



IrO₂-deposited Pt electrocatalysts for unitized regenerative polymer electrolyte fuel cells

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Abstract

An IrO₂/Pt electrocatalyst for the polymer electrolyte-type unitized regenerative fuel cell (URFC) was prepared by deposition of iridium oxide (IrO₂) particles on Pt black via a colloidal iridium hydroxide hydrate precursor, and URFC performance was examined. After the iridium hydroxide hydrate deposited Pt was calcined at 400 °C in air for 1 h, rutile-structure IrO₂ particles (20–50 nm dia.) were formed on Pt particle clusters. TEM and pore volume distribution analysis revealed that the microstructure of the deposited IrO₂/Pt catalyst was different from the mixed IrO₂/Pt catalyst. The cell using the deposited IrO₂/Pt (20 at % Ir) catalyst showed similar fuel cell performance with the mixed IrO₂/Pt electrode of higher Pt content (10 at % Ir) while maintaining water electrolysis performance. Consequently, 51% round-trip energy conversion efficiency at a current density of 300 mA cm⁻² was attained.

1. Introduction

A regenerative fuel cell (RFC) is an energy storage device using hydrogen as an energy medium [1–4]. RFCs have the advantages of long-term energy storage (free from self-discharge) and theoretically higher energy densities compared to secondary batteries. However, the RFC system is usually rather complicated and expensive due to the use of two separate electrochemical cells: a fuel cell and a water electrolyser [5, 6].

The unitized regenerative fuel cell (URFC) is an electrochemical cell working both as fuel cell and as water electrolyser, so that it is expected that a simpler and more compact RFC system can be constructed by using URFC. So far, such a URFC system has been developed for space applications [7, 8]. Figure 1 shows schematic diagrams of a polymer electrolyte-type URFC in fuel cell (PEFC) and water electrolyser (PEWE) operation. During PEFC operation, oxygen reduction and hydrogen oxidation take place, and during PEWE operation water decomposition (oxygen evolution) and proton reduction (hydrogen evolution) reactions take place. The most important technical problem is the development of the bifunctional electrode for oxygen reduction and evolution with high efficiency [9–11]. Previously, we reported a preparation of IrO₂ of high specific surface area using a colloidal iridium hydroxide hydrate precursor, and characterization of the URFC

performance of mixed catalysts of the IrO₂ and commercially available Pt black [12]. The round-trip energy conversion efficiency (total conversion efficiency of electric power → hydrogen → electric power) of a URFC showed the highest values (49% at 300 mA cm⁻², 42% at 500 mA cm⁻²) at an Ir content of 10–30 at % in the O₂ electrode. However, since these efficiencies are significantly lower than those of batteries, further efforts are necessary to improve the efficiency of the URFC.

To improve the efficiency of the URFC a new preparation method of IrO₂/Pt catalysts was developed by modifying the previous method. In this paper characterization of the IrO₂/Pt catalyst prepared by the new method and the URFC performance are reported with comparisons to the previous IrO₂/Pt catalyst.

2. Experimental details

2.1. Preparation and characterization of IrO₂/Pt black electrocatalysts by deposition method

Deposition of IrO₂ on Pt black was conducted by a procedure similar to that previously used for synthesizing IrO₂ fine powder [12]. An appropriate amount of hexachloroiridium(IV) acid hydrate (H₂IrCl₆ · xH₂O)

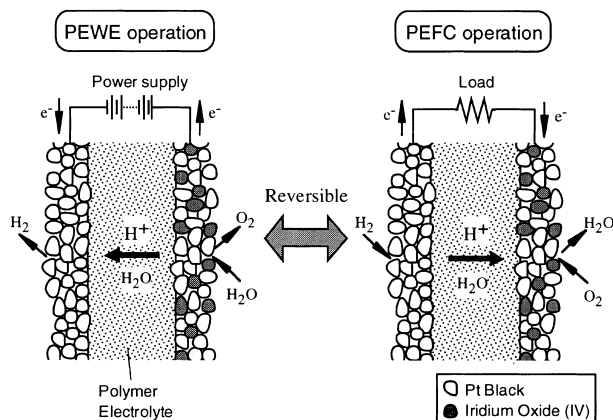


Fig. 1. Schematic diagram of the operation of a polymer electrolyte-type URFC.

