Short communication

Electrocatalytic activity of iridium oxide nanoparticles coated on carbon for oxygen reduction as cathode catalyst in polymer electrolyte fuel cell

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ABSTRACT

The iridium oxide nanoparticles supported on Vulcan XC-72 porous carbon were prepared for cathode catalyst in polymer electrolyte fuel cell (PEFC). The catalyst has been characterized by transmission electron microscopy (TEM) and in PEFC tests. The iridium oxide nanoparticles, which were uniformly dispersed on carbon surface, were 2–3 nm in diameter. With respect to the oxygen reduction reaction (ORR) activity was also studied by cyclic voltammetry (CV), revealing an onset potential of about 0.6 V vs. an Ag/AgCl electrode. The ORR catalytic activity of this catalyst was also tested in a hydrogen–oxygen single PEFC and a power density of 20 mW cm^{-2} has been achieved at the current density of 68.5 mA cm^{-2}. This study concludes that carbon-supported iridium oxide nanoparticles have potential to be used as cathode catalyst in PEFC.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are regarded as efficient power generator for stationary and mobile applications, due to their high power density, near-zero pollutant emission and low operating temperature. It is based on two electrochemical reactions: the oxidation of hydrogen at the anode and reduction of oxygen at the cathode. In PEFCs, carbon-supported platinum (Pt/C) is usually used as cathode catalyst, due to its high activity towards oxygen reduction [1]. However, limited Pt reserves, supply and high price will prohibit the widespread use of the PEFC in such huge fuel cell market. On the other hand, the overpotential for the oxygen reduction reaction (ORR) needs to be reduced. In the short-term, catalysts containing low amounts of Pt are the priority, but in the long-term, non-Pt-based material would be the better solution [2]. Various approaches have been conducted to overcome these problems: alloying Pt with other metals has been attempted, modification of carbons [3], and searching for other suitable compounds to replace Pt in PEFCs, such as transition metal oxides [4–7], transition metal chalcogenides [8] and metal coordination polymer [9–11].

Iridium (Ir) is one of the stable metals among Pt-group metals in acidic solution [12] and also has been the subject of many electrochemical studies. The surface of Ir has a strong affinity for OH or O species to form a surface with oxide coverage. As we know, IrO$_2$ has been used as anode for oxygen evolution reaction (OER) in many industrial electrochemical processes [13] and is one of a typical material that resists corrosion in acidic solution. It has also been evaluated that the formation of iridium oxide is probably responsible for the ORR activity in acidic solution [14]. From the viewpoint of catalyst design, iridium oxide could be a feasible candidate of the non-Pt-based catalyst for PEFC.

In the present study, we are interested in the ORR activity of iridium oxide catalyst and the performance of iridium oxide as cathode catalyst in PEFC. As we know, the catalyst should be deposited on porous nanostructure materials in order to increase the specific surface area, which is the prerequisite to obtain an acceptable catalytic performance [15]. Carbon is an ideal supporter of electrocatalyst for PEFC. Carbon has the essential properties of high electronic conductivity, anti-corrosive and the low cost. In general, the conventional support carbon black (Vulcan XC-72) is used for the dispersion of Pt nanoparticles. It is the first study that the novel carbon-supported iridium oxide nanoparticles were synthesized as an alternative catalyst for the PEFC cathode reaction. The catalytic activity for the ORR of carbon-supported iridium oxide catalyst was evaluated by electrochemical measurement and the performance of carbon-supported iridium oxide was also evaluated as cathode catalyst in a single PEFC.

2. Experimental

2.1. Catalyst preparation

The carbon-supported iridium oxide nanoparticles were prepared according to a process described previously [16]. The iridium

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oxide catalyst was coated onto Vulcan XC-72 carbon by dispersing iridium chloride hydrate (IrCl$_3$·nH$_2$O) (Wako Pure Chemical Industries, Ltd.) in a 3:1 mixture of water and isopropanol by sonicating for 20 min. The Vulcan XC-72 carbon black (Cabot Specialty Chemicals, Inc.) was then added and the mixture sonicated for a further 20 min. The resulting solution was boiled for 1 h. After boiling for 1 h, ammonia solution (Wako Pure Chemical Industries, Ltd.) was added until pH reached 12 and filtration of the mass. Then the mass took place by heating at 450 °C in air and washing with distilled water. The resulting powder was dried at 110 °C in air. The complete decomposition of Vulcan XC-72 in the presence of oxygen occurs at 460 °C [9]. High temperature decomposition notwithstanding, the carbon support remains stable in the calcination temperature.

