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.

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 ℃). 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.

EXPERIMENTAL

Preparation of HP-IrO$_2$/Ti electrode of the RDE equipment

The highly porous iridium oxide electrode with a Ti disk substrate, HP-IrO$_2$/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 IrCl$_3$) 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 IrO$_2$ 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 La(NO$_3$)$_3 \cdot$6H$_2$O) was dropped onto the IrO$_2$-coated Ti disk followed by drying (60°C, 10 min) and calcination (450°C, 10 min) in air. The procedure was repeated twice, and all traces of lanthanum species were then completely removed using 0.5 M H$_2$SO$_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 C$_2$H$_5$OH/H$_2$O (C$_2$H$_5$OH:H$_2$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.

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.

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 La(NO$_3$)$_3$·6H$_2$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 IrO$_2$-La$_2$O$_3$ particles from the MPTi sheet followed by filtration. The filtrated IrO$_2$-La$_2$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$_2$SO$_4$ 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 C$_2$H$_5$OH/H$_2$O (C$_2$H$_5$OH:H$_2$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.

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 × 20 mm × 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 La(NO$_3$)$_3$·6H$_2$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$_2$SO$_4$ 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.

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.

RESULTS AND DISCUSSION

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 linear sweep voltammetry, of the HP-IrO$_2$/Ti electrode prepared at 450°C by dip-coating was high, 0.84 V vs. RHE, when determined in 0.5 M H$_2$SO$_4$ at 60°C without rotation of the electrode, while those of the valve metal oxide electrodes, TiO$_x$/Ti, ZrO$_x$/Ti and TaO$_x$/Ti, prepared at 450°C by dip-coating were 0.91, 0.81 and 0.82 V vs. RHE, respectively[19], (b) The electric

conductivity of iridium oxide is much higher than those of the valve metal oxides. The high durability of iridium oxide coatings has already been demonstrated in industry; e.g., IrO_2-Ta_2O_5/Ti electrodes have generally been used as oxygen-evolving anodes in electroplating processes in acidic solutions[20]. A conceptual drawing of the novel cathode is shown in Fig. 1.

Figure 2 (a) shows a scanning electron microscopy (SEM) image of an as-received MPTi composed of interconnected titanium particles of 5–20 μm in diameter and 0.1 mm in thickness. After chemical etching of the MPTi sheet with oxalic acid solution to remove the surface titanium oxide layer (Fig. 2 (b)), the outer and inner surfaces of the MPTi were coated with an HP-IrO_2 layer by dip-coating. SEM images of an etched surface of the MPTi and an HP-IrO_2/MPTi electrode are shown in Figs. 2 (c) and (d).

Fundamental characteristics of HP-IrO_2 coated on a Ti disk substrate

Prior to clarifying the fundamental characteristics of the HP-IrO_2 catalyst layer coated on the MPTi, a few basic characteristics of the HP-IrO_2 catalyst coating were examined using an HP-IrO_2/Ti electrode with a non-porous titanium disk substrate, Ti. Figure 3 shows cyclic voltammograms of an HP-IrO_2/Ti before and after the severe durability test (10,000 potential cycles of the test electrode in O_2-saturated solution between 1.0 and 1.5 V vs. RHE at 500 mV s^{-1} at 30°C). As shown in these voltammograms, little change of the pseudo-capacitance was observed even after the 10,000 times of potential cycling. In Fig. 4, linear sweep voltammograms (LSVs) for the ORR of an HP-IrO_2/Ti before and after the durability test are presented. The fact that a limiting current was not observed even at 3,000 rpm strongly suggests that the HP-IrO_2 layer had a highly porous structure which was too small to easily contribute to

the ORR, other than larger pores which could easily contribute to the ORR in the solution. The specific activity, the current density per geometric surface area, at 0.75 V vs. RHE at 3,000 rpm was -0.90 mA cm$^{-2}_{(geometric)}$.