was dissolved in 0.038 M NaOH aqueous solution (stoichiometry: $\text{H}_2\text{IrCl}_6/\text{NaOH} = 1/9$) and held at 40 °C for 4 h with continuous stirring and nitrogen bubbling. After the solution had cooled to room temperature, platinum black (Johnson Matthey, specific surface area: $26.1 \text{ m}^2 \text{ g}^{-1}$) was suspended in the solution and ascorbic acid (200 mg) was added to the solution to avoid air oxidation of the iridium complex. The pH of the solution was then lowered to about 8 by the dropwise addition of 0.1 M HClO_4 solution. After the solution had been left for a day, the precipitate was separated, washed with distilled water several times, and dried under vacuum to obtain a mixture of iridium hydroxide hydrate/platinum black. Finally, the mixture was calcined at 400 °C for 1 h in air to give IrO_2 -deposited Pt black electrocatalyst. BET specific surface area of the obtained rutile-type IrO_2 catalyst showed maximum at the calcination temperature of 400 °C as previously reported [12]. The IrO_2 deposited Pt black powder was characterized by the following techniques: crystal structure and crystallite size of the powder determined by XRD (Jeol JDX-8020), specific surface area and pore volume distribution determined by gas absorption (Micrometrics ASAP2010), morphology and elemental analysis by TEM (Hitachi H-9000) and EPMA (Horiba EMAX-3700).

2.2. Preparation of membrane and electrode assembly and evaluation of URFC performance

Details of the electrode and MEA preparation procedures were described previously [12]. The IrO_2 -deposited Pt black powder obtained was made into a PTFE-bonded porous sheet (PTFE content: 15 wt %) and then Nafion[®] solution was impregnated into the porous sheet ($0.8 \text{ mg Nafion}^{\text{®}} \text{ cm}^{-2}$) to increase the number of electrochemical active sites on the electrode. A Pt black electrode sheet was also prepared by the same procedure. An IrO_2 -deposited Pt black electrode (oxygen electrode) and a Pt black electrode (hydrogen electrode) prepared by similar procedures as the oxygen electrode were hot-pressed onto both sides of a pretreated

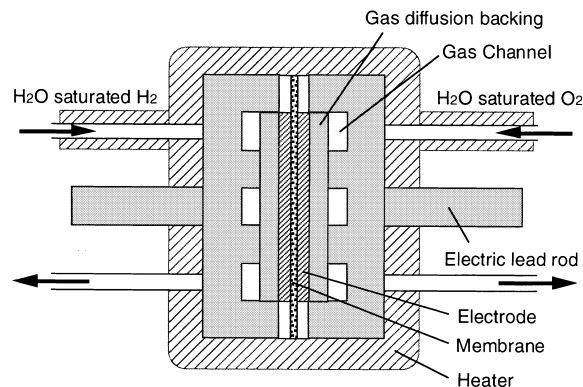


Fig. 2. Schematic illustrations of the cross-sections of a single cell of a URFC.

Nafion[®] 115 membrane at 160 °C for 60 s to obtain MEA.

Evaluation of URFC performance was conducted by a single cell with an active electrode area of 10 cm^2 (geometric). A schematic diagram of a cross-section of the single cell during fuel cell operation is shown in Figure 2. The MEA was clamped between end plates into which straight flow channels were machined. During fuel cell operation, the single cells were usually operated at 80 °C on H_2/O_2 with anode/cathode pressures of 0.30/0.30 MPa. Humidification of the reactant gases was accomplished by bubbling the gases through heated water-filled bottles that were kept at 80 °C. During water electrolysis operation, purified water was supplied to the bottom of the single cell instead of humidified gases. The cells and water reservoir were kept at 80 °C with atmospheric pressure.