2.2. Catalyst characterizations

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100 transmission electron microscope. The carbon-supported iridium oxide sample was placed in a vial containing acetone and then was ultrasonically agitated to form homogeneous slurry. Some drops of slurry were dispersed on a holey, amorphous carbon film on a copper grid for analysis.

The electrochemical characterization was performed with a CHI-611C potentiostat (ALS Co., Ltd.). A standard three-electrode cyclic voltammetry cell was used at room temperature. Pt wire and Ag/AgCl electrode served as counter and reference electrodes, respectively. The working electrode of carbon-supported iridium oxide was prepared using Schmidt electrode method [17]. Briefly, 2.27 mg of the carbon-supported iridium oxide powder was dispersed in 100 μl of water by sonicating for 10 min. Then, 10 μl of the carbon-supported iridium oxide powder dispersion was dropped onto a mirror-polished glassy carbon (GC) electrode (0.07 cm^2 exposed surface). After drying at room temperature, 2 μl of the 5 wt.% Nafion alcoholic dispersion (Wako Pure Chemical Industries, Ltd.) was dropped onto the surface to stabilize the carbon-supported iridium oxide powder on the GC surface. For the ORR experiment, oxygen was bubbled into 0.1 M HClO$_4$ solution at room temperature for 30 min.

2.3. Catalyst activity evaluation

The carbon-supported iridium oxide catalyst was evaluated as the cathode catalyst in a single PEFC. The electrode was prepared as follows: mixing the carbon-supported iridium oxide catalyst with distilled water and 5 wt.% Nafion alcoholic dispersion solution. The catalyst was combined with distilled water to achieve a 1:10 ratio by weight. 5 wt.% Nafion alcoholic dispersion was added in an amount to reach a weight of catalyst and distilled water. The mixture was cooled in ice bath and then ultrasonically mixed for 2 min to form a homogeneous ink. Then paint the ink onto the 5 cm^2 prefabricated hydrophobic carbon cloth (Toyo Co.) by brush. The catalyst layer was 0.1 mm in thickness with iridium oxide loading of 0.07 mg cm^{-2}. Nafion 117 was used as fuel cell membrane (DuPont). The membrane was boiled in 3% hydrogen peroxide (H$_2$O$_2$) (Wako Pure Chemical Industries, Ltd.) solution and in 0.1 M sulfuric acid (H$_2$SO$_4$) (Wako Pure Chemical Industries, Ltd.) solution for 1 h to remove organic and mineral impurities, and then rinsed with distilled water. The anode was commercial Pt/C catalyst with Pt loading of 1 mg cm^{-2} (Toyo Co.). The MEA was fabricated by hot-pressing the anode and cathode to the Nafion 117 membrane at 120 °C for 40 min. The fuel cell measurement was operated at a cell temperature of 60 °C. During fuel cell operation, the anode side was fed by pure hydrogen and the cathode side was fed by pure oxygen with a flow rate of 80 ml min^{-1}. Both gases were humidified by passing them through water bath at a temperature of 57 °C. After waiting for 1 h at open circuit voltage (OCV), fuel cell performance was tested by recording polarization curve.

3. Results and discussion

3.1. Physical characterization of iridium oxide catalyst

In our approach, the carbon-supported iridium oxide nanoparticles were directly deposited on the carbon by heating isopropanol solution of iridium (III) salt and calcined at 450 °C in air. It was established that the particle morphology and size affect the properties of the catalyst [18]. The size and morphology of the catalyst were analyzed by TEM. Fig. 1(a) and (b) is the typical TEM images of carbon-supported catalyst. As shown, the particles were well dispersed on the carbon surface and the average size of the particles is around 2–3 nm, much large aggregates were not found but the amount of particles is few.

