Thin film electrocatalyst layer for unitized regenerative polymer electrolyte fuel cells

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Abstract

Thin film electrocatalyst layers with various PTFE and Nafion contents for unitized regenerative polymer electrolyte fuel cells (URFCs) were prepared by the paste method and the performance as URFC electrodes was examined. Comparing the terminal voltage versus current density curves of the URFC, it was found that the PTFE content in the electrocatalyst layer affected only the fuel cell performance; the electrode containing 5–7 wt.% PTFE was appropriate for the URFC. The Nafion content in the electrode affected both the fuel cell and water electrolysis performance; the electrode containing 7–9 wt.% Nafion showed good performance. The addition of a small amount of iridium catalyst (about 10 at.%) to the oxygen electrode layer significantly improved the URFC performance. Catalyst loadings can be reduced to <1/3 by using the electrode prepared by the paste method compared to the conventional one without degrading the URFC performance.
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1. Introduction

A regenerative fuel cell (RFC) is an energy storage device using hydrogen as the energy medium [1–5]. RFCs have the advantages of long-term energy storage, because of they are free from self-discharge, and theoretically higher energy densities compared to secondary batteries such as Ni/MH or Li-ion [6], however, the RFC system tend to be complicated and expensive because the RFC system usually consists of a separate fuel cell and water electrolyzer as shown in Fig. 1(a). A unitized regenerative fuel cell (URFC) is an electrochemical cell working both as the fuel cell and water electrolyzer as shown in Fig. 1(b) [7]. Compared to the conventional RFC system, a simpler and more compact system can be constructed by using the URFC because the URFC system uses only one electrochemical cell.

Most of the polarization in the URFC is caused by the oxygen redox reaction; oxygen reduction during fuel cell (FC) operation and oxygen evolution during water electrolysis (WE). Therefore, the development of an active catalyst for the oxygen redox reaction is quite important for improving the efficiency of the URFC [8–10]. As previously reported, the PTFE-bonded catalyst electrode prepared from Pt black and a high-surface-area IrO_2 showed good catalytic properties for oxygen reduction during fuel cell operation and for oxygen evolution during water electrolysis [11,12]. However, the catalyst loadings were rather high (about 8–10 mg cm^{-2}) in the previous study, because the electrode was prepared by roll-press method, in which the electrode have to be made into self-standing thin film. Thus, the reduction of the catalyst is very difficult under a certain catalyst loading, so that further efforts are necessary to develop another preparation method of electrode for URFC with reduced catalyst loadings.

In the present study, the thin film electrocatalyst layer for the URFC was developed to reduce the catalyst loading by modifying the preparation technique for the PEFC electrode. Comparing to PEFC electrode, contradicting water management is required for URFC electrode; appropriate hydrophobicity is required during fuel cell operation, on the other hand, hydrophilic property is necessary for water electrolysis. Therefore, the amount of hydrophobic PTFE and relatively hydrophilic Nafion in the electrode layer would be important for URFC. A variety of thin film electrodes were prepared and the effects of the PTFE and Nafion contents in the electrodes on the URFC performance (fuel cell and water electrolysis) were reported.

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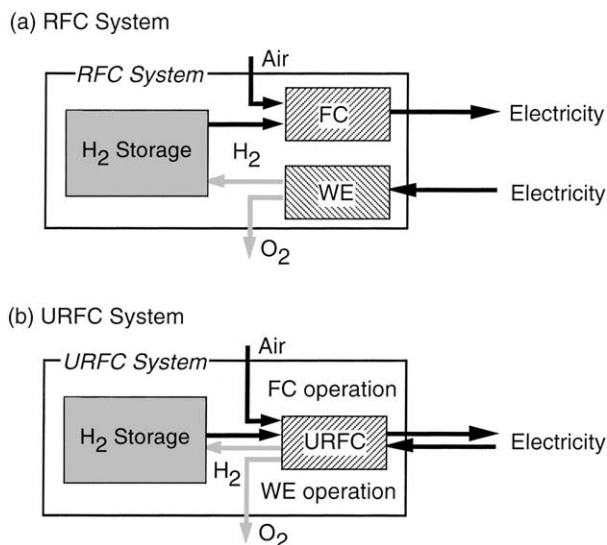*E-mail address:* ioroi-t@aist.go.jp (T. Ioroi).

Fig. 1. Concepts of a regenerative fuel cell (RFC) and a unitized regenerative fuel cell (URFC).

