



Short communication

Electrochemical studies of an unsupported PtIr electrocatalyst as a bifunctional oxygen electrode in a unitized regenerative fuel cell

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ABSTRACT

The electrochemical performance of an unsupported PtIr electrocatalyst was evaluated as a bifunctional oxygen electrode in a unitized regenerative fuel cell (URFC). The catalyst was a mixture of unsupported Pt black and Ir black catalysts in varying proportions. The performance of the unsupported PtIr catalyst was studied by using a rotating ring disc electrode (RRDE) and linear sweep voltammetry (LSV). In addition, a unit cell test was performed simultaneously in the electrolyzer and in the fuel cell mode to evaluate the performance and durability of PtIr catalysts. The catalyst composition consisting of 85 wt.% Pt and 15 wt.% Ir showed high oxygen evolution reactivity and comparable electrochemical activity compared to the unsupported Pt black catalyst. The URFC using Pt₈₅Ir₁₅ catalyst showed the highest round-trip efficiency when estimated at different current densities. The cycle performance of URFC with Pt₈₅Ir₁₅ catalyst was stable for 120 h at an applied current density of 0.5 A cm⁻².

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1. Introduction

The key issues in URFC development are the performance and stability of the bifunctional oxygen electrode (BOE). Currently, the preferred oxygen reduction catalysts demonstrate poor oxygen evolution performance, and the preferred oxygen evolution catalysts demonstrate poor oxygen reduction performance, which results in a decrease in the round-trip conversion efficiency (electric power → hydrogen storage → electric power) of URFCs. The peak separation between the oxygen reduction and oxygen oxidation is approximately 0.6 V. It is necessary to decrease this potential difference to less than 0.3 V [1].

The catalytic behavior of the catalyst in the BOE is affected by the size and composition of the metal nanoparticles, the interactions with the support, and the interactions between the metal components. The performance of the BOE varies significantly with the method used to prepare the electrode. Conventional methods such as adsorption, ion-exchange, or deposition of two metal precursors on the support often lead to the formation of metal particles that are relatively large and non-uniform in size and composition.

For BOE design, there is the additional requirement of an electrically conductive support for the catalysts. The typical support

material used in polymer electrolyte membrane (PEM) fuel cells is high-surface area carbon. However, carbon corrosion is disastrous at very positive potentials when the URFC is operated in the electrolyzer mode [2]. Sintering and dissolution of the metal catalyst on the carbon surface increases with carbon corrosion. The oxidation of the carbon surface leads to an increase in the hydrophilicity and affects water management, leading to increased mass transport losses. Carbon corrosion decreases the catalyst utilization due to a decrease in the electrical contact between the catalysts and the carbon current collector and subsequently increases the cell polarization. This effect causes the performance of the BOE to degrade quickly, which results in an inadequate performance for most applications.

Recently, it has been reported that Ir and IrO₂ exhibit good activity for the oxygen evolution reaction [3–5]. However, there are limited numbers of electrochemical studies that focus on the performance of PtIr catalysts as BOEs in both the electrolyzer and fuel cell modes.

The objective of this work is to study the electrochemical performance of unsupported PtIr electrocatalysts as bifunctional oxygen electrodes in URFCs. The catalysts used in our study were a mixture of unsupported Pt black and Ir black catalysts with varying Ir black content. The performances of the unsupported PtIr catalysts were studied using a rotating ring disc electrode (RRDE). In addition, a unit cell test was performed simultaneously to study the performance and durability of PtIr catalysts in electrolyzer and fuel cell modes.

