Effect of fabrication methods of bifunctional catalyst layers on unitized regenerative fuel cell performance

Guobao Chen a,b, Huamin Zhang a,* , Haipeng Ma a, Hexiang Zhonga

a Key Material Laboratory for PEMFCs, Dalian Institute of Chemical Physics, CAS, Dalian 116023, China
b Graduate School of the Chinese Academy of Sciences, CAS, Beijing 100039, China

ABSTRACT

In order to understand the origins of performance variations in unitized regenerative fuel cells (URFCs), bifunctional catalyst layers (BCLs) fabricated with two different methods, i.e., ink deposition on membrane or GDL, were designed in this paper. The performances of the two different methods were evaluated, and their reaction dynamics were measured by electrochemical impedance spectra. The different BCLs, caused by the different preparation processes, were found to influence the fuel cell performance. The cell potentials of the URFCs using platinum sprayed onto the gas diffusion layer (GDL) are above 0.100 V higher than those with platinum sprayed onto the membrane at 800 mA cm\(^{-2}\) in fuel cell (FC) mode. The mass transport resistances of the URFCs at different operation modes were also compared. It was proved that the platinum layer formed by applying platinum onto the GDL could prevent the cell from water flooding in FC mode. However, it was found that the cell performance changed slightly in water electrolysis mode with different BCLs. The electron conduction path was also found to be hindered by an IrO\(_2\) agglomerate, which led to a decrease in cell performance. The highest and lowest round-trip efficiencies of the URFC with different BCLs were 42.1\% and 22.3\%, respectively, at 800 mA cm\(^{-2}\).

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1. Introduction

A regenerative fuel cell (RFC) can be operated as an electrolyzer, splitting water into hydrogen and oxygen with the help of electric power from renewable energies. The RFC system can also create electrical power with the stored hydrogen and oxygen in the fuel cell (FC) mode. The mass transport resistances of the URFCs at different operation modes were also compared. It was proved that the platinum layer formed by applying platinum onto the GDL could prevent the cell from water flooding in FC mode. However, it was found that the cell performance changed slightly in water electrolysis mode with different BCLs. The electron conduction path was also found to be hindered by an IrO\(_2\) agglomerate, which led to a decrease in cell performance. The highest and lowest round-trip efficiencies of the URFC with different BCLs were 42.1\% and 22.3\%, respectively, at 800 mA cm\(^{-2}\).

In order to improve the round-trip efficiency of the URFC, one key issue is the fabrication of stable and highly active bifunctional catalyst layers (BCLs), which can be used for both oxygen reduction reactions (ORR) and oxygen evolution reactions (OER). It is well known that the best electrocatalyst for ORR is platinum (in its reduced form). Early research by Swette et al. [6], showed that iridium oxide (IrO\(_2\)) would be a good candidate for OER. So far, bifunctional electrocatalysts for oxygen redox reactions of the URFC have included Pt–Ir [7], Pt–Ru–Ir [8], Pt–IrO\(_2\) [9,10] and Pt–IrO\(_2–\)RuO\(_2\) [11,12], among which IrO\(_2\) and RuO\(_2\) were prepared by the Adams method [13]. However, the most applicable OER catalyst is iridium oxide since iridium and ruthenium suffer from instability [14].

Some of the above-described bifunctional oxygen electrode catalysts were obtained by mixing an efficient electrocatalyst for oxygen reduction-Pt black, and an efficient electrocatalyst for oxygen evolution-Ir or IrO\(_2\) or RuO\(_2\), while others were made by using alloyed Ptlr or PtlrO\(_x\) or PtlrO\(_x\). An OER catalyst does not exhibit a high catalytic activity for the oxygen reduction reaction, while an ORR catalyst may display a low catalytic activity for the oxygen evolution reaction. In addition, as we know, the reactions occurring at the cathode of the URFCs are the reduction and evolution of oxygen as follows:

\[ \text{O}_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l) \]  \hspace{1cm} (1)

\[ 2H_2O(l) \rightarrow \text{O}_2(g) + 4H^+ + 4e^- \]  \hspace{1cm} (2)
According to (1) and (2), in fuel cell mode, the oxygen gas is reduced to liquid water, but, in water electrolysis mode, the reactant is the liquid water and the product is oxygen gas. The different reactants and products in the two different modes also require a suitable bifunctional catalyst layer to obtain the highest round-trip efficiency.