2. Experimental

2.1. Preparation of electrocatalyst layer

The electrocatalyst layer for the oxygen electrode of the URFC was prepared in a manner similar to preparing the gas diffusion electrodes for a PEFC [13]. Commercially available platinum black fine powder (Johnson Matthey, specific surface area: 26.1 $m^2 g^{-1}$) and iridium black fine powder (Johnson Matthey, specific surface area: >20 $m^2 g^{-1}$) were mixed by the appropriate ratio. After the catalyst mixture was treated with a PTFE emulsion (Daikin, Polyflon) to increase the hydrophobic property of the catalyst, the catalyst/PTFE and 5 wt.% Nafion solution (Aldrich, 5 wt.% solution) were thoroughly mixed and the obtained catalyst/PTFE/Nafion slurry was applied to a PTFE sheet (Nitto Denko, 50 μm thick) using the doctor blade technique, and then dried in a vacuum oven at 80 °C for 1 h. The catalyst loadings were about 2–4 $mg cm^{-2}$ of Pt (and Ir). The electrocatalyst-coated PTFE sheets were placed on both sides of the pre-treated Nafion 115 membrane [14] and then hot-pressed at 150 °C to form the membrane electrode assembly (MEA).

2.2. Evaluation of URFC performance

Evaluation of the URFC performance was conducted using a single cell with an active electrode area of 10 cm^2. The test cell used for the performance evaluation was described in a previous paper [12]. The I–V characteristics of the URFC were measured galvanostatically and then the internal resistance of the cell was also determined by current interrupting method. During the fuel cell operation, the test cell was operated at 80 °C with H_2/O_2 at pressures of

0.30/0.30 MPa. The both gases were supplied to the cell at a rate of 100 $ml min^{-1}$ throughout the measurement. The corresponding fuel and oxidant utilization were calculated as 35 and 18% at 500 $mA cm^{-2}$, respectively. Humidification of H_2 was carried out by bubbling the H_2 through water contained in stainless steel bottle thermostated at 80 °C. Oxygen was supplied to the cell without humidification. During the water electrolysis operation, ultra-purified water (Organo, Puric-MX) was supplied from the water reservoir to the bottom of the both electrode side of the test cell and the produced H_2 and O_2 gases were evolved from the top of the cell. Water circulation was took place spontaneously by the evolved gas-lifting for H_2 electrode side, and water circulated at a rate of 75 $ml min^{-1}$ for O_2 electrode side. The cell and the water reservoir were kept at 80 °C and atmospheric pressure.

3. Results and discussion

In order to confirm the morphology of the prepared catalyst layer, the prepared MEA was observed by SEM. Fig. 2 shows a typical SEM image of the cross-section of a electrode/Nafion membrane. The electrode thickness was uniform throughout the electrode layer and the catalyst loading amount was about 3 $mg cm^{-2}$. Compared to the conventional PTFE-bonded catalyst layer prepared by the roll-pressing method [11,12], the thickness and the catalyst loading amount of the electrode by the paste method were reduced to 1/3.
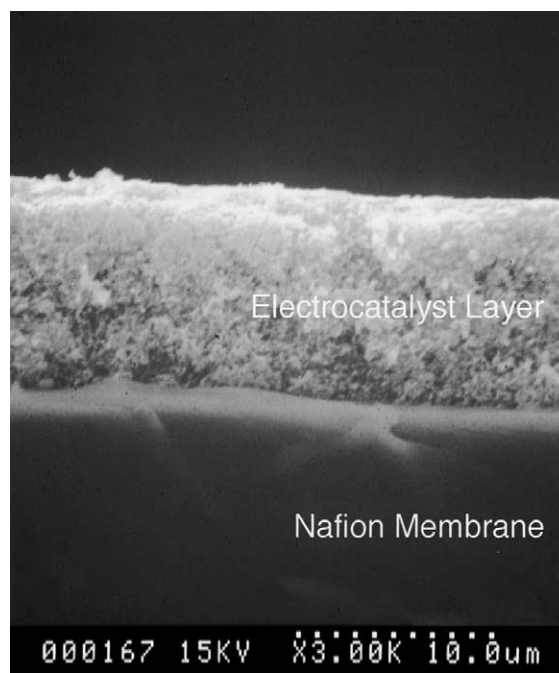

