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Description	

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Catalytic activity of carbon–supported iridium oxide for oxygen reduction reaction as a Pt-free catalyst in polymer electrolyte fuel cell

C. H. Chang[1], T. S. Yuen[2], Y. Nagao[1,*], H. Yugami[1]

[1]Department of Mechanical Systems and Design, Graduate School of Engineering, Tohoku University, 6-6-01 Aramaki Aza Aoba, Aoba-ku, Sendai 9808579, Japan, [2]Department of Mechanical and Aerospace Engineering, University of California, San Diego, California, USA

* Corresponding author: Tel.: + 81 22 795 4032; fax: + 81 22 795 4032.

E-mail address: y_nagao@energy.mech.tohoku.ac.jp (Y. Nagao).

Abstract

Iridium oxide supported on Vulcan XC-72 carbon black (IrO_2/C) as a cathode catalyst for polymer electrolyte fuel cell (PEFC) has been characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurement. The IrO_2 particles were 8-160nm in diameter. The oxygen electroreduction activity was studied by cyclic voltammetry (CV). It was found IrO_2/C had high oxygen reduction reaction (ORR) activity. The performance of the membrane electrode assemble (MEA) was also tested in a single PEFC showed that IrO_2/C catalyst would be potential candidates for use as cathode catalyst in PEFC.

Keywords: polymer electrolyte fuel cell; carbon-supported iridium oxide; oxygen reduction reaction; membrane electrode assemble

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are an alternative power generator for internal combustion engine in the mobile application and primary or secondary batteries in the stationary application, due to their high-energy density, low operation temperature (60-80℃) and low emission [1]. In PEFC, the electrical power generates based on two reactions: hydrogen is oxidized at the anode and oxygen is reduced at the cathode. Carbon–supported platinum (Pt/C) is usually used as cathode catalyst for the electroreduction oxygen in PEFC. However, there are many problems for the commercialization of PEFCs [2], at least partially, due to the high cost of platinum and the amount of its nature resource is too small to supply the huge market of fuel cell [3]. Some approaches to cost down and performance improvement have been researched for many years. Two major approaches to reduce catalyst cost are currently being actively studied: one is to reduce Pt loading, and the other one is to explore Pt-free catalysts. In the short-term, catalysts containing Pt is practical, but in the long-term, Pt-free catalysts would be the better way to overcome the problems for PEFCs.

The Pt-free cathode catalysts have attracted the most attention over many years. Pt-free cathode catalysts such as transition metal macrocyclic compounds [4,5], transition metal-oxide [6-8] and Ir-based chalcogenides [9] have been studied to exhibit good initial oxygen reduction performance in PEFCs. Since iridium oxide is one of the outstanding electrocatalyst for oxygen evolution [10], the carbon and titanium-supported RuO_2- IrO_2 electrode was used as oxygen-evolving anode has been studied [11]. It

also has been evaluated that IrO_2 is probably for the low oxygen reduction activity described previously [12,13]. The ORR activity of IrO_2/Ti in acidic solution has been published [14]. From the view point of catalyst design, modification of Ir might be a feasible way to improve the catalytic properties of catalyst.

The research presented in this paper, the novel carbon-supported iridium oxide (IrO_2/C) was synthesized as cathode catalyst to replace Pt/C in PEFCs. The structure and the electrocatalytic activities of synthesized carbon-supported IrO_2 catalyst were fully characterized. This study presents fundamental results of carbon-supported IrO_2 for ORR. The size of IrO_2 particles is expected to be small by using of the porous carbon as a substrate. The results could provide an idea to design less–expensive, more powerful and anti-corrosive cathode catalyst for PEFCs.

2. Experimental

2.1. Catalyst preparation

The preparation of carbon-supported IrO_2 was carried out as the follow steps. Appropriate amount (50mg/ml) of iridium chloride hydrate ($IrCl_3.nH_2O$, 99.9 %-Ir, %Ir-53.60, Strem Chemicals, Newburtport, MA) was dissolved with distillated water in beaker. Apply the $IrCl_3$ solution onto Vulcan XC-72 carbon black (Cabot Corporation, Billerica, MA) in a ceramic crucible. The resulting powder was then calcined at 450℃ in air for 10 minutes. Repeat the droping-calcination procedure six times.