Unfortunately, the size and amount of particles is too small to characterize by X-ray diffraction. But it was established that isolated transition metal nanoparticles showed the presence of an oxide layer due to the air exposure [19,20]. As shown in TEM images, the remarkable uniform small black dots are believed to be only iridium oxide particles on the carbon supporter.
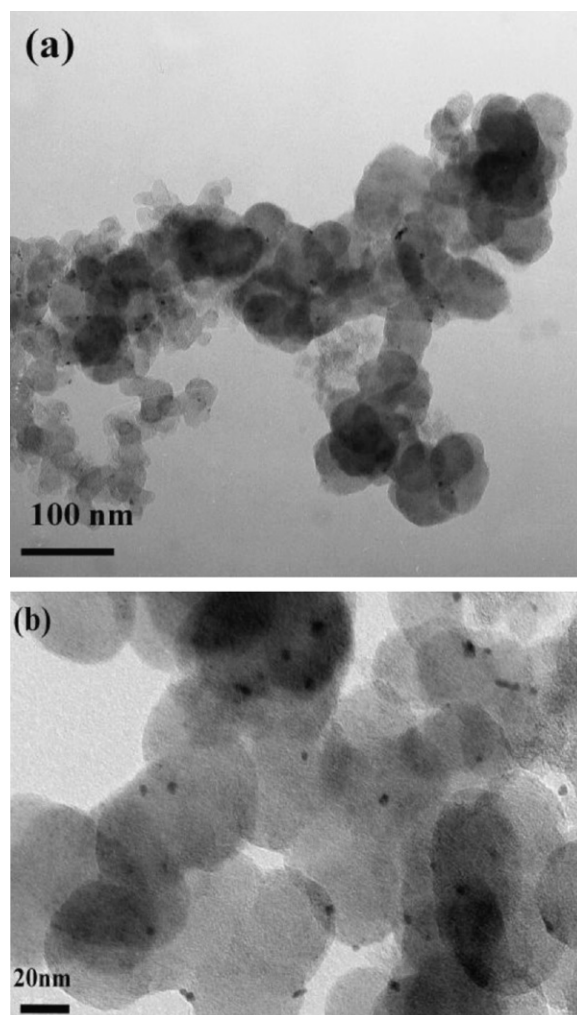

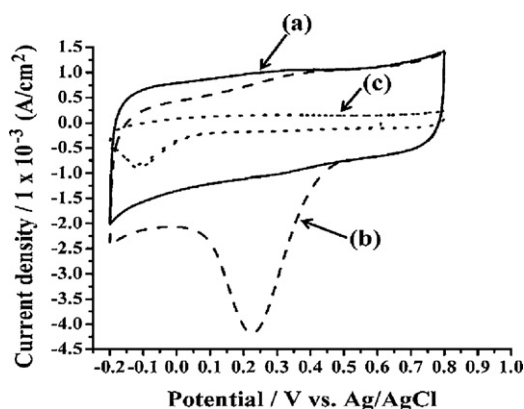Fig. 1. Typical TEM images of iridium oxide nanoparticles supported on Vulcan XC-72 carbon black.

Fig. 2. The cyclic voltammograms of carbon-supported iridium oxide catalyst coated glassy carbon electrode in N_2-saturated (line a) and O_2-saturated (line b) 0.1 M $HClO_4$ solution at room temperature and the cyclic voltammogram of Vulcan XC-72 carbon black without iridium oxide nanoparticles in O_2-saturated (line c) 0.1 M $HClO_4$ solution at room temperature. The scan rate is 50 mV s^{-1}.

3.2. Electrocatalytic activity of carbon-supported iridium oxide catalyst for ORR

The ORR activity of catalyst could be estimated by cyclic voltammetry. Fig. 2 shows the cyclic voltammograms of our carbon-supported iridium oxide catalyst coated glassy carbon electrode in N_2-saturated (line a) and O_2-saturated (line b) 0.1 M $HClO_4$ solution at room temperature, scan rate is 50 mV s^{-1}. As shown in Fig. 2, when sweeping the potential for carbon-supported iridium oxide catalyst coated glassy carbon electrode between 0.8 and −0.2 V (vs. Ag/AgCl) in N_2-saturation, the anodic and cathodic electric charges were almost equal, which were responsible for the typical double-layer capacitance, it has not produced any specific peak due to anodic dissolution in the cyclic voltammetry measurement. This also indicated that iridium oxide nanoparticles had electrochemical stability in acidic media between the swept potential ranges. In the presence of O_2, an additional cathodic current was observed as compared with those measured in N_2-saturated solution. The onset potential, E_{ORR}, for the ORR is defined by where the additional cathodic current attained to 20 μA cm^{-2} which was obtained by subtracting the voltammogram of the O_2-saturated solution during the cathodic scan from that of the N_2-saturated one. This additional cathodic current indicated that the as-prepared carbon-supported iridium oxide can catalyze the ORR with an onset reduction potential of 0.6 V (vs. Ag/AgCl). The onset potential for the ORR on IrO$_2$/C, IrO$_2$/Ti, RuO$_2$/Ti and Pt/C [21,22] was listed in Table 1. Although the onset potential of ORR on IrO$_2$/C is 0.6 V it was still lower than conventional Pt/C cathode catalyst.