There are several ways to prepare catalyst layers for a fuel cell: the so-called indirect decal method, the gas diffusion layer (GDL)-based method and the membrane-based method [15]. For the decal method, a transfer film is brushed with catalyst ink, dried and hot-pressed onto the electrolyte film. The GDL-based method implies that the catalyst ink is directly painted or sprayed onto the GDL. Fabricating the catalyst layers with the membrane-based method usually consists of spraying the catalyst ink directly onto a dry, blank membrane. The latter two methods have the advantage that the catalyst loading can be adjusted very precisely by simply weighing the membrane electrode assembly (or the GDL) before and after coating with the catalyst ink. Applying the electrodes by the decal method contains the risk of uneven or incomplete catalyst transfer from the transfer film to the membrane. We therefore restricted our research to the GDL- and membrane-based methods.

The water management, which is vital to ensuring the high performance and long life of the fuel cell, will differ in different fabrication processes. It has been shown that, if the cathode is flooded by excess water, the cell performance decreases [15]. Furthermore, the oxygen catalyst layers were made as shown in Fig. 1. Pt (Pt black, T.K.K. Corp.) and home-made IrO2 were used as bifunctional catalysts. IrO2 was made by proprietary modification of Adams-type fusion of the iridium salt in a nitrate flux [18]. All the bifunctional catalyst layers were prepared by spraying technique. To form C1 and C2, Pt and IrO2 were made as a mixed catalyst layer, whereas for other BCLs, Pt and IrO2 were divided to form individual catalyst layers, a Pt catalyst layer and an IrO2 catalyst layer, respectively. The spraying sequences of the Pt catalyst and IrO2 catalyst layers also varied as shown in Fig. 1. Four groups of BCLs, C1 and C2, C3 and C4, C5 and C6 and C7 and C8, had the same loading and were prepared from the same inks but differed in the locations of Pt and IrO2 layers. The BCL that applied Pt onto the GDL was named BCL1, while the BCL that applied Pt onto the membrane was named BCL2.

Prior to fabricating the electrodes, a homogeneous suspension composed of PTFE and carbon powder was sprayed onto waterproof carbon paper (TGP-060, Toray Inc.) to form the GDL with a sublayer [17]. The proton exchange membranes (PEMs, Nafion 1035, DuPont) were treated for 1 h in 5 wt.% H2O2 solution at 80 °C, 30 min in distilled water at 80 °C, 1 h in 0.5 M H2SO4 solution at 80 °C and finally 30 min in distilled water at 80 °C.

To prepare a hydrogen catalyst layer, a homogeneous ink consisting of Pt/C catalyst (28.4 wt.%, T.K.K. Corp.), Nafion solution (5 wt.% DuPont) and isopropanol was sprayed directly onto one side of a Nafion 1035 membrane. The prepared catalyst-coated membrane was then dried at room temperature for 24 h to evaporate the residual solvents. The Nafion content was 25 wt.% and the Pt/C loading was 0.5 mg cm⁻² for the hydrogen side.

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2. Experimental

2.1. Preparation of bifunctional catalyst layers and membrane electrode assemblies for URFCs

In this paper, eight bifunctional oxygen catalyst layers with two different preparation methods were designed. Pt and IrO2 catalysts were used as bifunctional catalysts. The performances of the URFCs in two different modes were evaluated. The electrochemical impedance spectra (EIS) of the URFCs were measured to study the effects of different bifunctional catalyst layers on cell performance, especially the round-trip efficiency of a URFC.

In the paper, eight bifunctional oxygen catalyst layers with two different preparation methods were designed. Pt and IrO2 catalysts were used as bifunctional catalysts. The performances of the URFCs in two different modes were evaluated. The electrochemical impedance spectra (EIS) of the URFCs were measured to study the effects of different bifunctional catalyst layers on cell performance, especially the round-trip efficiency of a URFC.