2.2. Catalyst characterization

X-ray diffraction analysis was performed on dry catalyst powder using a Philips X’pert MRD with Cu

K α radiation. The particle size of IrO_2 was also characterized by a JEOL JEM-2100 transmission electron microscopy (TEM). An ALS-CHI-611CX potentiostat (ALS Co., Ltd, Tokyo, Japan) and a convention three-electrode cell was used for electrochemical measurements. The working electrode was an IrO_2/C catalyst coated glassy carbon electrode. Pt wire and Ag/AgCl were used as counter and reference electrode, respectively. All potential in this work are quoted against Ag/AgCl electrode. The electrochemical measurements were carried out in 0.1M $HClO_4$ solution (Wako Pure Chemical Industries Ltd, Japan) at room temperature.

2.3 Catalyst evaluation

The single fuel cell device (ElectroChem, Inc.) test was conducted with 5cm^2 membrane electrode assemble (MEA) using IrO_2/C as cathode, commercial available anode with Pt loading 1 mg cm^{-2} (Toyo Corporation, Tokyo, Japan) and Nafion 117 membrane (DuPont) as the electrolyte to separate cathode from anode. The cathode was prepared by painting a cathode catalyst ink onto a piece of commercial available hydrophobic carbon cloth (Toyo Corporation, Tokyo, Japan). The cathode catalyst ink was prepared by mixing IrO_2/C (IrO_2 loading is 28wt. %), distillated water and 5% Nafion dispersion solution (Wako Pure Chemical Industries Ltd., Japan) in a ratio of 1:10:11 by mass. The MEA was fabricated by hot-pressing (60kgf cm^{-2}) the anode and cathode to the Nafion 117 membrane at 120℃ for 40 minutes. The single cell was operated at a temperature of 60℃and a relative humidity of 90% in our test station. Pure hydrogen (H_2) and pure oxygen (O_2) with a flow rate of 80ml/min were used as fuel.

3. Results and discussion

XRD was conducted to analysis the bulk structure and its support. Figure 1 shows the powder XRD pattern of carbon-supported IrO_2 powder. No presence of Ir in a metallic form was found. The characteristic peaks at are corresponding to the IrO_2 (2θ = 28.05°, 34.71°, 40.06°, 54.02°, 57.94°, 66.05°, 69.33°, 73.23°, 83.18° and 86.45°). The crystallite size was estimated at around 3.2-14.3nm based on the broadening of two peaks (28.05° and 34.71°) using the Scherrer equation ($k\lambda / \beta \cos\theta$, k = 0.9). It is well established that the particle size strongly affect the catalytic activity of the catalyst described previously [15]. With this in our mind, the size of the carbon-supported IrO_2 particles was analyzed by TEM. Figure 2(a) is the typical TEM image of carbon-supported IrO_2 catalyst. It can be seen that the IrO_2 nano-clusters and nano-particles were dispersed on the carbon surface, and the mean size is from 8 to160nm. Figure 2(b) and 2(c) are the high-resolution TEM image for area A (dotted line square) and size distribution of IrO_2 nano-particles, respectively. The most frequent size of the IrO_2 nano-particles was ~15 nm, and the average diameter was 27 nm. It showed that the formation of nano-clusters could be due to agglomeration of nano-particles when calcined at high temperature and high concentration of $IrCl_3$ solution during the preparation process. This result indicated that we need providing a uniform environment for the nucleation and growth metal oxide particles.

The oxygen reduction reaction (ORR) activity of catalyst could be estimated by cyclic voltammetry

(CV). Figure 3 shows the cyclic voltammograms of IrO_2/C catalyst coated glassy carbon electrode in N_2-saturation (solid line) and O_2-saturation (dotted line) 0.1M $HClO_4$ solution at room temperature, scan rate is 50mV/s. As could be seen, in N_2-saturation condition, we did not observe any redox peak but shows typical double-layer behavior on the surface. This result indicated that IrO_2 nanoparticles had a high electrochemical stability in acidic solution. In the presence of oxygen, an apparently reduction peak of oxygen commences at about 0.6V vs Ag/AgCl which showed IrO_2/C catalyst have ORR activity. This onset potential of ORR on IrO_2/C is almost comparable to that of IrO_2/Ti [13]. Such oxygen reduction reactions were also observed in other transition metal-oxide catalysts [8]. This result showed that the IrO_2/C might be used as a catalyst of cathode for PEFC.

