c) pieces of Nafion[®] 112 membrane (2 mm × 5 mm).

nitrogen bubbling. One wire of the DHE was used as the working electrode, and the other wire as the counter electrode. A galvanostat (HA-151, Hokuto Denko) was used to apply a reductive constant current while measuring the potential of the working electrode versus a Ag/AgCl reference electrode. In addition, in order to examine the applicability of the DHE on the cathode side of the PEMFC, the operation in a solution with oxygen bubbling was also tested.

2.3. Application for a PEMFC

The MEA of the PEMFC was made by hot-pressing electrodes onto each side of a Nafion[®] 117 membrane at 7 MPa for 1 min at 150 °C. Ten square centimeter circular pieces of a commercial gas diffusion electrode (GDE) (0.5 mg Pt cm⁻², E-TEK) were used for both the anode and cathode. The cell temperature was set at 80 °C. Gas feedings to the anode and cathode were fully humidified hydrogen and oxygen at 100 sccm and atmospheric pressure, respectively. Before placing the MEA in the cell, the DHE was mounted by an additional local hot-pressing on the anode side of the MEA between the edge of the GDE and gasket as shown in Fig. 2. The width of the space used for the mounting was that of the DHE unit, i.e., 2 mm. A constant current to operate the DHE was fed by a series connection of a dry battery (9 V, 6LR61) and an adjustable resistor (0–1 MΩ) adjusted beforehand, as a floating current source having no interference with other instruments.

In order to compare the potential of the DHE with the RHE, another MEA with both the DHE and RHE was made. The RHE was made by separating a circular area of Ø5 mm from the anode. The PEMFC was operated in the constant current mode using a galvanostat (HA-505G, Hokuto Denko), and the



Fig. 2. Photograph of a MEA with the DHE unit attached just outside the gas diffusion electrodes. The gap between the ends of the two Pt wires is ca. 1 mm.

potentials of the anode, cathode, DHE and RHE were measured against the ground potential using a datalogger (Model 8420, Hioki).

3. Results and discussion

From the results of the test operation of the DHE in an aqueous solution deaerated by nitrogen bubbling, it was found that at least $50 \mu\text{A}$ of reductive current was needed for the DHE to maintain a stable potential. Too small a current causes an unsteady potential above 0 V versus RHE. The steady-state potential of the DHE operated at $50 \mu\text{A}$ was about -5 mV versus RHE. On the other hand, the operation in an oxygen saturated solution needed a much higher current to consume the oxygen diffusing through the membrane, which resulted in a much higher overvoltage of the HER. This implies that the DHE we made is adequate for use only on the anode side of the PEMFC.

To investigate the stability of the DHE mounted on a PEMFC, the potential changes with time were measured. Fig. 3 shows the measurement results of the potential difference between the DHE and PEMFC anode every 0.5 s for 3 min. The PEMFC was operated at fixed currents in the range of 0 mA cm^{-2} (open circuit) to 500 mA cm^{-2} . At any current density, fluctuations of several millivolts were observed. This seems to be due to the potential changes of not only the DHE, but also the PEMFC anode. In any case, the magnitude of the fluctuations is ca. 5 mV, and the stability of the DHE is within this range.

The DHE potential includes a deviation from the thermodynamic potential caused by the overvoltage of the HER. To confirm the amount of the deviation, a PEMFC with both the DHE and RHE was operated. Fig. 4 shows the anode and cathode single potentials measured versus the DHE, together with the anode potential versus the RHE. An almost constant difference ($\approx 5 \text{ mV}$) between the anode potential versus the DHE and RHE was observed, which seems to be due to the

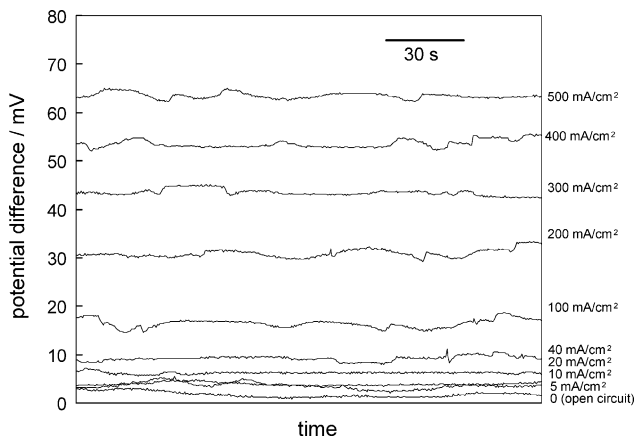


Fig. 3. Stability test: change in the potential differences between the DHE and PEMFC anode operated at fixed current densities. Data points were collected every 0.5 s.