3. Results and discussions

3.1. Characterization of IrO_2 -deposited Pt black

Details of the precipitation reaction of the iridium oxide precursor ($\text{Ir}(\text{OH})_3(\text{H}_2\text{O})_3$) from H_2IrCl_6 solution were described previously [12]. Figure 3 shows XRD patterns of the iridium hydroxide hydrate/Pt black obtained by the deposition method before and after calcination in air at 400 °C for 1 h. Before the calcination, the XRD peaks (Figure 3(a)) of the precipitates were assigned to Pt and iridium hydroxide hydrate. After the calcination (Figure 3(b)), all peaks assigned to hydroxide hydrate disappeared and new peaks indicated a rutile-structured IrO_2 . Therefore, the catalyst calcined at 400 °C turned out to be a rutile-type IrO_2 /Pt black mixture. To confirm the structure of the catalyst, TEM observations were conducted. TEM images of electrocatalysts by the deposition method, shown in Figure 4(a), reveal that IrO_2 particles were deposited on the Pt agglomerate surface (IrO_2 particles are shown by arrows in Figure 4(a)). On the other hand, the structure of the mixed IrO_2 /Pt catalyst was completely different from that of the deposited

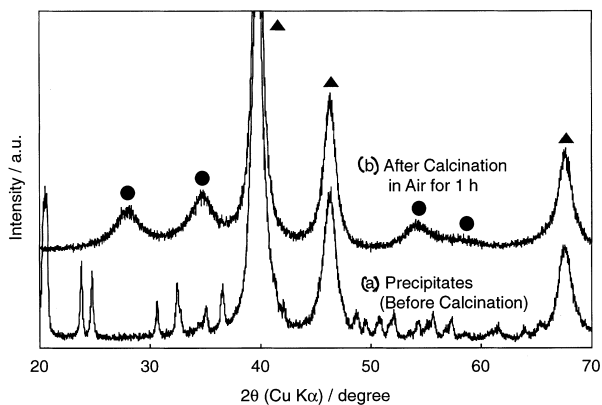


Fig. 3. X-ray diffraction patterns of precipitates by the deposition method: (a) precipitates before calcination, (b) precipitates after calcination in air at 400 °C for 1 h. Key: (▲) Pt and (●) IrO₂.

IrO₂/Pt, as shown in Figure 4(b). IrO₂ particles also aggregate in the mixed IrO₂/Pt catalyst, so that the dispersion of IrO₂ particles is relatively low. The mixed IrO₂/Pt catalyst was made by mixing Pt black powder (Figure 4(c)) and IrO₂ powder (Figure 4(d)) deposited from a homogeneous solution of the aqueous iridium complex. As shown in Figure 4(d), the IrO₂ powder consists of aggregated clusters of IrO₂ particles of size 30–50 nm. From the XRD pattern (Figure 3(b)), it was found that the crystallite size of the IrO₂ was about 3 nm determined by the Scherrer equation [13],

$$d = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (1)$$

where d is the diameter of the crystallite (Å), λ is wavelength of the X-rays (Å), β is full width at half maximum of the diffraction peak (radians) and θ_B is the Bragg angle of the peak. Thus, IrO₂ particles of 30–50 nm also consist of single-crystalline nanocrystallites. When the deposition reaction takes place in the supersaturated solution of iridium complex, subsequent nucleation would occur more easily on the surface of the nuclei than in the solution, thereby forming polycrystalline particles. These polycrystalline particles would aggregate further to form larger agglomerates. When Pt black particles are suspended in the solution, most of these polycrystalline iridium hydroxide hydrate particles stick on the Pt black aggregates to form the Pt/Ir(OH)₃(H₂O)₃ mixture, so that further aggregation of particles is prevented. This is the reason for the difference in morphology between the deposited IrO₂/Pt and mixed IrO₂/Pt electrocatalysts.

3.2. Evaluation of fuel cell/water electrolysis performance

The performance evaluation sequence was usually fuel cell operation followed by water electrolysis operation. Figure 5 shows the terminal voltage vs. current density

