



A gas-diffusion cathode coated with oxide-catalyst for polymer electrolyte fuel cells using neither platinum catalyst nor carbon catalyst-support



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ABSTRACT

To overcome the fundamental disadvantages of conventional cathodes for polymer electrolyte fuel cells (PEFCs), such as dissolution and migration of platinum-based catalysts and consumption of the carbon catalyst-support, a substantially novel gas-diffusion cathode has been proposed. The electrode was made of a porous oxide catalyst, which was coated on the inner and outer surfaces of a macro-porous titanium sheet substrate, using neither a platinum catalyst nor carbon catalyst-support. The suitability of this cathode for PEFCs, tested using a highly porous iridium oxide strongly coated on the macro-porous titanium sheet substrate, was confirmed by successful power generation. The gas-diffusion electrode functioned not only as the cathode but also as an anode of a PEFC.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted considerable research interest worldwide because they are promising not only for clean energy applications but also for distributed power supplies [1–3]. Platinum-based cathode catalysts loaded on carbon black or carbon nanotubes, e.g. Pt/C, PtCo/C, or Pt/Au/C [1–4], are likely to have serious unresolved disadvantages, such as dissolution and migration of catalyst metal and consumption of the carbon support, especially when PEFCs are operated under fluctuating loads [1–3,5–7]. Another issue that must be considered is that the consumption of the carbon catalyst-support will increase significantly when PEFCs are operated under conditions of widely fluctuating loads and at higher temperature (e.g. ~150°C). To enhance the reliability of PEFCs, the gas-diffusion cathode responsible for the oxygen reduction reaction (ORR) must be radically improved. Although various non-platinum cathode catalysts have been proposed [3,8–19], they generally use a carbon material as the cathode catalyst itself [8–12] or to provide electric conductivity to the less-conductive cathode catalyst particles such

as oxides and oxycarbonitrides [13–15,18]. However, the carbon in the catalyst layer of these non-platinum cathode catalysts can be unstable during power generation.

Here, we present a novel concept and a few basic results of a novel gas-diffusion cathode made of a highly porous oxide catalyst, which was strongly coated on the inner and outer surfaces of a macro-porous titanium sheet substrate, MPTi, using neither a platinum catalyst nor carbon support. The applicability of this electrode as a gas-diffusion anode for PEFCs will also be examined.

2. Experimental

2.1. Preparation of HP-IrO₂/Ti electrode of the RDE equipment

The highly porous iridium oxide electrode with a Ti disk substrate, HP-IrO₂/Ti, was prepared by almost the same procedure using a titanium disk substrate reported in the previous papers [16,17]. First, a removable Ti disk (6 mm in diameter) of homemade rotating disk electrode (RDE) equipment, developed in this study, was etched in oxalic acid solution at 80°C for 2 h. Next, a predetermined quantity of 1.2 μL solution (1-butanol solution containing 0.5 M IrCl₃) was dropped onto the top surface of the Ti disk. Then the disk was dried (60°C, 10 min) and heated (550°C, 10 min) in air to coat the top surface of the disk with a dense and thin IrO₂

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interface to prevent the electrolyte from touching the Ti substrate directly. After the procedure, 1.2 μL of solution (1-butanol solution containing 0.35 M IrCl_3 and 0.15 or 0.13 M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was dropped onto the IrO_2 -coated Ti disk followed by drying (60 °C, 10 min) and calcination (450 °C, 10 min) in air. The procedure was repeated twice, and all traces of lanthanum species were then completely removed using 0.5 M H_2SO_4 at 60 °C for 10 h. The electrode was then washed with distilled water followed by drying in air at 60 °C for 30 min. A typical amount of HP- IrO_2 loaded on the titanium disk determined by gravimetry was 1.1 mg cm^{-2} . Finally, 10 μL of a 0.025 wt% dispersion of an ionomer (Nafion[®], Aldrich) in a $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ ($\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}=4:1$, volume ratio) mixture was dropped onto the electrode surface, and the electrode was dried at 60 °C for 1 h in air and at room temperature for one night in the vacuum condition. Although the HP- IrO_2 layer adhered strongly to the Ti disk surface, the oxide layer was coated with the ionomer to make the electrode condition similar to that of the MEA described below.

2.2. Electrochemical measurements for the ORR and HOR on the HP- IrO_2/Ti electrode with a rotating disk electrode (RDE) equipped with a removable titanium disk electrode

A beaker-type electrolytic cell for the RDE was used. A bundle of carbon fibers, instead of a Pt plate, was used as the counter-electrode to avoid the deposition of Pt onto the test electrode through dissolution. A Luggin capillary, connected to a hydrogen electrode as a reference electrode, was placed in front of the working electrode at a distance of 2 mm. For the ORR and the HOR (hydrogen oxidation reaction) experiments, highly pure oxygen gas and highly pure hydrogen gas were bubbled into a 0.1 M HClO_4 solution at 30 °C, respectively. Prior to the voltammetry, all the HP- IrO_2/Ti electrodes used in this study were pre-treated in electrolytic solution by sweeping the electrode potential between 0.05 V and 1.5 V vs. RHE at 50 mV s^{-1} for 30 min.