Fig. 1. Schematic diagram of different bifunctional catalyst layers for URFCs. The four groups of BCLs, C1 and C2, C3 and C4, C5 and C6, C7 and C8, were the same electrode structure and catalyst loading; C1, C3, C5 and C7 sprayed Pt onto the gas diffusion layer (BCL1) while others applied Pt onto the membrane (BCL2).
respectively. The loading of Pt and IrO2 were the same with the BCLs.

The MEAs were fabricated by hot-pressing the anode and the cathode to the membrane at 160 °C and 0.8 MPa for 1 min and fitting into a test station. The active areas of the MEAs were all 5 cm².

2.2. Characterization of bifunctional catalysts and bifunctional catalyst layers

The BET specific surface areas and pore volumes of commercial platinum and home-made IrO2 catalysts were measured by the N2 adsorption method (ASAP2010 Micromeritics Instrument). The linear sweep voltammetry (LSV) tests of Pt and IrO2 catalysts were measured using a CHI 660 electrochemical station (CH Corp., USA). The catalyst layer on the glassy carbon electrode (GCE) (4 mm in diameter) was prepared as followed: a mixture containing 1 mL of ethanol, 5.00 mg of catalyst and 50 μL of Nafion solution (5 wt.%) was homogenized for 30 min in a ultrasonic bath. The mixture (25 μL) was cast onto a clean GCE surface and dried in air. All the measurements were carried out in a standard three-electrode cell. A Pt foil was served as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. A solution of 0.5 M H2SO4 was used as electrolyte. All tests were carried out after O2 bubbling for 30 min. The scan rate was 5 mV s⁻¹.

The changes in the surface of the GDL and the membrane sprayed with Pt and IrO2 catalyst layers were examined by means of a scanning electron microscope, respectively (SEM, Amray, KYKY model 1000B). The in-plane conductivity of the GDLs was measured using a four-point method [19].

2.3. Evaluation of URFC performance

The single cell test for the URFC performance evaluation was described in a previous paper [20]. During fuel cell operation, the URFC was operated at 80 °C with H2/O2 at pressures of 0.2 MPa. Pure hydrogen and oxygen were used and both were externally humidified before entering the cell by bubbling through water at 90 °C and 85 °C, respectively. During the water electrolysis (WE) operation, deionized water was pumped into the membrane electrode assembly from the water reservoir kept at 80 °C with atmospheric pressure. The polarization curves of URFCs were galvanostatically measured using a constant current supply. Before recording the point in the polarization curves, the URFC was held at the corresponding current for 5 min to ensure a steady state.

2.4. EIS measurements

Electrochemical impedance spectra of the URFCs in fuel cell mode were measured by the KFM2030 impedance meter (Kikusui, Japan), which was connected to the Fuelcell-Load & Impedance Meter software (Kikusui, Japan) for in situ EIS measurements. The maximal measured ac current for the sine signal was 165 mA over a frequency range of 100 mHz to 10 kHz. The cathodes were used as the working electrode, while the anodes of the single cells were used as the reference electrode and counter electrode, respectively.

The EIS of URFCs in water electrolyzer mode were conducted at 1.55 V using a Potentiostat (EG&G PAR, Model 2273A) for frequency measurements extending from 10 mHz to 100 kHz, and a 10 mV amplitude of sinusoidal potential perturbation was employed.

The impedance data were modeled by using ZSimpWin software.

3. Results and discussion

3.1. Characterization of bifunctional catalysts and bifunctional catalyst layers

The BET specific surface areas of Pt and IrO2 were 28.53 m² g⁻¹ and 32.01 m² g⁻¹, respectively. The pore volumes of commercial platinum and home-made IrO2 were 0.12 cm³ g⁻¹ and 0.05 cm³ g⁻¹, respectively, much lower than the carbon powers in the literature [19].

Fig. 2 shows the polarization curves of bifunctional catalysts in 0.5 M H2SO4. As can be seen from Fig. 2a, during the cathodic scan, Pt displays a much higher ORR catalytic activity than IrO2. The half-wave potential E½ (the potential corresponding to one-half of the diffusion current) of Pt was 0.566 V (vs. SCE), while that of IrO2 was lower than 0.208 V (vs. SCE), suggesting that the oxygen reduction reaction is most catalyzed by platinum. Fig. 2b shows the comparison of the potentiodynamic polarization curves for oxygen evolution on Pt and IrO2 catalysts. The current density on the IrO2 is obviously larger than that on Pt at potentials above 1.25 V (vs. SCE). The LSV test results confirm that platinum is the main ORR catalyst, while the iridium oxide is the primary OER catalyst.