Even after 10,000 potential cycles of the HP-IrO$_2$/Ti electrode between 1.0 and 1.5 V vs. RHE at 500 mV s^{-1}, there was only a 7 % (0.06 mA cm$^{-2}_{(apparent)}$) decrease in the current density of the electrode for the ORR at 0.75 V vs. RHE. The reason why the catalytic activity for the ORR decreased by 7 % in spite of the little change in the pseudo-capacitance after the durability test is unclear at present. In any case, the electrode was proved to be highly durable, although the high durability of iridium oxide coatings has already been well-documented, provided that the coatings have been prepared by the appropriate procedure. The ORR on the HP-IrO$_2$ obeyed the 4-electrons reaction over a wide range of potentials, as determined by a rotating ring disk electrode method (Fig. 5).

The performance of a PEFC with an MEA using a Pt/C anode and HP-IrO$_2$/MPTi cathode

The *I-E* and *I-W* curves for a (Pt/C)|membrane|(HP-IrO$_2$/MPTi) fuel cell under pure oxygen (atmospheric pressure) and hydrogen (atmospheric pressure) at 80°C is shown in Fig. 6. As demonstrated in this figure, considerable electric power was successfully generated with the PEFC, although the performance was not high enough for the practical use at present. The cell voltage at zero net current of the fuel cell including the overvoltage other than the electric motive force of the cell and the maximum power density were 0.89 V and 42 mW cm^{-2}, respectively. Here we denote the cell voltage at zero net current of the fuel cell as CVZC, which is often described with OCV (Open

Circuit Voltage). Although conditions for preparing the HP-IrO$_2$/MPTi cathode have not yet been optimized, the high values of both the CVZC and the power density are noteworthy.

Fundamental HOR characteristics of the HP-IrO$_2$/Ti electrode

In order to prove the possibility of a PEFC, where both cathode and anode are composed of oxide-coated gas-diffusion electrodes, the anodic characteristics for the hydrogen oxidation reaction, HOR, of the HP-IrO$_2$ catalyst layer were examined using an HP-IrO$_2$/Ti electrode as an oxide anode. As shown in Fig. 7, the HP-IrO$_2$/Ti electrode showed catalytic activity towards both the reduction of H$^+$[21, 22] and the oxidation of hydrogen in 0.1 M HClO$_4$ at 30°C, where the LSV curves depended on the initial electrode potential in the potential sweep to the positive potential. The HP-IrO$_2$/Ti electrode provides high catalytic activity for the HOR at 3,000 rpm; the current density for the HOR at 0.01 V vs. RHE was 0.63 mA cm^{-2}$_{(geometric)}$.

As a result, the HP-IrO$_2$ has been found to have catalytic activity for the HOR. Therefore, an MEA was assembled with HP-IrO$_2$/MPTi electrodes not only as the cathode, but also as the anode of a PEFC: (HP-IrO$_2$/MPTi)|membrane|(HP-IrO$_2$/MPTi).

The performance of a PEFC with HP-IrO$_2$/MPTi electrodes both for the cathode and the anode

The *I-E* and *I-W* curves for a (HP-IrO$_2$/MPTi)|membrane|(HP-IrO$_2$/MPTi) fuel cell under pure oxygen (atmospheric pressure) and hydrogen (atmospheric pressure) at 80°C is shown in Fig. 8. The CVZC and the maximum power density were 0.86 V and 34 mW cm^{-2}, respectively. Under pure O$_2$ (+0.2 MPa) and H$_2$ (+0.2 MPa), however, the

CVZC and the maximum power density improved to 0.91 V and 74 mWcm^{-2}, respectively. Under pure O_2 (+0.2 MPa) and H_2 (+0.2 MPa), however, the CVZC and the maximum power density improved to 0.91 V and 74 mW cm^{-2}, respectively. The success of the generation of this fuel cell is significant; however, the performance was not high enough for the practical use at present. Although the HP-IrO_2/MPTi electrode has been demonstrated to act also as the anode of the PEFC, not only iridium is expensive material but adaptation of the electrode to the anode of PEFCs requires a more detailed examination of the durability.