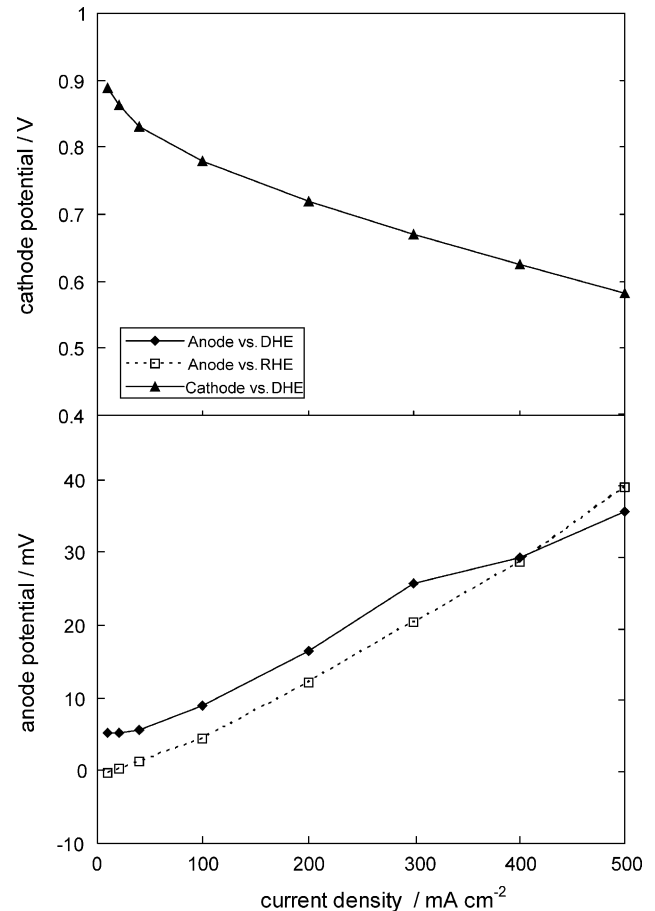


Fig. 4. Measurement of single electrode potentials of a PEMFC with a DHE and an RHE. The anode potential is plotted vs. both the DHE and RHE. Potential difference between them, which is about 5 mV, originated from the overvoltage of the DHE.

overvoltage of the HER at the DHE. This confirms that the DHE we made is adequate for measuring the single electrodes, considering the deviation from the thermodynamic potential, which can be estimated beforehand. In Fig. 4, the potential difference seems to be reversed at the higher current densities. This is probably due to the unexpected potential distributions in the lateral directions in the electrolyte membrane caused by the high current density.

A possible explanation for the fluctuations of the DHE potential with time is that the partial pressure of hydrogen gas in contact with the hydrogen evolution wire exceeds the environmental pressure and is not stable. There is room to improve the stability of the DHE by increasing the gas permeability in the electrolyte membranes composing the DHE, which is now under investigation.

4. Conclusions

As a compact DHE, a unit composed of two electrolyte membranes and two platinum wires between them was made. By operating in an aqueous acid solution, the proper current

to maintain a constant potential was found to be 50 μ A. Measurements of the potential difference between the anode and DHE in a PEMFC detected potential fluctuations in the range of ca. 5 mV, which defines the accuracy of the measurement using this DHE. The operation of a PEMFC with both the DHE and RHE confirmed that the DHE we made was adequate for measuring the single electrode potentials of the PEMFC, and there is a potential difference between the DHE and RHE of about 5 mV which came from the overvoltage of the HER.

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