The average thicknesses of the Pt and IrO2 layers were about 9.7 μm and 8.6 μm, respectively, as obtained by SEM. Since platinum is the main ORR catalyst as concluded above, the Pt layers may play an important role in the cell performance of the URFC in fuel cell mode, thus the surface morphology of Pt sprayed with the two different preparing methods should be further investigated. Fig. 3 shows the SEM images of the Pt and IrO2 layers on the gas diffusion layer and on the membrane. It is evident that the Pt particle layer formed by spraying onto the GDL shows a homogeneous and porous surface with small agglomerates of Pt particles and Nafion, as shown in Fig. 3a and b. In contrast, M-Pt presents several large cracks and a large conglomeration of Pt particles and Nafion. The bulky pores were formed when the Pt layer sprayed onto the membrane. The average pore size in M-Pt was about 2 μm, while that

![Figure 2](image-url)
in GDL-Pt was only 131 nm, as observed by the SEM images. It can be concluded that the microstructure of the platinum catalyst layer is improved by spraying onto the GDL. As shown in Fig. 3c and d, M-IrO₂ also displays more agglomerates than GDL-IrO₂. The large IrO₂ particles can fill into the large pores formed in M-Pt, which may hinder the oxygen transfer.

Fig. 4 shows the in-plane resistance $R_{\text{in-plane}}$ of different materials. A carbon paper (Toray-060) is used as a standard. The GDL firstly sprayed with an IrO₂ layer and then sprayed with a Pt layer was designated GDL-IrO₂–Pt. As seen from Fig. 4, the $R_{\text{in-plane}}$ of the GDL-Pt is nearly 6.96 mΩ cm, while that of the GDL-IrO₂ is 7.74 mΩ cm. The results confirm that the resistivity of IrO₂ is larger than that of Pt. It is worth noting that the $R_{\text{in-plane}}$ of the GDL-IrO₂ is nearly 20% higher than that of the conventional GDL and the $R_{\text{in-plane}}$ of the GDL-IrO₂–Pt is about 14% higher than that of the GDL-Pt. Therefore, it can be inferred that, in fuel cell mode, the electron conduction path tends to be hindered by the IrO₂ agglomerate.

### 3.2. Effect of bifunctional catalyst layers on cell performance

Variations of cell performances with different bifunctional catalyst layers in fuel cell mode and in water electrolysis mode are presented in Figs. 5 and 6, respectively. It can be seen that the cell performances of the URFCs are quite different between the two preparation methods in FC mode, while they change slightly in water electrolysis mode. The cell potentials at different current densities $j₁ = 100 \text{ mA cm}^{-2}$ and $j₂ = 800 \text{ mA cm}^{-2}$ are presented in Table 1.

As shown in Fig. 5, it is apparent that the performances of the URFCs with BCL1 are considerably better than those using BCL2, especially at high current densities. Taking C₁ and C₂ as an example, it can be noted that the cell potential of the URFC with C₁ is 0.100 V higher than the URFC using C₂ at 800 mA cm$^{-2}$, though their cell potentials were the same at 100 mA cm$^{-2}$. The URFC employing C₄

