Stack Performance of Proton Exchange Membrane Based Unitized Reversible Fuel Cells

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Abstract

Proton exchange membrane (PEM) based unitized reversible fuel cells (URFCs) have attractive features as a key component of hydrogen utilization systems. To determine if drawbacks that do not appear in a small-scale single cell of a URFC are significant when a URFC has larger cells in a stack configuration required for commercial applications, a pilot-scale URFC system was successfully operated in both the electrolysis and fuel cell operation modes and both its overall stack performance and the performance variation between cells were measured. No significant drawbacks due to larger cells or stacking were detected in either mode. Local hydrogen pressure at the generation point during electrolysis mode and local flooding during fuel cell mode is examined based on experimental data.

Keyword(s): Unitized reversible fuel cell, Pilot-plant, Local hydrogen pressure, Local flooding

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1. Introduction

Recently, hydrogen is attracting attention as an energy carrier for the temporary storage buffer of intermittent renewable energy, such as solar and wind⁹. For this purpose, hydrogen is typically produced by a water electrolyzer powered by a renewable energy source (RES), such as a photovoltaic system or wind turbine, and is then stored in various forms, such as compressed, metal hydride, or liquefied. Such stored hydrogen can be used as fuel for power generation devices such as fuel cells. Hydrogen utilization systems composed of an electrolyzer, storage apparatus, and fuel cell have been studied by many countries for several decades. Compared with secondary batteries, hydrogen storage has several advantages in its high energy density and long-term stability.

In typical operation of a hydrogen utilization system, there is no overlap time between its two operation modes, electrolysis (EL) and fuel cell (FC) modes. A proton exchange membrane (PEM) electrolyzer and a proton exchange membrane fuel cell (PEMFC) both use a common PEM as the electrolyte, and have a similar cell/stack design. From a technical viewpoint, a unitized cell/stack of these two electrochemical devices is possible. Unitized reversible fuel cells (URFCs) based on a PEM have been studied for several decades²-⁵ as an energy device for space⁶-⁸ or terrestrial applications⁹,¹⁰. As an energy-conversion device, URFCs have several advantages over the discrete installation of an electrolyzer and a fuel cell: 1) reduced cost of the total system, 2) higher operating ratio per individual device, 3) lower maintenance, and 4) smaller footprint.

In previous experimental studies¹¹-¹³, we evaluated a URFC using a small-scale single cell of an URFC (electrode area of 27 cm²) aiming to optimize cell components such as the gas diffusion layer (GDL) and flow channels in a bipolar plate. In a real-scale URFC system, each cell should have a larger electrode area (several hundred cm²) and cells should be piled up into a stack. Drawbacks that did not appear in the small-scale single cell might be significant when larger cells are in a stack, such as nonuniform electrical contact in a catalyst layer (CL)/GDL- or GDL-bipolar plate, and the nonuniform distribution of gases and liquids due to partial closing of flow channels. These nonuniformities might produce current spots or overconcentration of reactant (liquids or gases), and consequently degrade the total stack performance. To determine if these drawbacks are significant when a URFC has larger cells in a stack configuration required for commercial applications, in this study, a pilot-scale URFC system was operated in both the EL and FC modes and then both its overall stack performance and the performance variation between cells were measured.

2. Principle of a Unitized Reversible Fuel Cell (URFC)

PEM electrolysers and PEMFCs both are based on PEM technology and have a similar cell configuration, consisting of a membrane electrode assembly (MEA) including GDLs, and bipolar plates with flow channels. The fabrication method of MEAs can be divided into two categories based on the process used to apply the CL, that is, catalyst-coated membrane (CCM) and catalyst-coated substrate (CCS)¹⁴. In fabricating a CL, inks or slurries containing catalyst are directly applied either to a GDL...
substrate or a PEM. Applying the catalyst inks to a GDL substrate forms a two-layer structure called a CCS, whereas applying to both sides of the PEM forms a three-layer structure called the CCM. Two CCSs are combined either with a PEM or with one CCM sandwiched between two GDLs, thus forming a five-layer MEA. Nowadays, an MEA for a PEMFC is commonly fabricated using the CCM process, whereas either the CCM or CCS process is used for a PEM electrolyzer. The configuration of a URFC with a PEM is the same as these PEM-based devices. Either process of CL application can be used to fabricate an MEA of a URFC.