Fig. 2. Scanning electron micrograph of a cross-section of the electrode prepared by paste method. Catalyst loading amount was 3 $mg cm^{-2}$.
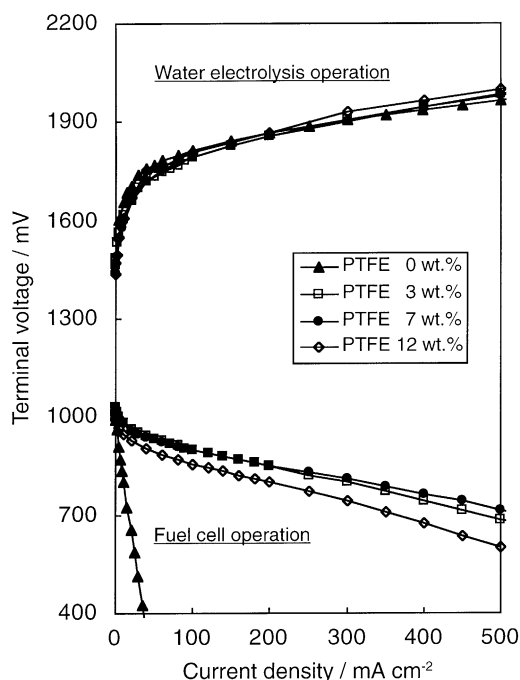
Fig. 3. Terminal voltages vs. current density curves of 10 cm^2 URFCs with various PTFE loadings in the oxygen electrode. PTFE content: 0–12 wt.%, Nafion content: 9 wt.%. Fuel cell: the cell operated with H$_2$/O$_2$ at 80 °C, respective pressures of 0.30/0.30 MPa, respective flow rate of 100/100 ml min^{-1}, humidification temperature of 80 °C. Water electrolysis: the cell operated with purified water at 80 °C and atmospheric pressure.

Fig. 4. Terminal voltages vs. current density curves of 10 cm^2 URFCs with various Nafion loadings in the oxygen electrode. PTFE content: 6.3 wt.%, Nafion content: 1.5–14 wt.%. Fuel cell: the cell operated with H$_2$/O$_2$ at 80 °C, respective pressures of 0.30/0.30 MPa, respective flow rate of 100/100 ml min^{-1}, humidification temperature of 80 °C. Water electrolysis: the cell operated with purified water at 80 °C and atmospheric pressure.

3.1. PTFE and Nafion contents in the electrode

In order to investigate the effect of the PTFE and Nafion contents in the paste electrode on the URFC performance, the paste Pt electrodes with various PTFE (0–12 wt.%) and Nafion (1.5–14 wt.%) contents were prepared and both the fuel cell and water electrolysis performances were examined. In this section, an iridium catalyst was not used for the oxygen electrode in order to focus our attention on the effects of the PTFE and Nafion contents and to exclude the experimental error factor caused by the difference in the iridium content between the electrodes prepared by different batches.

Fig. 3 shows the terminal voltage versus current density curves of URFC with the electrode containing 0–12 wt.% PTFE with 9 wt.% Nafion. Without PTFE, the fuel cell performance was very poor, which was probably due to catalyst wetting in the electrode. With the increasing PTFE content, the fuel cell performance was improved and showed a maximum at around 7 wt.% PTFE content. Increasing the PTFE loading by more than 7 wt.%, a performance degradation of the fuel cell occurred. On the other hand, all of the I–V curves for water electrolysis in Fig. 3 are almost on the same trace, it was indicated that the water electrolysis performance scarcely depended on the PTFE content. The reason why PTFE content only affected fuel cell performance is not clear at the present
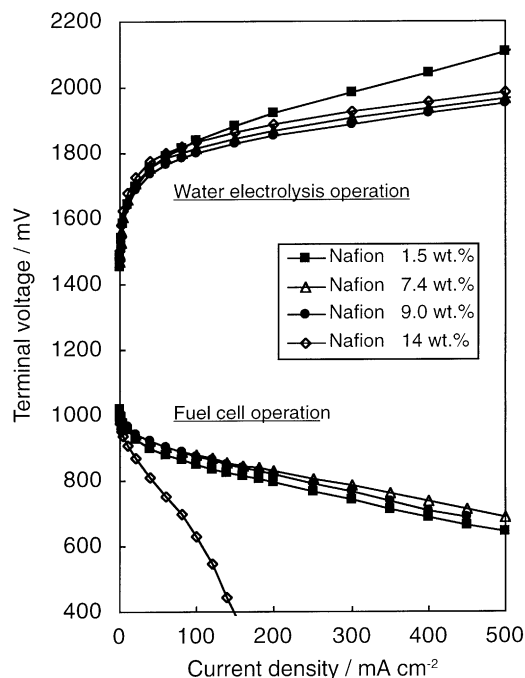
state, however, the performance degradation of the fuel cell at >10 wt.% PTFE could not be ascribed to the increase in the resistivity of the electrode, because the internal resistance of the cell at >10 wt.% PTFE determined by the current interrupting method is similar to that of the cell <10 wt.% PTFE.