<table>
<thead>
<tr>
<th>Catalyst layer type</th>
<th>Fuel cell mode</th>
<th>Water electrolysis mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{j₁}$/V</td>
<td>$E_{j₂}$/V</td>
</tr>
<tr>
<td>C₁</td>
<td>0.861</td>
<td>0.674</td>
</tr>
<tr>
<td>C₂</td>
<td>0.861</td>
<td>0.573</td>
</tr>
<tr>
<td>C₃</td>
<td>0.863</td>
<td>0.565</td>
</tr>
<tr>
<td>C₄</td>
<td>0.833</td>
<td>–</td>
</tr>
<tr>
<td>C₅</td>
<td>0.865</td>
<td>0.672</td>
</tr>
<tr>
<td>C₆</td>
<td>0.846</td>
<td>0.565</td>
</tr>
<tr>
<td>C₇</td>
<td>0.848</td>
<td>0.620</td>
</tr>
<tr>
<td>C₈</td>
<td>0.847</td>
<td>0.359</td>
</tr>
<tr>
<td>GDL-Pt</td>
<td>0.872</td>
<td>0.722</td>
</tr>
<tr>
<td>M-Pt</td>
<td>0.871</td>
<td>0.667</td>
</tr>
<tr>
<td>GDL-IrO₂</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>M-IrO₂</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
had no fuel cell performance at 400 mA cm\(^{-2}\), while the URFC using C3 still obtained 0.565 V at 800 mA cm\(^{-2}\). It is evident that the URFCs adopting C5 and C7 also received 0.107 V and 0.261 V higher than those using C6 and C8 at 800 mA cm\(^{-2}\), respectively. The results indicate that the performance has not been significantly influenced by the location of sprayed platinum for lower current densities. This has been observed to occur only at higher current densities.

Studies on the enhancing performance of URFCs with Pt applied onto the GDL have revealed that the location of platinum in the catalyst layer plays a crucial role on cell performance of the URFC in...
FC mode. As mentioned above, platinum is the main ORR catalyst, so the area of effective interface between Pt and the oxygen gas can exert a heavy influence on the cell performance in fuel cell mode. For higher current densities, the water produced in the ORR process will fill into the large pores of M-Pt in BCL2 and induces flooding in the catalyst layer. These factors resulted in a decrease in the effective interface areas between the catalyst and the reactant oxygen.

Fig. 6 reveals that the changes in cell performance with the two preparation methods are ruleless in the water electrolysis mode. The URFCs with C1 and C7 have a lower performance than the URFCs employing C2 and C8, respectively. However, the URFCs using C3 and C5 show a slight enhancement in comparison to those with C4 and C6, respectively. As calculated from Table 1, the difference in cell potentials in these eight BCLs was not more than 0.050 V, both at 100 mA cm\(^{-2}\) and at 800 mA cm\(^{-2}\). This illustrates that the location of the catalyst layers slightly influences the performance of the URFCs in WE mode.

The performances of cells using the pure Pt and IrO\(_2\) layers, in comparison to the BCLs, are shown in Fig. 7. Their cell potentials at 100 mA cm\(^{-2}\) and 800 mA cm\(^{-2}\) are also recorded in Table 1. It is interesting to note that the Pt layer sprayed onto the GDL outperforms the Pt layer sprayed onto the membrane in FC mode. When in water electrolysis mode, it is clear that the IrO\(_2\) layers had better performance than the Pt layers. The cell potentials with Pt layers were above 1.950 V at 800 mA cm\(^{-2}\), about 0.350 V higher than those with IrO\(_2\) layers, which confirms that IrO\(_2\) is the main OER catalyst. However, the cells using IrO\(_2\) layers had no performance in FC mode because of the low ORR catalytic activity of IrO\(_2\).

### Electrochemical Impedance Spectroscopy (EIS)

#### 3.3. EIS analysis of the URFCs

To further study the change of the effective interface areas between the catalyst and the reactant, electrochemical impedance spectra of the URFCs both in fuel cell mode and in water electrolysis mode were measured.

The dynamic EIS response of a cell can provide information about the interfacial kinetics, electrode transport process, and membrane hydration [21,22]. Generally, the anodic polarization is very small and can be neglected. Thus, the obtained impedance spectra mainly reflect the cathodic polarization.

Figs. 8 and 9 show Nyquist plots of URFC single cells in fuel cell mode and in water electrolysis mode, respectively. The \(R_\Omega\) (\(R_1\)) (\(R_2\)) combination is chosen as the equivalent circuit (EC) fitting our experimental data. Fig. 10 shows a schematic representation of the EC. It was found from the spectra that the small loop (usually not apparent) at the highest frequency (HF) was overlapped by a large loop at the middle high frequency (MHF). The small loop is due either to the ionic ohmic drop/double layer charging inside the active layer in the granular electrode structure, or to electronic contact problems between the electronic supply and the gas diffusion layer [23,24]. The large loop appears to be most interesting, since it may provide information on a diffusion process responsible for an important part of the total resistance.