In order to evaluate the ORR catalytic activity of the IrO_2/C catalyst prepared in this study, MEA was fabricated with IrO_2/C as the cathode catalyst. The PEFC assembled with such an MEA was tested using our test station. Figure 4 shows the polarization and power density curves obtained from a single PEFC at 60℃. The open circuit voltage (OCV) is around 0.80V at 60℃. At a cell voltage of 0.2V, the polarization curve shows the limiting current density of 34mA cm^{-2} and the maximum power density 6.8mW cm^{-2}. This result is pretty far to that of conventional Pt/C cathode catalyst in PEFC performance. This initial result indicated that the IrO_2/C MEA performance could be improved by optimization in the catalyst preparation process to obtain smaller and well-dispersed IrO_2 nano-particles. More optimization work and synthesis parameters are underway in order to improve ORR catalytic activity and stability.

4. Conclusions

In this study, the carbon-supported IrO_2 nano-particles as cathode catalyst for oxygen reduction reaction in PEFC were prepared by droping-calcination process at 450 °C. The IrO_2 nano-clusters and nano-particles, which were dispersed on carbon, were 8-160nm in diameter. We have demonstrated the carbon-supported IrO_2 catalyst showed an onset potential for oxygen reduction reaction at 0.6V (vs Ag/AgCl) in 0.1M $HClO_4$ solution. It showed that IrO_2 behaves as an active and stable catalyst for ORR in acidic condition. The results of cell performance presented here (maximum power density is 6.8mW cm^{-2}) suggest that the carbon-supported IrO_2 catalyst in this study could be a promising cathode catalyst for PEFCs. Nevertheless, the power performance of the PEFC reported here is still lower than conventional PEFCs. The carbon-supported IrO_2 was used as cathode catalyst is the initial step to develop anti-corrosive, more powerful and less-expensive cathode catalyst for PEFCs in the future. Further study of the preparative process is now under way and hopefully will lead to better performance of IrO_2/C catalyst.

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Figure captions

Fig. 1 Powder XRD patterns of IrO_2/C catalyst calcined in air at 450℃.

Figs.2 (a) TEM image of IrO_2 nanoparticles supported on Vulcan XC-72 carbon black. (b) High-resolution TEM image acquired for area A. (c) Size distributions of IrO_2 nano-particles from the TEM image.

Fig. 3 The cyclic voltammogram of IrO_2/C catalyst in N_2-saturation (solid line) and O_2-saturation (dotted line) 0.1M $HClO_4$ solution at room temperature, scan rate is 50mV/s.

Fig. 4 Polarization and power density curves of the single cell adopting IrO_2/C as cathode catalyst at 60℃. Hydrogen flow rate: 80ml/min and oxygen flow rate 80ml/min. Fuel cell operated at RH 90%.