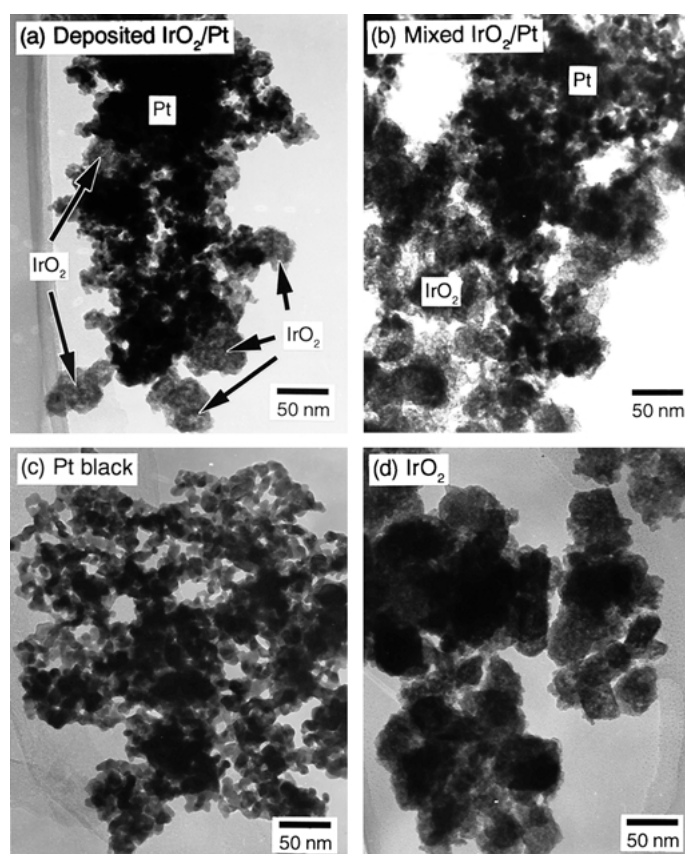


Fig. 4. Transmission electron microphotographs of (a) deposited IrO₂/Pt, (b) mixed IrO₂/Pt, (c) Pt black, and (d) IrO₂.

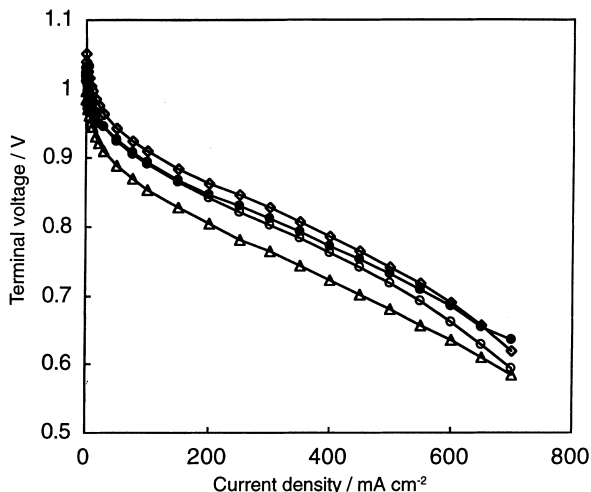


Fig. 5. Terminal voltage against current density curves of URFCs during fuel cell operation. Key: (\diamond) Pt, (\bullet) deposited IrO_2/Pt (20%/80%), (\circ) mixed IrO_2/Pt (10%/90%) and (Δ) mixed IrO_2/Pt (30%/70%).

curves during fuel cell operation for a cell using the deposited IrO_2/Pt electrocatalyst (20 at % Ir) in the oxygen electrode along with the curves for the cells using Pt black (0 at % Ir) and the mixed IrO_2/Pt electrocatalysts (10 and 30 at % Ir) in the electrode. In the case of the mixed IrO_2/Pt cell performance decreased with increasing IrO_2 content, due to IrO_2 being less active for oxygen reduction than Pt. Interestingly, the cell using the deposited IrO_2/Pt (20 at % Ir) showed better performance than the mixed IrO_2/Pt (10 at % Ir). This indicates that the Pt electrocatalyst in the deposited IrO_2/Pt is more effectively used during fuel cell operation. This difference in fuel cell performance is probably due to electrode morphologies, which will be discussed below.

The terminal voltage against current density curves for water electrolysis operation are shown in Figure 6. During water electrolysis, the voltage decreased dramatically with introduction of IrO_2 to the oxygen electrode. As for water electrolysis, the performance increased with increasing IrO_2 content regardless of the preparation procedure of IrO_2/Pt catalyst. Therefore, the fuel cell performance was successfully improved whilst maintaining the high water electrolysis performance by using the deposited IrO_2/Pt electrocatalysts.