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2. Experimental

2.1. Preparation of PtIr catalyst ink

Physical mixtures of commercially available Pt black and Ir black catalysts with Pt black:Ir black compositions of 100:0, 85:15, 70:30, and 40:60 were prepared and used as BOE catalysts. The catalyst was dispersed in de-ionized water instead of isopropyl alcohol (IPA) due to Pt black agglomeration in the conventional IPA solution. The ink was prepared by mixing the catalyst (10 mg) with 1 ml of de-ionized water for 30 min in an ultrasonic bath. The catalyst ink used to prepare the electrode for fuel cell testing contains 20% by weight of Nafion ionomer. Ten microliters of the ink was loaded on a glassy carbon disk electrode (GCE). After drying, a 5 μL mixture of 1:20 Nafion solution (5 wt.% Nafion dispersion, DuPont Co. Ltd.) and methyl alcohol was applied to the GCE.

2.2. Electrochemical studies

The electrochemical properties of the physically mixed PtIr black catalysts were characterized by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. To determine the electrochemical surface area, an estimated amount of catalyst ink was placed on the glassy carbon electrode of the RRDE (0.196 cm^2), and the CVs of the catalysts were recorded in a 0.5 M H_2SO_4 solution purged with nitrogen (N_2). To evaluate the ORR polarization, the LSV of catalysts was performed in 0.5 M H_2SO_4 under oxygen (O_2). The experiments were carried out at a scan rate of 5 mV s^{-1} using a Pine Potentiostat-Model AFCBP1.

2.3. Membrane and electrode assembly (MEA) preparation and unit cell test

The catalyst ink was applied to the GDL (LT140W ELAT[®], E-TEK), followed by drying at 80 $^\circ\text{C}$. The catalyst loadings in the electrodes were between 1 and 6 mg cm^{-2} . The MEAs were prepared by hot-pressing the electrodes onto a Nafion[™] 112 membrane at 140 $^\circ\text{C}$ with 800 psi for 3 min.

The MEA performance of the URFC was measured in a single cell with an electrode area of 5 cm^2 . In the fuel cell mode, humidified hydrogen and oxygen were supplied to the anode and cathode at a constant flow rate of 150 $\text{cm}^3 \text{min}^{-1}$. The measurements were performed at 75 $^\circ\text{C}$. In the electrolyzer mode, de-ionized water heated at 70 $^\circ\text{C}$ was supplied to the bifunctional oxygen electrode at constant flow rate of 60 $\text{cm}^3 \text{min}^{-1}$ [6–8].

The performance of the URFC in the cycle test was evaluated by measuring the voltage transients at a constant current density of 0.5 A cm^{-2} . The duration of each cycle was 24 h, with 12 h in the electrolyzer mode and 12 h in the fuel cell mode [9]. Additionally, an electrolyte drying time of 2.5 min at the transition between the two modes was used in order to switch from the electrolyzer mode to the fuel cell mode.

3. Results and discussion

The performance of the PtIr catalysts was studied with cyclic voltammetry. Fig. 1 shows the electrochemical activity of PtIr (hydrogen adsorption and desorption peaks) as a function of Ir black content. As shown in Fig. 1, the desorption peak of hydrogen decreases with increasing of Ir black content in the PtIr catalyst. The results indicate that the electrochemical active surface area of the Pt₈₅Ir₁₅ catalyst is comparable to that of the Pt black catalyst (Pt₁₀₀Ir₀).

Fig. 2(a) shows linear sweep voltammograms obtained for various PtIr catalyst compositions. The PtIr catalyst shows well-defined mass transfer and kinetic regions similar to those obtained for

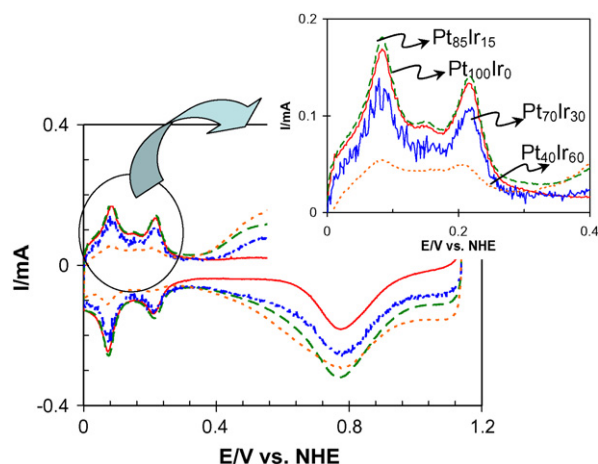


Fig. 1. CV curves showing the effect of Ir content on the catalytic activity of PtIr catalysts.