\(R_\Omega\) represents the impedance at the intersection of the high frequency (HF) curve with the real axis. It is attributed to the internal resistance of the cell, including the total ohmic resistance of the cell, which can be expressed as a sum of the contributions from uncompensated contact resistance and ohmic resistance of the cell components, such as membrane, catalyst layer, backing, end plate and that between each of them [25]. \(R_1\) represents the resistance that arose by the abovementioned potential fact at the HF small loop and \(R_2\) is the resistance for a mass-transfer process in the oxygen reduction or oxygen evolution [24]. \(Q_1\) and \(Q_2\) are so-called constant phase elements (CPE) [26].

As shown in Fig. 8, we measured the electrochemical impedances of the two kinds of the URFCs operating at 100 mA cm\(^{-2}\) and 800 mA cm\(^{-2}\) with the equivalent circuit shown in Fig. 10.

#### Table 2

Parameters evaluated from fit of EIS in FC mode at 100 mA cm\(^{-2}\) and 800 mA cm\(^{-2}\) with the equivalent circuit shown in Fig. 10.

<table>
<thead>
<tr>
<th>Catalyst layer type</th>
<th>(j_1 = 100) mA cm(^{-2})</th>
<th>(j_2 = 800) mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(R_\Omega) (m(\Omega) cm(^2))</td>
<td>(R_1) (m(\Omega) cm(^2))</td>
</tr>
<tr>
<td>C1</td>
<td>98.7</td>
<td>40.6</td>
</tr>
<tr>
<td>C2</td>
<td>88.7</td>
<td>27.4</td>
</tr>
<tr>
<td>C3</td>
<td>95.7</td>
<td>22.1</td>
</tr>
<tr>
<td>C4</td>
<td>153</td>
<td>85.9</td>
</tr>
<tr>
<td>C5</td>
<td>90.1</td>
<td>13.1</td>
</tr>
<tr>
<td>C6</td>
<td>103</td>
<td>67.4</td>
</tr>
<tr>
<td>C7</td>
<td>120</td>
<td>24.3</td>
</tr>
<tr>
<td>C8</td>
<td>101</td>
<td>52.8</td>
</tr>
<tr>
<td>GDL-Pt</td>
<td>112</td>
<td>80.9</td>
</tr>
<tr>
<td>M-Pt</td>
<td>79.2</td>
<td>21.8</td>
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</tbody>
</table>
Fig. 8. Nyquist plots of URFC single cells in fuel cell mode at 100 mA cm\(^{-2}\) and 800 mA cm\(^{-2}\) with different types of bifunctional catalyst layers. C1, C3, C5, C7 and GDL-Pt sprayed Pt onto the gas diffusion layer while others applied Pt onto the membrane.

and 800 mA cm\(^{-2}\) in fuel cell mode. Table 2 shows the calculated results from the simulated data of EIS in FC mode at 100 mA cm\(^{-2}\) and 800 mA cm\(^{-2}\) with the equivalent circuit shown in Fig. 10 by ZView. As seen in Table 2, when the current density was 100 mA cm\(^{-2}\), the \(R_\Omega\) and \(R_2\) values of the URFCs with various BCLs in FC mode were similar, except for that of the URFC using C4. The \(R_\Omega\) and \(R_2\) values of the URFC with C4 reached 153 m\(\Omega\) cm\(^2\) and 1764 m\(\Omega\) cm\(^2\), respectively, much higher than the others. These values cannot be measured at 800 mA cm\(^{-2}\) due to the lack of cell performance. The large mass transport resistance may result from the large agglomerates of IrO\(_2\) layers and the high resistivity of IrO\(_2\). It is worth noting that when the current densities of URFCs increase from 100 mA cm\(^{-2}\) to 800 mA cm\(^{-2}\), the mass transport resistances of the URFCs are all reduced. The reason is likely that there is a
lower influence of kinetics on impedance at high currents. However, the $R_2$ with different type of BCLs varied evidently. As presented in Table 2, the mass-transfer resistances of the URFCs with BCL1 were much lower than those with BCL2 at high current density. The difference of $R_2$ between the two kinds of BCLs obtained more than 150 mΩ cm$^2$ at 800 mA cm$^{-2}$. The distinction of $R_2$ between C5 and C6 even reached 317.2 mΩ cm$^2$. As a comparison, we can find that the $R_2$ of GDL-Pt was nearly 160 mΩ cm$^2$ larger than that of M-Pt at 800 mA cm$^{-2}$. This suggests that the cells using Pt applied layers onto the GDL can prevent the cell from water flooding when large amounts of water are produced in the cell reaction. It is interesting to note that the $R_2$ of the C3 was 70 mΩ cm$^2$ and 280 mΩ cm$^2$ larger than GDL-IrO$_2$ at 100 mA cm$^{-2}$ and 800 mA cm$^{-2}$, respectively. As mentioned above, the electron conduction path tends to be hindered by a IrO$_2$ agglomerate. Thus, at high current density, the mass-transfer resistance increased quickly due to the limited electron conduction. In conclusion, the higher mass transport resistance is the major factor contributing to the lower cell performance in FC mode at high current density, as shown in Fig. 5.