As described above, this improvement in URFC performance is likely due to the microstructure of the electrocatalysts, because the deposited IrO_2/Pt and the mixed IrO_2/Pt show nearly the same specific surface area ($34.6 \text{ m}^2 \text{ g}^{-1}$ and $35.3 \text{ m}^2 \text{ g}^{-1}$, respectively), while the structures of the mixed and the deposited IrO_2/Pt were significantly different, as determined from the TEM images. To investigate the microstructure of the electrode more precisely, pore volume distributions of the electrocatalysts were examined by the nitrogen adsorption method (Figure 7). The pore volume distribution was considerably different between the IrO_2 and the Pt black: the IrO_2 showed a relatively sharp peak at a pore

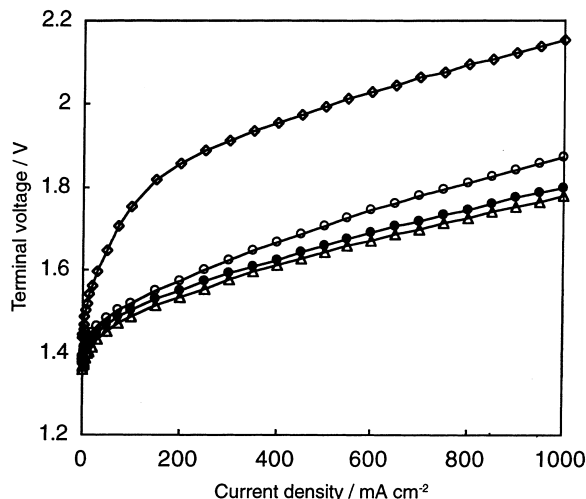


Fig. 6. Terminal voltage against current density curves of URFCs during water electrolysis operation. Key: (\diamond) Pt, (\bullet) deposited IrO_2/Pt (20%/80%), (\circ) mixed IrO_2/Pt (10%/90%) and (Δ) mixed IrO_2/Pt (30%/70%).

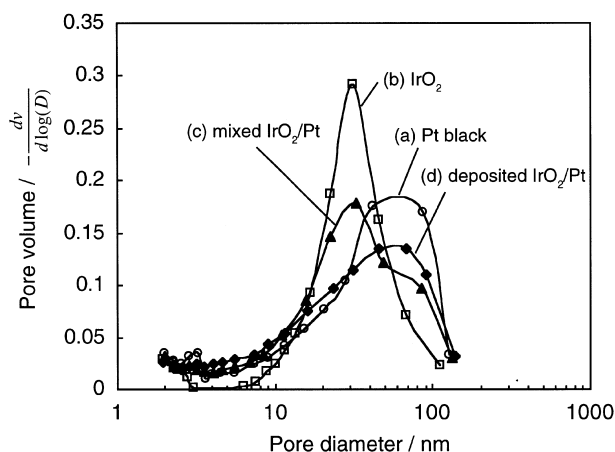


Fig. 7. Pore volume distribution of (a) Pt black, (b) IrO_2 , (c) mixed IrO_2/Pt and (d) deposited IrO_2/Pt .

diameter of 30 nm, whereas the Pt black had a broad peak around 30–100 nm with a tail on the smaller pore diameter side. As for IrO_2/Pt , the distribution of the mixed IrO_2/Pt was solely an addition of the distribution of the Pt black and the IrO_2 , however the distribution of the deposited IrO_2/Pt electrocatalyst was very similar to that of the Pt black. This suggests that the structure of the electrode layer using the deposited IrO_2/Pt is similar to the Pt black electrode. Based on the TEM images and the pore distribution analyses, the electrode structure of the two kinds of IrO_2/Pt may be schematically illustrated as in Figure 8. In the deposited IrO_2/Pt catalyst, it is relatively easy to maintain the conduction path of electrons along Pt agglomerates because the deposited IrO_2 particles are dispersed (Figure 8(a)). However, the electron conduction path tends to be hindered by IrO_2 agglomerates in the mixed IrO_2/Pt catalysts as shown in Figure 8(b). Although IrO_2 is a good electronic conductor ($\rho = 49 \mu\Omega \text{ cm}$ at 300 K) as a metal oxide, the