oxygen reduction on the Pt black catalyst. However, in the activation controlled region (0.8–0.9 V), the PtIr catalyst with a high concentration of Ir shows slightly less activity towards the oxygen reduction reaction (ORR) than the pure Pt black catalyst. The Pt₄₀Ir₆₀ catalyst shows the lowest onset potential for oxygen reduction due to lower activity of the Ir catalyst for ORR.

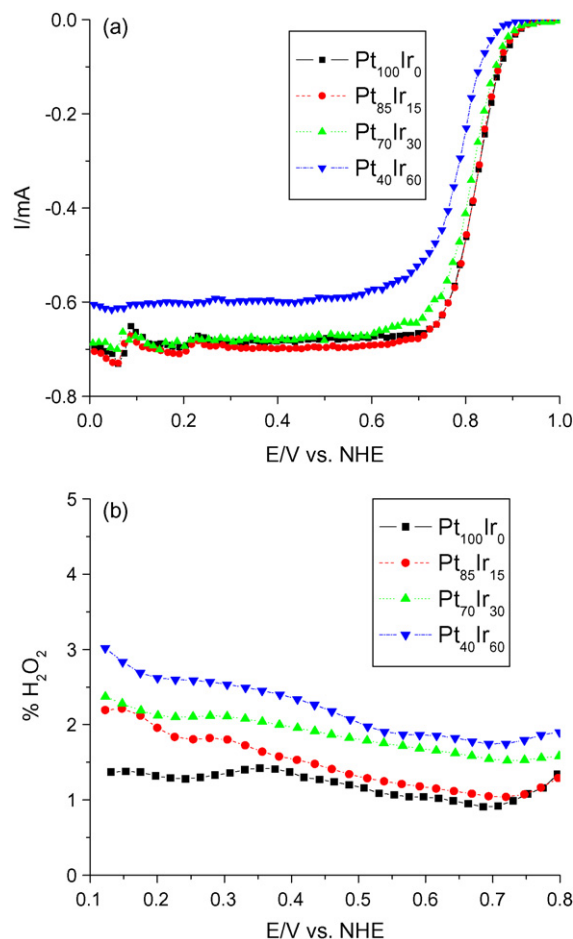


Fig. 2. (a) Activity of the oxygen reduction reaction measured with LSV as a function of various compositions of PtIr catalysts. (b) H_2O_2 formation during ORR in 0.5 M H_2SO_4 saturated with oxygen. Rotation speed of the electrode is 900 rpm.