Fig. 4 shows the terminal voltage versus current density curves of the URFC with the electrode containing 1.5–14 wt.% Nafion with 6.3 wt.% PTFE. The Nafion content affected both the fuel cell and water electrolysis performances, in particular, significant degradation occurred during the fuel cell operation when the Nafion content was relatively high. The terminal voltages of the URFC during the fuel cell operation and water electrolysis at 200 mA cm^{-2} were replotted as a function of the Nafion content in Fig. 5. It was found from Fig. 5 that both the fuel cell and water electrolysis performances were good at 7–9 wt.% Nafion. The performance degradation at <7 wt.% Nafion was probably due to the lack of effective reaction sites, i.e. the interface between Pt and Nafion electrolyte. The URFC performance also degraded at >9 wt.% Nafion, which was ascribed to the increasing resistance of mass transfer such as O$_2$ or H$_2$ gas diffusion into the electrode or gas desorption from the electrode. Based on these results, it would be concluded that the appropriate PTFE and Nafion contents in the URFC electrode are around 5–7 and 7–9 wt.%, respectively.
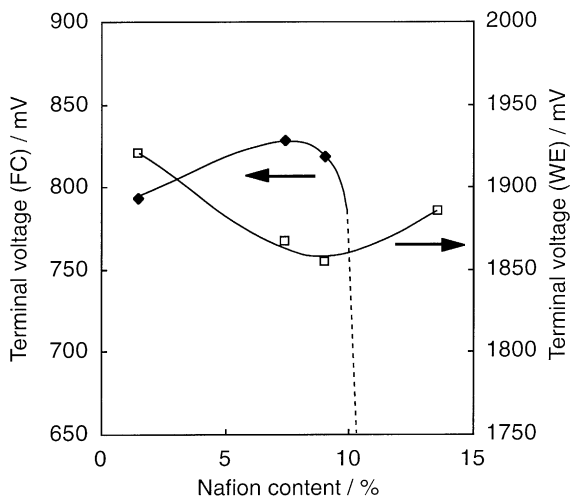
Fig. 5. Terminal voltages of the cell during fuel cell and water electrolysis operation at 200 mA cm^{-2} as a function of Nafion content in the oxygen electrode. Experimental conditions: see Fig. 4.

3.2. Iridium content in the oxygen electrode

As reported in previous papers [11,15], the addition of iridium metal or iridium oxide to the oxygen electrode dramatically improved the water electrolysis efficiency, however, the efficiency of the fuel cell operation decreased. Therefore, the iridium content in the oxygen electrode is an
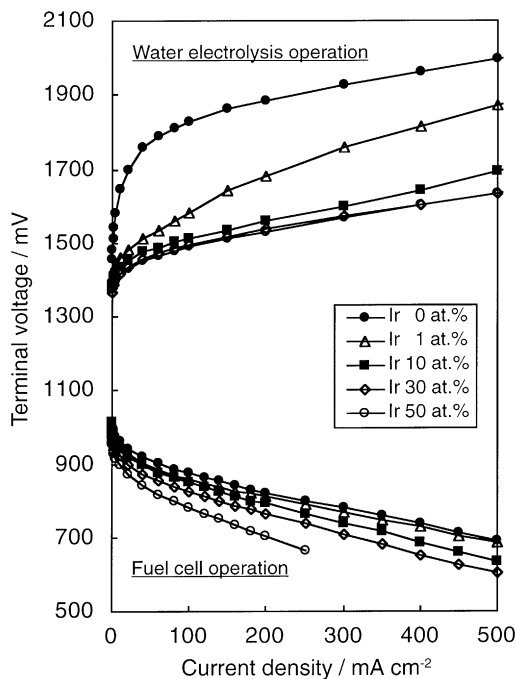

Fig. 6. Terminal voltages vs. current density curves of URFCs with various iridium contents in the oxygen electrode. Iridium content: 0–50 at.%, PTFE content: 6 wt.%, Nafion content: 5 wt.%. Fuel cell: the cell operated with H$_2$/O$_2$ at 80 °C, respective pressures of 0.30/0.30 MPa, respective flow rate of 100/100 ml min^{-1}, humidification temperature of 80 °C. Water electrolysis: the cell operated with purified water at 80 °C and atmospheric pressure.
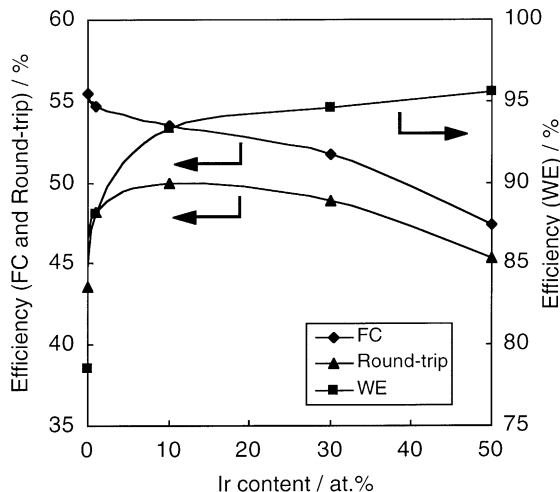