A schematic of reactant/product transport during both operation modes of a URFC is shown in Fig. 1. In the EL mode, the following reactions occur at both electrodes by electric power input from the source.

\[ 2H^+ + 2e^- \rightarrow H_2(g) \]  
\[ H_2O(l) \rightarrow 1/2O_2(g) + 2H^+ + 2e^- \]

The overall reaction thus can be expressed as,

\[ H_2O(l) \rightarrow H_2(g) + 1/2O_2(g) \]

Liquid water is supplied to the anode as fuel (reactant) for the electrolysis, where it is dissociated into molecular oxygen (O₂), protons (H⁺), and electrons (e⁻). Protons formed at the anode migrate through the PEM to the cathode where they are reduced to molecular hydrogen (H₂). In this migration, water molecules (H₂O) accompany the migrating protons due to electro-osmotic drag. Thus, the PEM is kept wet without an outside water supply to the cathode, and therefore water as a reactant is supplied only at the anode during typical EL operation.

In the FC mode, because reduction and oxidation at each electrode are reversed from that in the EL mode, the role of anode/cathode is also reversed, namely, the H₂ and O₂ electrode, respectively. H₂ and O₂ are respectively supplied to the anode and cathode, and then oxidized and reduced as follows.

\[ H_2(g) \rightarrow 2H^+ + 2e^- \] at anode
\[ 1/2O_2(g) + 2H^+ + 2e^- \rightarrow H_2O(l) \] at cathode

The overall reaction during FC operation is completely opposite that during EL as follows:

\[ H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \]

To maintain a sufficiently high proton conductivity of the PEM, the PEM has to be hydrated. The reactants of H₂ and O₂ are thus humidified during transport to the cell. Equation (5) shows, however, that liquid water is generated at the cathode. Excess liquid water would then accumulate at the CL/GDL interface and thus cause severe degradation of the cell performance because O₂ transport to the CL is hindered by accumulated water, which is called “flooding”. Because FC performance is sensitive to the hydration state of the PEM and CL, the amount and state (liquid/vapor) of water in the cell must be carefully managed for stable operation.

### 3. Experimental Apparatus

The URFC stack and its balance of plants (BOP) were designed and manufactured by Takasago Thermal Engineering Co. (Japan). All components were enclosed in a cabinet (1,280 mm width × 740 length × 1,361 height mm); URFC stack, a pipeline system for gas and liquid including gas-liquid separators, valves, pumps, an air-blower, a control system including a control panel, a DC-power supply, an electric load, and a chiller.

#### 3.1 URFC Stack

Figure 2 shows a schematic of the stacking configuration of the cells. (Not shown are the sealing components such as gasket and manifold.) In the cells in the present URFC stack, the MEAs were fabricated using the CCM process, and thus a composite of CCM sandwiched between two GDLs served as the MEA. As shown in Fig. 2, the MEA was rectangular with an area of 250 cm², and 10 cells were piled up to form a stack. Table 1 lists the
specifications of an individual cell and of the stack. The total weight of this stack including both end-plates (made of stainless steel) was about 55 kg. The stack temperature \(T_{\text{stack}}\) was measured with a sheathed thermocouple (Type T) inserted into the body of one end-plate, with the tip of the sheath placed at the center of the electrode area. The stack had six fluid connections at one of the end-plates (right-hand side in Fig. 2), that is, the inlet and outlet lines for each fluid of \(H_2\), \(O_2\) (or air), and cooling water. Each fluid line passed through the bipolar plates and membranes. Each gas (\(H_2\) and \(O_2\) (or air)) was distributed to one side of each cell by using manifolds. Carbon, which is a typical material for the GDL and bipolar plate for a PEMFC, cannot be used for the oxygen electrode of a URFC (i.e., the cathode in the FC mode), because the potential of the oxygen electrode during EL mode is so cathodic that carbon material tends to corrode. Therefore, in the present URFC, a titanium (Ti)-felt was applied as the oxygen-electrode GDL, whereas carbon paper, which is a typical GDL substrate of a PEMFC, was used as the hydrogen-electrode GDL. For the bipolar plate, to facilitate the cooling-water path between the cells, two plates must be placed back-to-back. In this case, the potential of these two plates must be equal due to sufficient surface contact. Because the bipolar plates simultaneously function both as a cathode and anode, all bipolar plates must be resistant against high cathodic potential. Therefore, all the bipolar plates equipped here were made of Ti. However, Ti bipolar plates are costly, typically accounting for half the total cost of the stack\(^{10}\). Therefore, to reduce the number of bipolar plates, in our system, two bipolar plates (i.e., cooling water path) were placed only between every other cell (rather than between each cell) as shown in Fig. 2. Each bipolar plate had a terminal to measure the cell voltage.