Table 3 shows the parameters evaluated from the simulated data of EIS in WE mode at 1.55 V with the equivalent circuit shown in Fig. 10 by ZView. It is clearly observed that though the $R_2$ value of GDL-IrO$_2$ was nearly twice as the $R_2$ of GDL-IrO$_2$, the mass transport resistances of the various URFCs were all near 700 mΩ cm$^2$ and there is no coherence in the variation of $R_2$ with the two types of BCLs. This can be explained by the fact that the effective interface area between IrO$_2$ and water in the BCLs was affected slightly by the fabrication methods.

### 3.4. Round-trip efficiencies of the URFCs

The round-trip efficiency $\varepsilon_{RT}$ is used for comparison of the different bifunctional oxygen electrode since the variations in electrode preparation influence the cell performance in FC and WE mode in a different way. This variable compares energy gained in FC mode to the energy needed for gas production in WE mode. It can be calculated from the operating voltages in fuel cell and water electrolysis mode at the current density $j$ [4].

$$\varepsilon(j)_{RT} = \frac{P(j)_{FC}}{P(j)_{WE}} = \frac{U(j)_{FC}}{U(j)_{WE}}$$

The round-trip efficiencies were calculated, at 100 mA cm$^{-2}$ and 800 mA cm$^{-2}$, with the polarization curves of the URFCs shown in Figs. 5 and 6. Fig. 11 shows these efficiency values for different cells. C3 and C4 were not compared because of C4 having no discharge at 800 mA cm$^{-2}$. As expected from the voltage against current density characteristics, the cells with Pt sprayed onto the
GDL displayed significantly higher round-trip efficiency than those with Pt sprayed onto the membrane at high current density. The highest improvement was the URFC using C7, which gained 15.6% higher than the URFC using C8 at 800 mA cm\(^{-2}\). This is mainly caused by the highest enhancement of fuel cell performance at this current density. As shown in Fig. 11, the highest and lowest of the round-trip efficiencies of the URFC were 42.1% and 22.3%, respectively, at 800 mA cm\(^{-2}\), so it can be concluded that the high round-trip efficiency of the URFC can be obtained if the right fabrication method is used.

4. Conclusion

In this study, the effect of the preparation method of bifunctional catalyst layers on the performance of URFCs was investigated. Pt layers formed by spraying onto the GDL showed a more homogeneous and porous surface than that sprayed onto the membrane, which prevented the URFC from water flooding at high current density in fuel cell mode. The current densities of the URFC with Pt layers sprayed onto the GDL are above 0.100 V higher than those using Pt layers sprayed onto the membrane at 800 mA cm\(^{-2}\), though they were nearly the same at 100 mA cm\(^{-2}\). The difference of mass transport resistances between the two kinds of BCLs obtained more than 150 mΩ cm\(^{2}\) at 800 mA cm\(^{-2}\). The results also showed that the electron conduction path tends to be hindered by an IrO\(_2\) agglomerate, which induces an increase in the mass-transfer resistance. Cell performances were also found to change slightly with different catalyst layers in water electrolysis mode. The highest and lowest of the round-trip efficiencies of the URFC were 42.1% and 22.3%, respectively, at 800 mA cm\(^{-2}\).

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