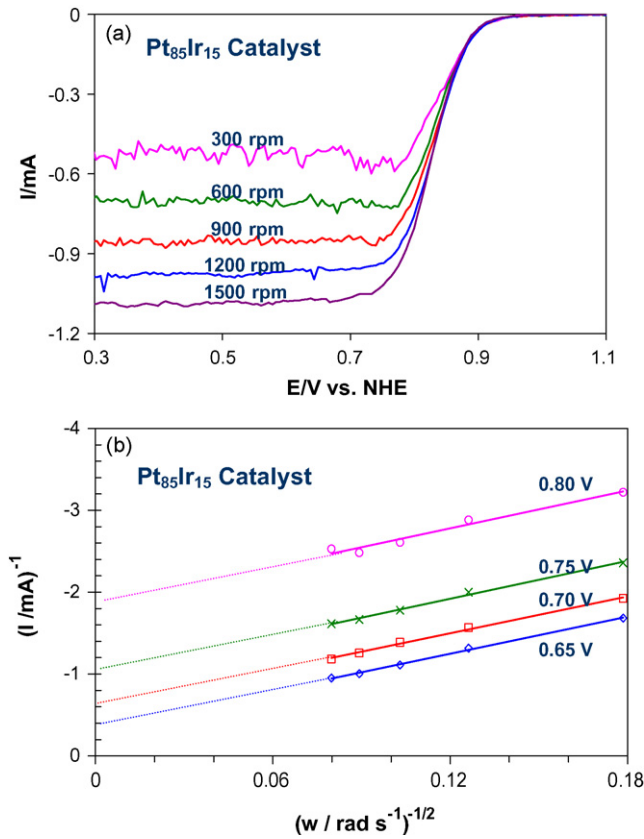


Fig. 3. (a) Oxygen reduction polarization curves obtained on the Pt₈₅Ir₁₅ catalyst at different rotation speeds, and (b) Levich–Koutecky plots obtained for the Pt₈₅Ir₁₅ catalyst at 0.8, 0.75, 0.7, and 0.65 V (vs. NHE).

The formation of hydrogen peroxide (H₂O₂) is a critical criterion for the choice of a suitable catalyst in fuel cells. Oxygen may be reduced partially to H₂O₂ or completely to H₂O. The generation of H₂O₂ leads not only to the loss of the intrinsic activity of the catalyst,

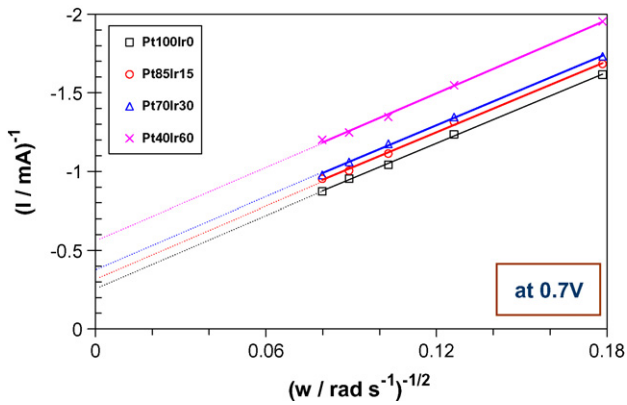


Fig. 4. Levich–Koutecky plots for ORR on Pt₁₀₀Ir₀, Pt₈₅Ir₁₅, Pt₇₀Ir₃₀, and Pt₄₀Ir₆₀ catalysts at 0.7 V in oxygen saturated 0.5 M H₂SO₄ solution.

Table 1
Kinetically limited current, I_k , produced at 0.7 V vs. NHE during oxygen reduction on PtIr catalysts with various compositions.

Catalyst	I_k (mA)
Pt ₁₀₀ Ir ₀	3.85
Pt ₈₅ Ir ₁₅	3.23
Pt ₇₀ Ir ₃₀	2.56
Pt ₄₀ Ir ₆₀	1.72

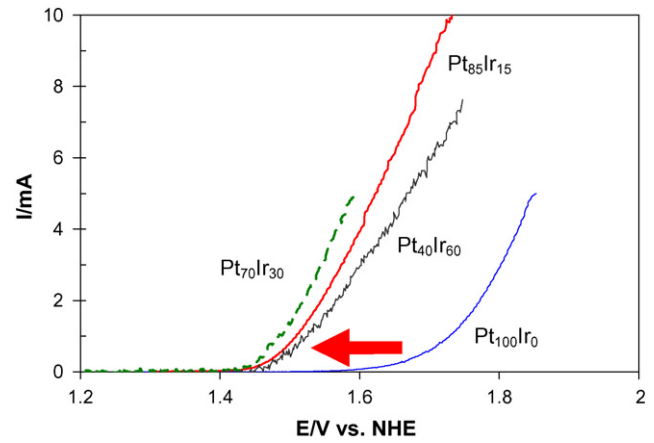


Fig. 5. The effect of Ir content in PtIr catalysts on OER.