### 3.2 Balance of Plant (BOP)

There were six major line systems: inlet and outlet lines of \(H_2\), inlet and outlet lines of air/\(O_2\), electrolysis-water circulation line, and cooling-water circulation line. The outlet line of \(H_2\) and part of the outlet line of air/\(O_2\) were used for both EL and FC modes. In the EL mode, deionized (DI) water stored in the \(O_2\)-water separator tank was fed into the URFC stack using a circulation pump for electrolysis water. Along with liquid water, the produced oxygen at the anode by electrolysis was released from the stack and fed back to the separator tank to remove the water. Oxygen gas was released from the tank and exhausted to the atmosphere. Simultaneously, hydrogen was produced at the cathode. Because liquid water migrated from the anode (\(O_2\) side) to the cathode (\(H_2\) side) through the membrane by electro-osmosis drag during electrolysis, hydrogen gas was also released with liquid water. Hydrogen was separated from the liquid water at the \(H_2\)-water separator tank and finally dried by cooling with a heat exchanger. Hydrogen pressure (\(P_{\text{H2}}\)) was regulated with a back pressure valve in the range between 0.1 to 1.0 MPa (abs). Because the line pressure of the oxygen side was always slightly higher than 0.1 MPa, a differential pressure existed between the anode and cathode when hydrogen was compressed at the anode.

In the FC mode, \(H_2\) gas was supplied to the anode and air to the cathode. Note that the anode and cathode during FC mode are

### Table 1 Specifications of URFC stack.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\text{H}_2) side</th>
<th>(\text{O}_2) side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Nafion 115</td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pt</td>
<td>Pt+IrO(_2)</td>
</tr>
<tr>
<td>Gas diffusion layer</td>
<td>(\text{H}_2) side</td>
<td>Carbon paper</td>
</tr>
<tr>
<td>(Current collector)</td>
<td>(\text{O}_2) side</td>
<td>Titanium felt</td>
</tr>
<tr>
<td>Bipolar plate</td>
<td>Titanium (Pt coated)</td>
<td></td>
</tr>
<tr>
<td>Cell/Stack configuration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrode active area</td>
<td>250 cm(^2)</td>
<td></td>
</tr>
<tr>
<td>Number of cells in series</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>
opposite that during EL mode as shown in Fig. 1. In the recirculation system for the H₂ gas supply, residual H₂ released from the stack was recirculated with a recirculation pump. The flow rate of recirculated H₂ was fixed at 25 L/min, which corresponds to a stoichiometric ratio of 2.9 at current density of 0.5 A cm⁻². To maintain a sufficiently high hydrogen purity, the recirculation line was opened at a moment (e.g., 1 sec) and hydrogen was fully discharged every 5 min. The stoichiometric ratio of H₂ was nearly 1. Air was supplied by an air blower (BLW) and was humidified with a membrane humidifier during transport to the stack. The membrane humidifier acted as a moisture exchanger between the air inlet and outlet lines, that is, by transferring moisture from the exhausted air containing higher moisture to the inlet air. The flow rate of air was fixed at 48 L/min, and the dew point of introduced air at this flow rate was about 60 °C.