The role of oxide ion vacancy in the oxide-coated gas-diffusion electrode

To design highly active gas-diffusion electrodes, it is important to guarantee the electrical conduction through the current collector to the catalyst surface. The gas-diffusion cathode proposed in this study, the electrical resistance of the MPTi support, which is the current collector itself, is composed of interconnected titanium micro-particles, and hence, the electrical resistance of the MPTi sheet is negligible. Electrical resistance occurs mainly (a) through the bulk of the oxide catalyst particles themselves and the interface between the oxide catalyst particles connecting to each other to form the oxide catalyst layer, and (b) at the interface between the oxide catalyst layer and the titanium support. For the HP-IrO_2/MPTi electrode, the resistance from (a) and (b) are unlikely to be high, because IrO_2 exhibits metallic conductivity. Even if an oxide catalyst does not have metallic conductivity, the oxide-coated titanium electrode acts as a catalyst electrode, provided the oxide layer is thin and contains many oxide ion vacancies. The oxide ion vacancy in metal oxides can generally be created by heating them or by heating them in vacuum at a high temperature; however, vacancies are also

created for the oxides prepared by calcination of precursors at low temperature, e.g., 450°C. In spite of the considerably low electric conductivity of the valve metal oxides coated on a Ti disk substrate: TiO_x/Ti, ZrO_x/Ti and TaO_x/Ti, all these oxide-coated electrodes showed high catalytic activity for the ORR[19]. This suggests that the oxide ion vacancy in these oxides was stable under the polarization. Moreover, heat-treatment of the oxides under a reducible atmosphere, e.g., under hydrogen, increases not only the amount of oxide ion vacancies but also the electric conductivity, as has been utilized to control the electric properties of n-type titanium dioxides, TiO_{2-x}. The oxide ion vacancy may act as the active sites for the ORR[14, 17, 19]; that is, the electron density of the surface metal ions surrounding the oxide ion vacancy will be enhanced compared to the other normal metal ions on the surface, and they may behave as adsorption sites for oxygen molecules[23]. Concerning the potential for resistance (b) pointed out above, the interface between the oxide coating and the titanium support formed by the dip-coating is usually stable; that is, the oxide coating adheres to the titanium substrate strongly, forming a mixed oxide interface layer.

SUMMARY

In conclusion, this study demonstrated successful power generations of PEFCs with a substantially novel oxide-coated gas-diffusion cathode. The important results of this study are as follows: (a) A gas-diffusion electrode composed of oxide catalyst, a highly porous iridium oxide in this study, which was strongly coated on inner and outer surfaces of a macro porous titanium sheet substrate has been reported for the first time. (b) The oxide-coated gas-diffusion electrode using neither platinum catalyst nor carbon

support has functioned not only as the cathode but the anode of PEFCs. (c) The ORR on the HP-IrO$_2$ obeyed the 4-electrons reaction over a wide range of potentials. (d) It has been found that IrO$_2$ shows catalytic activity for the oxidation of hydrogen in acidic solution. (e) The PEFCs composed of two different MEAs, (Pt/C)|membrane|(HP-IrO$_2$/MPTi) and (HP-IrO$_2$/MPTi)|membrane|(HP-IrO$_2$/MPTi), have functioned well.

This type of gas-diffusion electrode should be widely studied in order to realize stable and highly reliable PEFCs; however, the iridium oxide electro-catalyst, which was used as a test oxide catalyst of this gas-diffusion electrode should be replaced by a less-expensive oxide catalyst in near future. Our approach to creating novel gas-diffusion cathodes may pave the way for the worldwide development of PEFCs, although the performance of the cathode still needs to be improved. Other than the search for a less-expensive catalyst providing high catalytic activity for the ORR, the macro-porous metal support should also be improved; i.e., the MPTi sheet support must be made thinner, and the inner specific surface area of the MPTi sheet should be larger to allow it to carry more oxide catalyst.