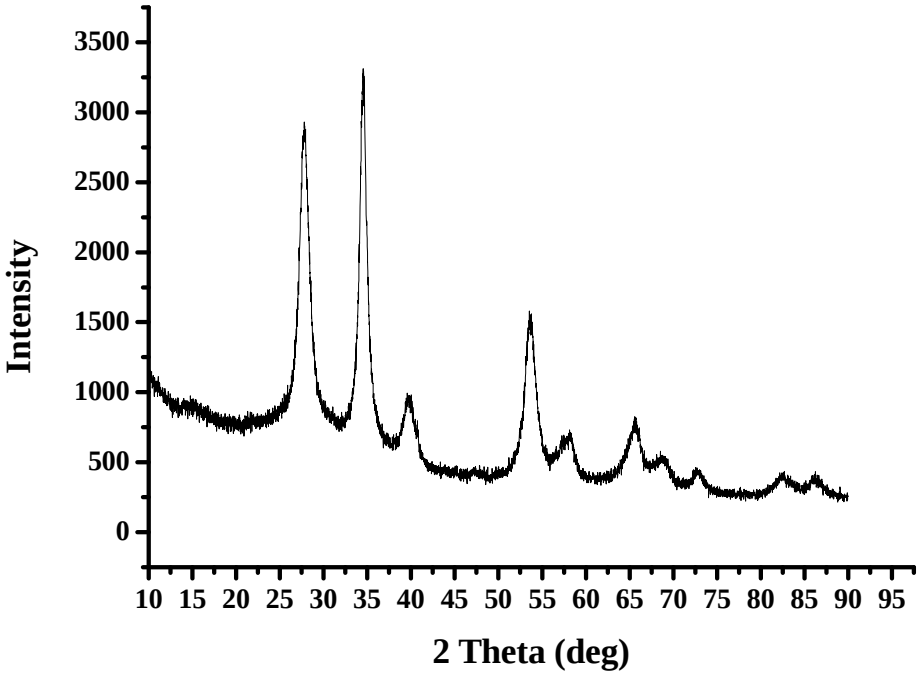
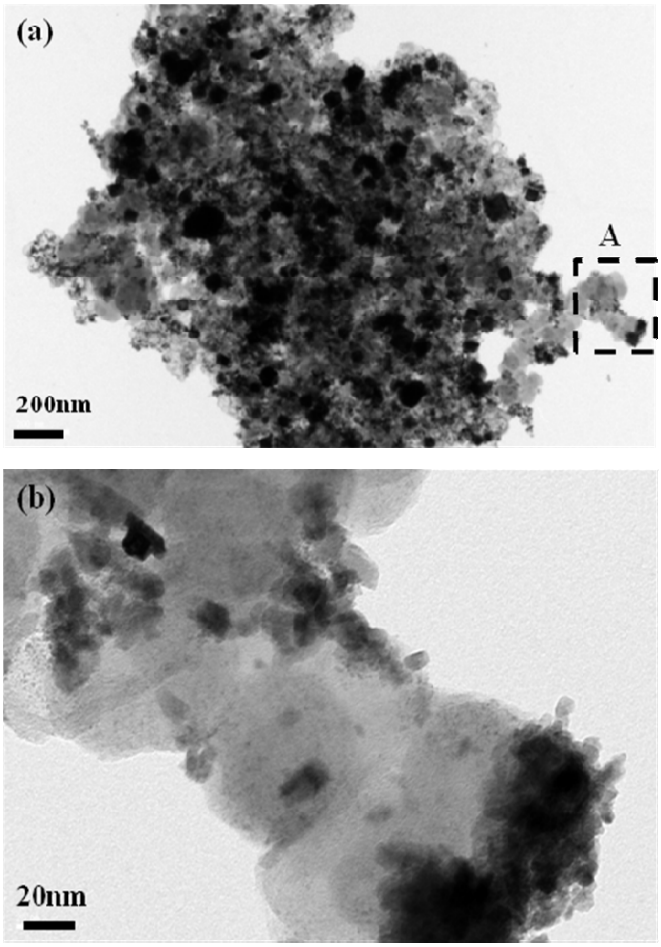

Intensity
3500
3000
2500
2000
1500
1000
500
0
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
2 Theta (deg)

Fig. 1


(a)
A
200nm
(b)
20nm
(c)
Distribution / %
Diameter / nm
0
5
10
15
20
25
0
20
40
60
80
100
120
140
160