During both EL and FC modes, T_stack of the URFC was controlled using circulating cooling water. In this cooling-water loop, when T_stack reached a target temperature, cold water was supplied to the heat exchanger from the chiller. The temperature of the cooling water was measured at the inlet and outlet of the stack, and this temperature difference was then used to calculate the extracted thermal energy.

Using this URFC system (the URFC stack and its BOP), the stack current (I_stack) – stack voltage (V_stack) characteristics were measured at various operating conditions for both modes of EL and FC. The cell voltage (Vcell) variations were also obtained at the same time.

4. Results and Discussion

The URFC stack performance measured under nominal operating conditions at various T_stack is summarized in Table 2. Under nominal operation condition for the EL mode stack current I_stack = 250 A, hydrogen pressure P_H₂ = 1.0 MPa, power input for electrolysis (W_stack) was about 4.4 kW, when the Faraday (current) efficiency was near 1. In the FC mode, I_stack of nominal operation (i.e., the maximum I_stack for stable operation) was varied with T_stack. The maximum power output (W_stack = 0.8 kW) was obtained at T_stack = 70 °C and I_stack = 125 A. Details of the stack performance for both operation modes are described in the following sections.

4.1 Electrolysis (EL) Operation

The variable parameters for EL operation were T_stack and P_H₂. Figure 3 shows the measured I_stack – V_stack characteristics of EL under different T_stack, when P_H₂=1.0 MPa. Because the overpotentials were relatively small during EL operation and the joule heat generated from the stack was lower than that during FC operation, T_stack was limited to under 60 °C. As expected, the EL performance was improved at higher T_stack, because the overpotential of both activation and ohmic decreased as T_stack was increased. The difference in V_stack (i.e., ΔV_stack) between different T_stack increased with increasing I_stack. Comparison of V_stack at T_stack = 40 and 60 °C shows that ΔV_stack ≈ 1.0 V at I_stack = 250 A, and thus the difference in W_stack for EL at these two temperatures was 0.25 kW. T_stack should be as high as possible to obtain a high stack performance.

![Fig. 3 Current (I_stack) – voltage (V_stack) characteristics of EL mode at various stack temperature (T_stack) at pressure of produced hydrogen (P_H₂) of 1.0 MPa.](image)

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Stack performance of URFC at nominal operating conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Electrolysis mode</td>
</tr>
<tr>
<td>Stack temperature T_stack [°C]</td>
<td>40</td>
</tr>
<tr>
<td>Stack current I_stack [A]</td>
<td>250</td>
</tr>
<tr>
<td>Stack voltage V_stack [V]</td>
<td>18.4</td>
</tr>
<tr>
<td>Stack power (DC) W_stack [kW]</td>
<td>4.6</td>
</tr>
<tr>
<td>Hydrogen pressure (abs) P_H₂ [MPa]</td>
<td>1.0</td>
</tr>
<tr>
<td>Produced/introduced hydrogen flow rate F_H₂ [L/min]</td>
<td>17.4</td>
</tr>
</tbody>
</table>
performance, though the maximum $T_{stack}$ is around 80 °C due to the limitation of thermal stability of the PEM. The variation in cell voltage ($V_{cell}$) between the cells at $T_{stack} = 40$ and 60 °C is shown in Fig. 4, when $P_{H2} = 1.0$ MPa and $I_{stack} = 250$ A. At both levels of $T_{stack}$, the difference in $V_{cell}$ between all 10 cells was very small. The maximum $V_{cell}$ difference was 17 mV at $T_{stack} = 40$ °C and 22 mV at 60 °C. $V_{cell}$ variations observed at other operating conditions (various $T_{stack}$, $P_{H2}$, and $I_{stack}$) reveal that $V_{cell}$ difference during EL was small regardless of $T_{stack}$, $P_{H2}$, and $I_{stack}$. Consequently, no significant drawback due to larger cells or to stacking of the cells was observed in EL mode, that is, neither nonuniformity in the electric contact of CL-GDL and GDL-bipolar plates nor nonuniformity in the distribution of gases and liquids were observed.