but also contributes to the deterioration of the membrane electrode assembly [9–12]. The percentage of H₂O₂ produced was estimated with the following equation [11–14]:

$$\%H_2O_2 = \frac{(200 I_R/N)}{(I_D + I_R/N)} \quad (1)$$

where I_R is the ring current, I_D is the disc current, and N is the collection efficiency. In this work, the value of N was taken as 0.39 [12–14]. As shown in Fig. 2(b), the formation of hydrogen peroxide (H₂O₂) in the potential region of 0.7 V (a typical operating potential)

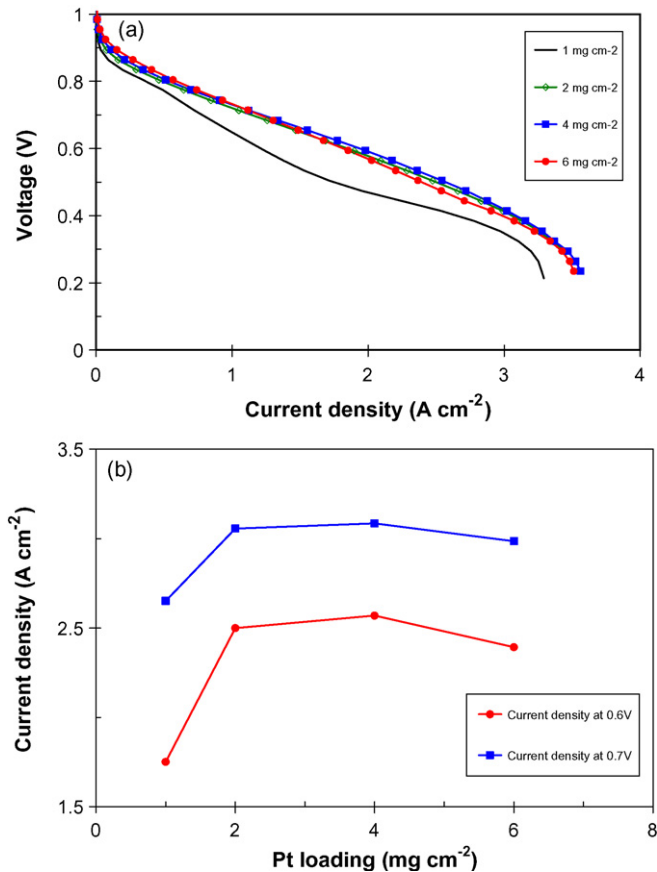


Fig. 6. (a) Polarization curves obtained in fuel cell mode with the following Pt black catalyst loadings: 1.0, 2.0, 4.0, and 6.0 mg cm⁻². A commercial E-TEK platinum catalyzed electrode was used as the anode with a loading of 0.5 mg cm⁻². (b) The current densities were estimated at 0.6 and 0.7 V vs. NHE.