Fig. 7. Energy conversion efficiencies for fuel cell (FC), water electrolysis (WE), and round-trip of URFCs as a function of iridium content (based on the thermoneutral potential, $-\Delta H/nF$). Experimental conditions: see Fig. 6.

important factor for maximizing the URFC performance. Fig. 6 shows the terminal voltage versus current density curves of the URFC with the oxygen electrode containing 0–50 at.% iridium with 6 wt.% PTFE and 5 wt.% Nafion. The significant decrease in the terminal voltage for water electrolysis occurred with the addition of only a small amount of iridium. The cell voltage for fuel cell operation decreased with the increasing iridium content, however, these decreases were much smaller than that for the water electrolysis.

Based on the results shown in Fig. 6, the energy conversion efficiency of the fuel cell, water electrolysis and round-trip operations (electric power → hydrogen → electric power) can be calculated using the previously reported equations, based on the thermoneutral potential, $-\Delta H/nF$ [11]. These calculated efficiencies at 200 mA cm^{-2} are shown in Fig. 7 as a function of iridium content in the oxygen electrode. As expected from the terminal voltage versus current density curves, the efficiency of the fuel cell decreased and the efficiency of the water electrolysis increased with an increase in the iridium content. Consequently, the efficiency curve of the round-trip had a maximum at around 10 at.% Ir. This result agreed well with the previous result for the URFC using the electrode prepared by the roll-press method.

3.3. URFC performance of paste and roll-press electrodes

For comparison of the utilization efficiency of the catalyst, the terminal voltage versus catalyst-mass-normalized current curves of the URFC using the paste electrode and the roll-press electrode are shown in Fig. 8. Preparation of the roll-press electrode was described in the previous paper [11]. The oxygen electrode of the both cells contained a 10 at.% Ir catalyst. The catalyst loading amounts of the paste and
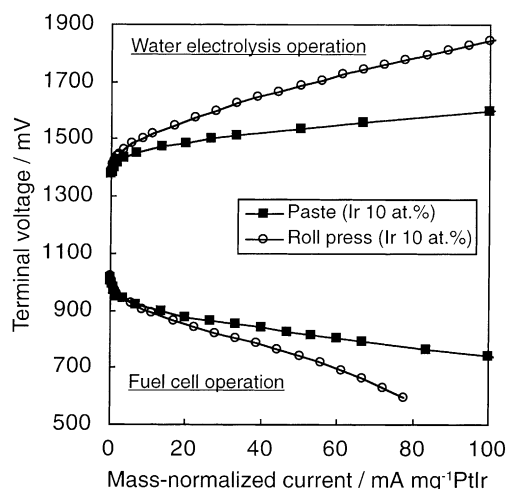
Fig. 8. Terminal voltages vs. mass-normalized current curves of URFCs using the oxygen electrodes prepared by paste and roll-press methods. The paste electrode; iridium content: 10 at.%, PTFE content: 6 wt.%, Nafion content: 5 wt.%. The roll-press electrode; iridium content: 10 at.%, PTFE content: 15 wt.%, Nafion content: 9 wt.% [11]. URFC operation conditions: see Fig. 6.

roll-press electrode were 3 and 9 mg cm^{-2}, respectively. As can be seen in Fig. 8, the paste electrode cell showed a higher terminal voltage during fuel cell operation and a lower voltage during water electrolysis at a given normalized current than the roll-press electrode cell, which suggested that the electrocatalyst in the paste electrode was utilized more effectively than that in the roll-press electrode during both operation modes. Therefore, it was concluded that utilization of the paste electrode for the URFC is an effective way to reduce the loading amount of the electro-catalyst.

4. Conclusions

The electrodes for the URFC were prepared by the paste method and the performance of the URFC using these electrodes were examined. The electrode containing 5–7 wt.% PTFE and 7–9 wt.% Nafion was appropriate for the URFC. The addition of about 10 at.% Ir to the oxygen electrode significantly improved the URFC performance. Although more study is required to further decrease the catalyst loading, this study showed that utilization of the paste electrode is an effective way to reduce the loading amount of the URFC electrocatalyst.

Acknowledgements

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