Figure 5 shows the effect of $P_{H2}$ on EL performance under the same $T_{stack}$ (40 and 60 °C) The $I_{stack}$ -- $V_{stack}$ performance at atmospheric $P_{H2}$ (0.1 MPa) was better than that at higher $P_{H2}$, although the difference in performance between $P_{H2} = 0.6$ MPa and 1.0 MPa was relatively small. Based on the data in Fig. 5, $\Delta V_{stack}$ was relatively independent of $I_{stack}$, and the $I_{stack}$ -- $V_{stack}$ curve was shifted depending on the $P_{H2}$ change, indicating negligible pressure dependency on overpotentials (activation and ohmic).

Theoretical decomposition voltage of water ($V_{EL,rev}$) can be derived from Eq. (3) as,

$$V_{EL,rev} = E_{rev} + \frac{RT}{2F} \ln \left( \frac{P_{H2}P_{O2}^{1/2}}{P_{H2}^{1/2}} \right)$$

where $E_{rev}$ is reversible potential of EL, $R$ is gas constant, $T$ is temperature of reaction field (i.e., $T_{stack}$ in this case), $F$ is the Faraday constant, $P_{H2}$ and $P_{O2}$ represent produced gas pressure of H$_2$ and O$_2$, respectively, and $a_{H2O}$ is activity of reactant water. $E_{rev}$
Stack Performance of Proton Exchange Membrane Based Unitized Reversible Fuel Cells.

can be derived from the Gibbs energy of Eq. (3)\(^1\) and is 1.208 V at \(T=50^\circ\text{C}\). If we assume \(E_L\) under atmospheric conditions, then \(P_{\text{H}_2}, P_{\text{O}_2}\), and \(a_{\text{H}_2}\) can be considered unity (i.e., \(P_{\text{H}_2} = P_{\text{O}_2} = a_{\text{H}_2} = 1\)), and thus the second term in the right-hand side in Eq. (7) would be zero. The \(V_{E_L,th}\) due to pressure change from \(P_{\text{H}_2}\) to \(P'_{\text{H}_2}\) under constant temperature can be expressed as,

\[
\Delta V_{E_L,th} = \frac{RT}{2F} \ln\frac{P'_P}{P_P}
\]  

(8)

Substituting \(T_{\text{stack}} (50^\circ\text{C})\) for \(T\) in Eq. (8), the calculated \(\Delta V_{E_L,th}\) is 25 mV at a \(P_{\text{H}_2}\) change from 0.1 to 0.6 MPa, and as 32 mV at 0.1 to 1.0 MPa. The corresponding measured \(\Delta V_{\text{stack}}\) in Fig. 6 was on average 32 mV and 38 mV per cell, respectively. The measured \(P_{\text{H}_2}\) represented an average pressure in the compressed hydrogen compartment, which is the region from the flow channel in the stack through the pipe to the back-pressure valve. The disagreement between the theoretical and measured voltage difference (\(\Delta V_{E_L,th}\) and \(\Delta V_{\text{stack}}\), respectively) suggests that the local hydrogen pressure at the hydrogen generation point in the electrode is significantly higher than \(P_{\text{H}_2}\), and the pressure difference between local and average would increase with increasing \(P_{\text{H}_2}\). If we assume the local hydrogen pressure at generation point under atmospheric pressure condition is equal to the average pressure (i.e., \(P_{\text{H}_2} = 0.1\) MPa), the calculated \(P'_{\text{H}_2}\) corresponding to measured \(\Delta V_{\text{stack}}\) of 32 mV (at 0.1 to 0.6 MPa) and 38 mV (at 0.1 to 1.0 MPa) is 1.0 MPa and 1.5 MPa, respectively. These results indicate that the calculated local pressure was significantly higher than the average hydrogen pressure (i.e., measured \(P_{\text{H}_2}\)).