Figs. 2

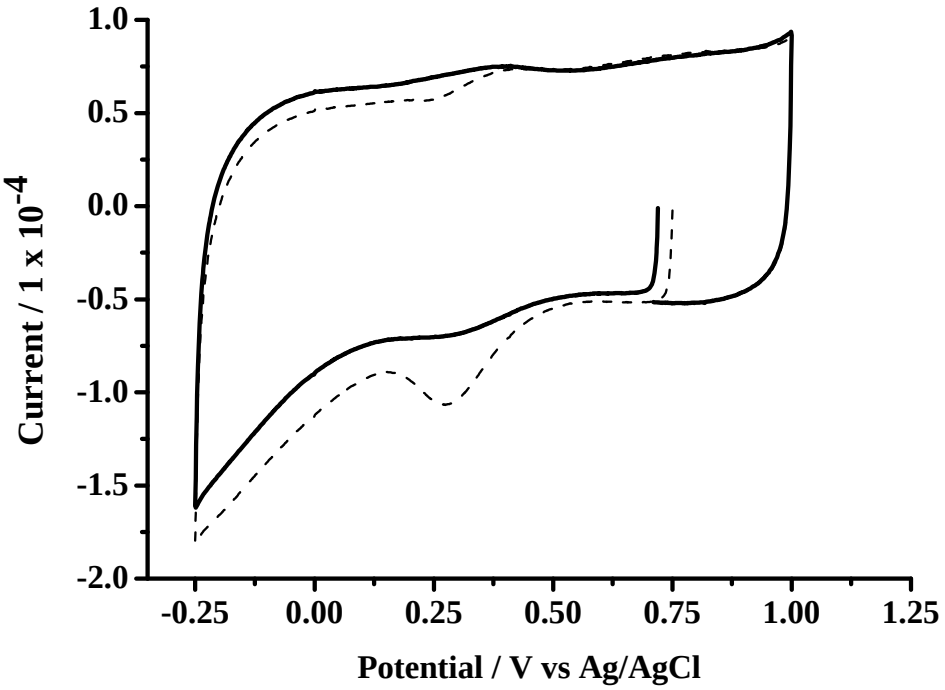

1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
Current / 1 x 10-4
-0.25
0.00
0.25
0.50
0.75
1.00
1.25
Potential / V vs Ag/AgCl

Fig. 3

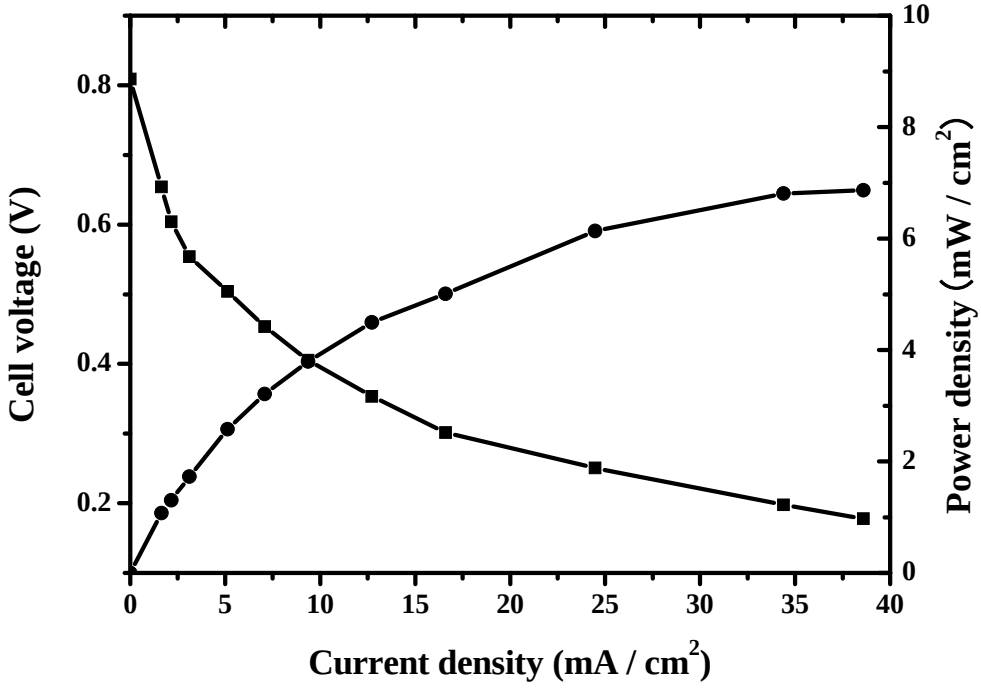

Cell voltage (V)
Power density (mW / cm^2)
Current density (mA / cm^2)
0.2
0.4
0.6
0.8
0
2
4
6
8
10
0
5
10
15
20
25
30
35
40

Fig. 4