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Figure captions

Fig. 1. A conceptual drawing of an HP-IrO$_2$/MPTi cathode.

Fig. 2. (a) An SEM image of the as-received macro-porous Ti sheet substrate, MPTi. (b) The MPTi after being chemically etched with oxalic acid solution. (c) and (d) SEM images of an HP-IrO$_2$/MPTi electrode observed at two different magnifications.

Fig. 3. Cyclic voltammograms of the HP-IrO$_2$/Ti electrode showing the durability of the electrode after repetitive potential cycles between 1.0 V and 1.5 V vs. RHE at 500 mV s^{-1} in O$_2$-saturated 0.1 M HClO$_4$ at 30°C. The number of potential cycles: a; the first sweep after the pre-treatment, b; 100 times, c; 1,000 times, d: 10,000 times.

Fig. 4. Linear sweep voltammograms for the ORR (a) before and (b) after the durability test (10,000 potential cycles of the test electrode in O_2-saturated solution between 1.0 and 1.5 V vs. RHE at 500 mV s^{-1}) of an HR-IrO$_2$/Ti electrode at 30°C. The rotating speed of the electrode in O_2-saturated solution for (a) and (b): a; 0, b; 500, c; 1,000, d; 1,500, e; 2,000, f; 2,500, g; 3,000 rpm.

Fig. 5. (a) The ring current and disk current, respectively, of an HP-IrO$_2$/Ti electrode by the RRDE in O_2-saturated 0.1 M HClO$_4$ at 30°C at the test electrode rotating speed of 2,000 rpm. (c) Number of electrons contributing to the reduction of one oxygen atom on the HP-IrO$_2$/Ti electrode calculated from the voltammograms of (a) and (b).

Fig. 6. The cell voltage and power density *vs*. current density for a PEFC: (Pt/C, 20 wt%Pt)|(membrane, Nafion$^{®}$ 117)|(HP-IrO$_2$/MPTi), under pure H$_2$ (atmospheric pressure) and pure O$_2$ (atmospheric pressure) at 80°C.

Fig. 7. (a) Linear sweep voltammograms of an HP-IrO$_2$/Ti for the HOR at the anodic potential sweep rate of 5 mV s^{-1} in 0.1 M HClO$_4$ at 30°C. a; a LSV measured in N$_2$-saturated 0.1 M HClO$_4$. The rotating speed of the electrode in H$_2$-saturated solution: b; 0, c; 500, d; 1,000, e; 1,500, f; 2,000, g; 2,500, h; 3,000 rpm.

Fig. 8. The cell voltage and power density *vs*. current density for the PEFC: (HP-IrO$_2$/MPTi)| membrane (Nafion$^{®}$ 117)|(HP-IrO$_2$/MPTi), under pure O$_2$ (atmospheric pressure) and H$_2$ (atmospheric pressure) at 80°C (squares; □ and ■) or under pure O$_2$ (atmospheric pressure + 0.2 MPa) and H$_2$ (atmospheric pressure + 0.2 MPa) at 80°C (circles; ○ and ●).

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Ti sheet substrate composed of inter-connected Ti particles

Ionomer

Highly porous oxide catalyst layer coated on a macro porous Ti sheet substrate

Y. Takasu, et al. Fig. 1

(a)

10 μm

(c)

SE   WD22.5mm 20.0kV x2.5   10 μm

(b)

SE   WD21.9mm 20.0kV x2.   10 μm

(d)

50 nm

Y. Takasu, et al. Fig. 2

Y. Takasu, et al. Fig. 3

(a)

(b)

(c)

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Y. Takasu, et al. Fig. 6

Y. Takasu, et al. Fig. 7

Y. Takasu, et al. Fig. 8