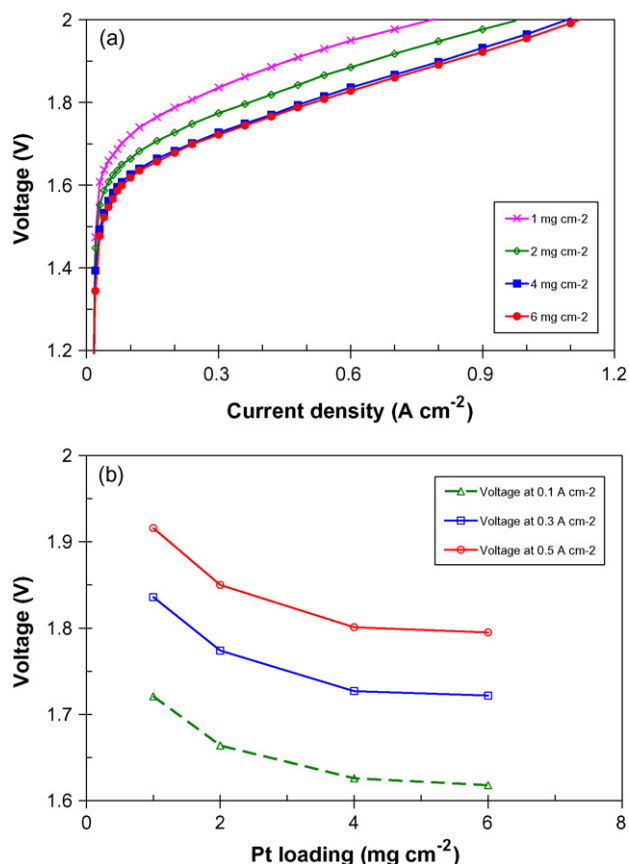


Fig. 7. (a) Polarization curves obtained using the same Pt black catalyst loadings as in Fig. 6. (b) The voltages were measured at applied current densities of: 0.1, 0.3, and 0.5 A cm⁻².

for all PtIr catalysts is approximately 2%. This value is similar to that of the unsupported Pt catalyst.

Fig. 3(a) shows polarization curves for oxygen reduction on Pt₈₅Ir₁₅ catalysts at different rotation speeds. The measurements were conducted using a potential scan rate of 5 mV s⁻¹. The results indicate that ORR is under mixed kinetic and diffusion control over a wide range of potentials [15]. The kinetic control regions are in the range from 0.7 to 0.9 V vs. NHE, while diffusion control is in the range from 0.3 to 0.7 V vs. NHE. As shown in Fig. 3(a), well-defined limiting currents were observed as a function of the rotation rate. To determine the number of electrons involved in the ORR, first order kinetics with respect to oxygen concentration was assumed. Under such conditions, the current is related to the rotation speed [11,14,16,17] by the following equation:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{B\omega^{1/2}} \quad (2)$$

where I is the current, I_k is the kinetic current, B is the Levich slope and ω is the rotation speed of the RRDE. The Levich slope is given by

$$B = 0.62 nFAcD^{2/3} \nu^{-1/6} \quad (3)$$

where n is the number of electrons transferred per O₂ molecule, F is the Faraday constant, A is the electrode surface area, c is the concentration of O₂ in the solution, D is the diffusion coefficient of O₂ in the solution, and ν represents the kinetic viscosity of the solution [15]. The Levich slope was estimated to be 0.13, which, according to Eq. (3), results in $n = 4$ for $A = 0.196$ cm². Fig. 3(b) shows the Levich–Koutecky plots obtained in the potential range of 0.65–0.8 V vs. NHE. A linear relationship can be observed between I^{-1} and $\omega^{-1/2}$. The slopes are nearly constant, which indicates that the elec-