In order to evaluate the electrocatalytic activity of carbon-supported iridium oxide for ORR without the potential effect of carbon black (Vulcan XC-72) on the behavior of carbon-supported iridium oxide catalyst, the carbon black without iridium oxide nanoparticles was also prepared using the same steps. Fig. 2 also shows the cyclic voltammogram of carbon black without iridium oxide nanoparticles coated glassy carbon electrode in O_2-saturated (line c) 0.1 M $HClO_4$ solution at room temperature, scan rate is 50 mV s^{-1}. As shown in Fig. 2, there is an apparent reduction potential for ORR at 0.1 V (vs. Ag/AgCl). The present results showed that
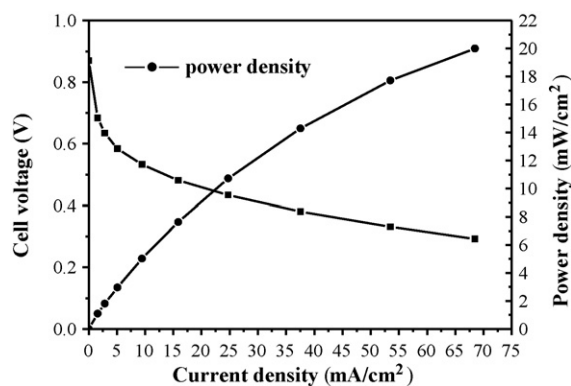

Fig. 3. Polarization and power density curves of the single cell adopting carbon-supported iridium oxide as cathode catalyst at 60 °C. Hydrogen flow rate: 80 ml min^{-1} and oxygen flow rate: 80 ml min^{-1}. Fuel cell operated at RH 90%.

electrocatalytic activity of carbon-supported iridium oxide for ORR is higher than that of carbon black (Vulcan XC-72).

3.3. Performance of carbon-supported iridium oxide catalyst in single PEFC

In order to evaluate the ORR activity of the carbon-supported iridium oxide catalyst prepared in this study, the fuel cell devices test were conducted with 5 cm^2 membrane electrode assembly (MEA) using prepared carbon-supported iridium oxide as the cathode catalyst and were tested in our test station. Fig. 3 shows the performance of fuel cell device with prepared carbon-supported iridium oxide cathode catalyst at the catalyst loading of 0.07 mg cm^{-2}. For the MEA, open circuit voltage (OCV) of 0.87 V was observed. The catalyst generates current density of 68.5 mA cm^{-2} and a power density of 20 mW cm^{-2} at 0.29 V. Although a power density of about 20 mW cm^{-2} was achieved in this study it was still a little far to that of conventional Pt/C cathode catalyst in PEFC performance. However, the cell performance could be improved by the optimization of the catalyst preparing process including the amount variation of precursor of iridium oxide.

4. Conclusions

Carbon-supported iridium oxide nanoparticles were prepared using IrCl$_3 \cdot n$H$_2$O as the iridium oxide precursor to develop a new catalyst for ORR. The present results indicated (CVs and OCV) that carbon-supported iridium oxide, but not carbon, behaves as an active catalyst for ORR in acidic solution. Fuel cell performance was tested by recording polarization curve, at a cell voltage of 0.29 V, the single cell performance test results showed a current density of 68.5 mA cm^{-2} with a power density of 20 mW cm^{-2} at 60 °C. Although the electrocatalytic activity of carbon-supported iridium oxide nanoparticle is still lower than that of Pt, using carbon-supported iridium oxide nanoparticle as cathode is considered a new potential candidate towards the development of less-expensive and anti-corrosive oxide electrode for cathode in PEFC. Further study of the preparative process is now under way and hopefully will lead to better performance of carbon-supported iridium oxide catalyst.

Acknowledgements

Table 1
The onset potential for the ORR on carbon-supported iridium oxide, IrO$_2$/Ti, RuO$_2$/Ti and Pt/C catalyst.

Catalyst	Pt/C [22]	RuO$_2$/Ti [21]	IrO$_2$/Ti [21]	IrO$_2$/C
E_{ORR} (V vs. Ag/AgCl)	0.81	0.30	0.54	0.6

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