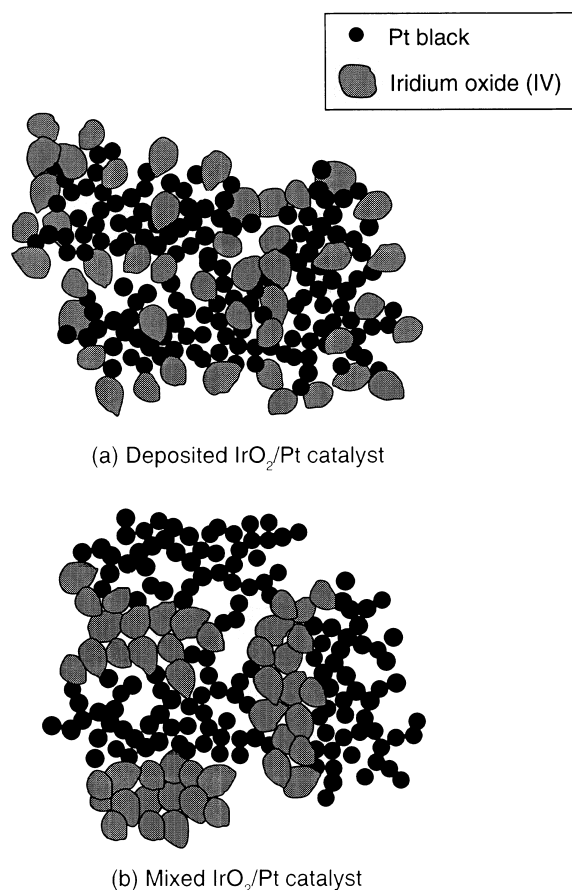


Fig. 8. Schematic diagram of (a) deposited IrO₂/Pt and (b) mixed IrO₂/Pt.

Table 1. Energy conversion efficiency of URFC during fuel cell, water electrolysis and round-trip at 300 and 500 mA cm⁻²

Catalyst/(Ir at %/Pt at %)	Current density /(mA cm ⁻²)	ϵ_{FC} /%	ϵ_{WE} /%	$\epsilon_{R.T.}$ /%
Pt	300	56	77	43
Mixed IrO ₂ /Pt(10%/90%)		55	91	49
Mixed IrO ₂ /Pt(30%/70%)		52	93	49
Deposited IrO ₂ /Pt(20%/80%)		55	93	51
Pt	500	50	74	37
Mixed IrO ₂ /Pt(10%/90%)		49	86	42
Mixed IrO ₂ /Pt(30%/70%)		46	90	41
Deposited IrO ₂ /Pt(20%/80%)		50	89	44

resistivity of IrO₂ is five times larger than that of Pt (9.85 $\mu\Omega$ cm at 293 K) [14]. Therefore, the Pt catalyst in the mixed IrO₂/Pt electrode may not be used effectively, which causes the performance decrease in the fuel cell operation.

Based on the above terminal voltage against current density characteristics, the energy conversion efficiency of the fuel cell, water electrolysis and the round-trip efficiency can be calculated using the equations previously reported [12]. Table 1 shows these efficiency values

for cells using Pt, deposited IrO₂/Pt (20 at % Ir) and mixed IrO₂/Pt (10 and 30 at % Ir) catalysts for oxygen electrode. As expected from the voltage against current density characteristics, the deposited IrO₂/Pt shows comparable ϵ_{FC} to the mixed IrO₂/Pt (10 at % Ir) and comparable ϵ_{WE} to the mixed catalyst (30 at % Ir). Consequently, the deposited IrO₂/Pt catalyst shows higher $\epsilon_{R.T.}$ than the simply mixed IrO₂/Pt catalysts: 2–3% higher $\epsilon_{R.T.}$ was attained for the deposited IrO₂/Pt (20 at % Ir).

4. Conclusions

A IrO₂/Pt electrocatalyst for URFC was prepared by deposition of iridium hydroxide hydrate on Pt black particles in aqueous solution. After the calcination procedure, IrO₂ particles (20–50 nm dia.) were deposited on Pt particle clusters, which possessed a completely different structure compared to the mixed IrO₂/Pt catalysts. The fuel cell performance was improved by using the deposited IrO₂/Pt catalyst as an oxygen electrode without diminishing the water electrolysis performance. In this study, uniformly dispersed IrO₂ in Pt black is found to effectively improve URFC performance.

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