2.3. Electrochemical measurements for the ORR by rotating ring disk electrode method (RRDE)

Rotating ring disk electrode (RRDE) equipment with a glassy carbon disk (GC) electrode (6 mm in diameter), a platinum ring electrode, and a bundle of carbon cloth counter electrode and hydrogen electrode was used to elucidate the reaction process for the ORR on the HP- IrO_2 cathode. Since it was difficult to replace the GC electrode of the RRDE equipment with a removable titanium disk electrode, HP- IrO_2 powder was put on the GC electrode. The HP- IrO_2 powder was prepared as follows: a MPTi sheet was soaked in the coating solution (1-butanol solution containing 0.5 M IrCl_3 and 0.21 M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) followed by drying (60 °C, 10 min) and calcination (300 °C, 10 min) in air. This procedure was repeated twice. The electrode was then ultra-sonicated in distilled water to remove the $\text{IrO}_2\text{-La}_2\text{O}_3$ particles from the MPTi sheet followed by filtration. The filtrated $\text{IrO}_2\text{-La}_2\text{O}_3$ particles were dried and calcined (450 °C, 20 min) in air, and then all traces of lanthanum species were removed using 0.5 M H_2SO_4 at 60 °C for 10 h to prepare HP- IrO_2 fine particles. After filtration, the HP- IrO_2 particles were ground and then washed with distilled water followed by drying in air at 60 °C for 30 min. A small amount of HP- IrO_2 particles (0.2 mg) was put on the GC electrode of the RRDE using a dispersion of HP- IrO_2 in water. Finally, 10 μL of a 0.025 wt% dispersion of the ionomer in a $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ ($\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}=4:1$, volume ratio) mixture was dropped onto the electrode surface to fix the HP- IrO_2 powder onto the GC electrode, and the electrode was dried at 60 °C for 1 h in air and at room temperature for one night in the vacuum condition. The HP- IrO_2/GC electrode was rotated at 2000 rpm in the voltammetry.

2.4. Preparation of HP- IrO_2/MPTi electrodes for the MEAs

To prepare the electrode for the MEA, a macro-porous Ti sheet, MPTi (TIPOROUS[®], Osaka Titanium Technologies Co., Ltd.), was used as the substrate of the oxide catalyst. First, the MPTi (20 mm \times 20 mm \times 0.1 mm) was etched with 10% oxalic acid at 80 °C for 1 h, and then rinsed with deionized water. Next, the MPTi was soaked in the coating solution (1-butanol solution containing 0.5 M IrCl_3 and 0.21 M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) followed by drying (60 °C, 10 min) and calcination (450 °C, 10 min) in air. This procedure was repeated twice, and the lanthanum species were then removed using 0.5 M H_2SO_4 at 60 °C for 10 h. The electrode was then washed with distilled water followed by drying (60 °C, 30 min) in air. A typical amount of HP- IrO_2 loaded on the MPTi determined by gravimetry was 16 mg cm^{-2} . Both the loading amount and the state of the highly porous iridium oxide, HP- IrO_2 , coated over the MPTi have not yet been optimized because they are not easy to coat HP- IrO_2 in suitable thickness and state on the entire surface of the inner surface of porous titanium sheet substrate, MPTi. The optimization of the coating conditions is a future problem.

Finally, the ionomer mixture was sprayed toward the HP- IrO_2/MPTi electrode, and the electrode was dried at 60 °C for 1 h in air at room temperature for one night in the vacuum condition. The (Pt/C)|membrane|(HP- IrO_2/MPTi) MEA was prepared with the conventional Pt/C (20 wt%, 1 mg cm^{-2} , EC-20-10-7: Electro Chem. Inc.) anode, the IrO_2/MPTi cathode and a Nafion[®] membrane (N-117) by pressing them under 0.7 MPa at 130 °C for 3 min. The (HP- IrO_2/MPTi)|membrane|(HP- IrO_2/MPTi) MEA was prepared with the two HP- IrO_2/MPTi electrodes and a Nafion[®] membrane (N-117) by pressing them under 0.7 MPa at 130 °C for 3 min. For both MEAs, carbon paper (IGRACET GDL10CA: SGL Carbon Group) was attached to the anode and cathode for the power generation test.

2.5. Power generation tests

Two different MEAs, (Pt/C)|membrane|(HP- IrO_2/MPTi) and (HP- IrO_2/MPTi)|membrane|(HP- IrO_2/MPTi), were tested under pure hydrogen and oxygen at 80 °C. The power generation tests under atmospheric pressure of H_2 and O_2 were carried out at a laboratory of Shinshu University and EIWA corporation separately, and the tests under H_2 (atmospheric pressure + 0.2 MPa) and O_2 (atmospheric pressure + 0.2 MPa) were carried out at EIWA corporation.

3. Results and discussion

3.1. Concept of the next-generation gas-diffusion cathode

We have been examined the ORR activity of a few oxide electrodes which were prepared by dip-coating using a titanium disk substrate [16,17,19]. This methodology has various benefits: (a) its preparation procedure is easy, (b) it can be applied for various kinds of oxide catalysts, (c) it needs no carbon support, (d) the oxide catalysts can be prepared at a low temperature and (e) the interface between the catalyst oxide coating and the titanium substrate is usually strong due to the formation of a mixed oxide interface layer. In this study, these benefits were utilized to prepare a novel gas-diffusion oxide cathode; that is, a macro-porous titanium sheet, MPTi, was used as the substrate of oxide catalyst layer.

To test the availability of the oxide-coated catalyst for the novel gas-diffusion electrode, we have selected the electrode coated with a highly porous iridium oxide, HP- IrO_2 , prepared by dip-coating with the help of lanthanum oxide to form a highly porous structure [16,17]. The reasons why we have chosen it were as follows: (a) the onset potential for the ORR, where the cathodic current for the ORR becomes clear in the cathodic potential sweep of an electrode in

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