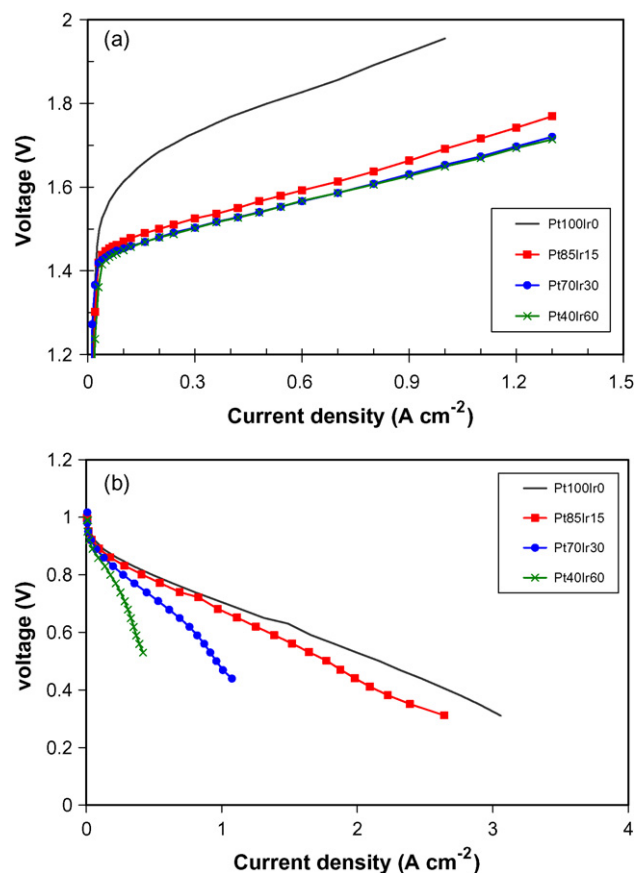


Fig. 8. Polarization curves obtained using various composition of PtIr catalyst with a catalyst loading of 4 mg cm⁻². The temperatures in the electrolyzer mode (a) and in the fuel cell mode (b) were 70 and 75 °C, respectively.

trochemical reaction follows first order kinetics. In addition, the n values for the reaction are almost the same. Similar results were also obtained for the Pt₁₀₀Ir₀, Pt₇₀Ir₃₀, and Pt₄₀Ir₆₀ catalysts.

Fig. 4 shows the relationship between I^{-1} and $\omega^{-1/2}$ for various compositions of PtIr catalysts at 0.7 V. The observed parallelism of the slopes indicates that the number of electrons (n) involved in the ORR is close to four in the electron reduction path of O₂. The kinetically limited currents, I_k , are summarized for various catalyst compositions in Table 1. The value of I_k is determined from the y-intercept of the I^{-1} vs. $\omega^{-1/2}$ plots.

Fig. 5 shows the oxygen evolution reaction (OER) reactivity of PtIr catalysts as a function of the catalyst composition. The onset potential for OER for the unsupported Pt black catalyst is approximately 1.6 V, while the estimated OER for the PtIr black catalyst is approximately 150 mV more negative. The results indicate that the PtIr black catalyst is more effective as a catalyst for the oxygen evolution reaction than the pure Pt black catalyst is. In the case of PtIr catalysts, the oxygen evolution rate increases with increasing Ir content in the PtIr catalyst, up to 30 wt.%.

The polarization curves obtained in the fuel cell mode for MEAs prepared with different Pt loadings are shown in Fig. 6(a). As shown in this figure, the cell performance increases with increasing Pt loading. The dependence of the current density measured on the Pt catalyst at 0.6 and 0.7 V is shown in Fig. 6(b). The performance increases with increasing Pt loading up to 4.0 mg cm⁻². Further increase of Pt loading to 6 mg cm⁻² results in a negligible decrease in the current density.

Fig. 7(a) shows that the cell performance in the electrolyzer mode increases with increased Pt loading. The cell voltages estimated at different current densities as a function of Pt loading are

Table 2

Round-trip conversion efficiency of URFCs estimated for various compositions of PtIr catalysts at current densities of 0.5 and 1.0 A cm⁻².

Current density (A cm ⁻²)	Composition (Pt:Ir)	V _{FC} (V)	V _{WE} (V)	ε _{RT} (%)
0.50	100:0	0.798	1.799	44
	85:15	0.774	1.565	49
	70:30	0.720	1.545	47
	40:60	0.380	1.543	25
1.00	100:0	0.705	1.955	36
	85:15	0.683	1.658	41
	70:30	0.470	1.653	28
	40:60	0.313	1.649	19