4.2 Fuel cell (FC) Operation

Figure 7 shows the \(I_{\text{stack}} - V_{\text{stack}}\) characteristics of the FC mode under \(T_{\text{stack}} = 70\) and 60 \(^\circ\text{C}\). When \(I_{\text{stack}} > 50\) A, a significant difference is evident. The rapid decrease in \(V_{\text{stack}}\) at \(T_{\text{stack}} = 60\) \(^\circ\text{C}\) indicates “flooding”, that is, condensed liquid water in the cell/stack accumulated at the electrode and hindered the mass transport of reactive gases to the electrode surface. The dew point of air passing through the membrane humidifier was estimated at around 60 \(^\circ\text{C}\) under the constant flow rate of the air regardless of \(T_{\text{stack}}\). Therefore, the relative humidity (RH) of the air in the cathode gas channel would be around 100% when \(T_{\text{stack}} = 60\) \(^\circ\text{C}\).

Figure 8 shows the variation in \(V_{\text{cell}}\) in all 10 cells during FC mode at current density of 0.4 A/cm\(^2\) (i.e., 100 A). As shown in Fig. 8a, the difference in \(V_{\text{cell}}\) between the cells was small at \(T_{\text{stack}} = 70\) \(^\circ\text{C}\), and the maximum difference was about 30 mV. Contrary to this, at \(T_{\text{stack}} = 60\) \(^\circ\text{C}\) (Fig. 8b), the difference in \(V_{\text{cell}}\) difference was large, and the maximum difference was about 300 mV, and cells of high \(V_{\text{cell}}\) alternated with those of low \(V_{\text{cell}}\). The significant difference in \(V_{\text{cell}}\) observed at \(T_{\text{stack}} = 60\) \(^\circ\text{C}\) might be caused not by unexpected nonuniformity caused by larger cells or by

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stacking of the cells but by the temperature difference between the cells. As mentioned above, each pair of cells in this stack configuration shared a common distribution of cooling water (see Fig. 2), and thus, there might be a temperature difference between the individual cells in each pair, although the temperature of each cell was not measured in the present experiments. The yield of flooding sensitively depends on RH. In the cells of lower temperature, RH of the air in the cathode gas channels would exceed 100 %. Because $V_{\text{cell}}$ at this lower temperature would therefore be degraded due to severe flooding, $V_{\text{stack}}$ would be degraded. Consequently, for FC mode, $T_{\text{stack}}$ should be higher than 70 °C for stable operation with this URFC stack.

5. Conclusions

To determine if drawbacks that do not appear in a small-scale single cell of a URFC are significant when a URFC has larger cells in a stack configuration required for commercial applications, a pilot-scale URFC system was successfully operated in both EL and FC modes and both its overall stack performance and the performance variation between cells were measured.

In EL mode, the stack performance was improved by increasing $T_{\text{stack}}$. Experimental data revealed that the difference in $V_{\text{cell}}$ between cells during EL is small regardless of $T_{\text{stack}}$, $P_{\text{H2}}$, and $I_{\text{stack}}$. Correspondingly, no significant degradation in stack performance due to enlargement or stacking of the cells was observed in EL operation. However, the effect of $P_{\text{H2}}$ change on EL performance revealed that the local H$_2$ pressure at the hydrogen generation point in the electrode is significantly higher than the average of H$_2$ pressure in the compressed hydrogen compartment (the region from the flow channel in the stack through the pipe to the back-pressure valve).

In FC mode, the $I_{\text{stack}}-V_{\text{stack}}$ curve at $T_{\text{stack}} = 60$ °C was severely degraded when $I_{\text{stack}} > 50$ A, significantly different from the $I_{\text{stack}}$-independent curve at $T_{\text{stack}} = 70$ °C. In addition, the difference in $V_{\text{cell}}$ between the cells was significant at $T_{\text{stack}} = 60$ °C compared with that at 70 °C. This significant difference in $V_{\text{cell}}$ observed at $T_{\text{stack}} = 60$ °C might be caused not by any unexpected defect due to larger cells or to stacking of the cells but by a temperature difference between the cells.

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