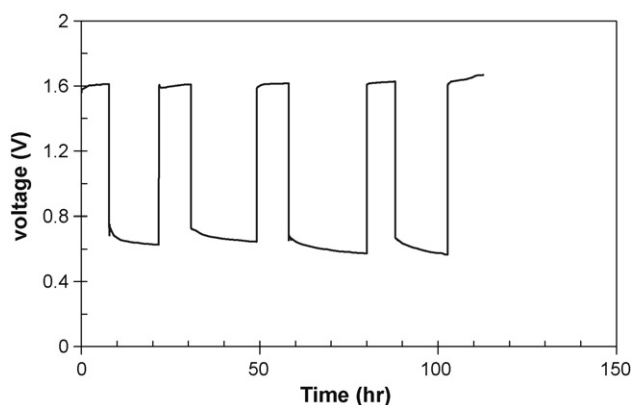


Fig. 9. The cycling stability test was performed using a current density of 0.5 A cm⁻². The catalyst (Pt₈₅Ir₁₅) loading was 4 mg cm⁻².

presented in Fig. 7(b). These decrease with increased Pt loading up to 4 mg cm⁻². With further increases in the Pt loading, the voltage reaches a plateau, indicating that the optimum catalyst loading in the catalyst layer for URFC is 4 mg cm⁻². In addition to the fact that the fuel cell performance reaches a plateau at 2 mg cm⁻², according to the results reported in this study, higher catalyst loading is more effective for high energy conversion efficiency in URFCs.

The performance of bifunctional oxygen electrodes with PtIr catalysts as an active material for oxygen reduction and the oxygen evolution reaction was tested using a 5 cm² single cell. Fig. 8(a) and (b) shows the polarization curves of the URFC with a catalyst-coated electrode (CCE) with unsupported PtIr catalyst. In the electrolyzer mode (Fig. 8(a)), the performance of unsupported PtIr catalyzed MEA is higher than that of unsupported Pt catalyzed MEA due to the higher oxygen evolution reactivity of the PtIr catalyst. This fact indicates that the oxygen evolution reaction takes place predominantly on the Ir catalyst. In the fuel cell mode (Fig. 8(b)), the performance of unsupported PtIr catalyzed MEA is lower than that of the unsupported Pt catalyzed MEA due to the lower oxygen reduction reactivity of PtIr catalyst.

The round-trip energy conversion efficiencies (ε_{RT}) during water electrolysis and fuel cell operation were calculated using a previously reported equation [1,3]:

$$\epsilon_{RT} = \frac{V_{FC}}{V_{WE}} \quad (4)$$

where V_{FC} and V_{WE} are the cell voltages for the fuel cell and water electrolyzer, respectively, at a given current density. Table 2 summa-

rizes the efficiency values of URFCs estimated for different current densities. The results indicated that the composition of 85 wt.% Pt and 15 wt.% Ir shows the highest round-trip energy conversion efficiency.

The cycle performance of the MEA with a Pt₈₅Ir₁₅ catalyst is shown in Fig. 9. During the cycling test, a current density of 0.5 A cm⁻² was applied to the cell. The results indicate that the cycle performance of the URFC with Pt₈₅Ir₁₅ catalyst is stable for 120 h at an applied current density of 0.5 A cm⁻².

4. Conclusion

Bifunctional electrocatalysts for the oxygen electrode of a URFC were prepared with unsupported Pt and Ir black catalysts. The electrochemical active surface area and oxygen reduction reactivity of the Pt₈₅Ir₁₅ catalyst was comparable to those of the unsupported Pt black catalyst (Pt₁₀₀Ir₀). With increasing Ir content in the PtIr catalyst, the activity towards ORR decreases compared with that of the unsupported Pt black catalyst due to the lower activity of the Ir catalyst for ORR. In spite of the lower activity of PtIr catalysts for ORR, the onset potential for OER for the PtIr black catalyst is about 150 mV more negative than that of the Pt black catalyst is, which implies that the unsupported PtIr black catalyst is more effective than the Pt black catalyst for the oxygen evolution reaction. The URFC using the Pt₈₅Ir₁₅ catalyst shows good initial performance and durability in the cycle test for 120 h at an applied current density of 0.5 A cm⁻².

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