INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2014) 1–8

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Enhancement of proton exchange membrane fuel cell performance by titanium-coated anode gas diffusion layer

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ARTICLE INFO

Article history:
Received 31 May 2014
Received in revised form
7 October 2014
Accepted 13 October 2014
Available online xxx

Keywords:
Titanium
Gas diffusion layer
Proton exchange membrane fuel cells
Sputtering

ABSTRACT

Titanium was coated onto an anode gas diffusion layer (GDL) by direct current sputtering to improve the performance and durability of a proton exchange membrane fuel cell (PEMFC). Scanning electron microscopy (SEM) images showed that the GDLs were thoroughly coated with titanium, which showed angular protrusion. Single-cell performance of the PEMFCs with titanium-coated GDLs as anodes was investigated at operating temperatures of 25 °C, 45 °C, and 65 °C. Cell performances of all membrane electrode assemblies (MEAs) with titanium-coated GDLs were superior to that of the MEA without titanium coating. The MEA with titanium-coated GDL, with 10 min sputtering time, demonstrated the best performance at 25 °C, 45 °C, and 65 °C with corresponding power densities 58.26%, 32.10%, and 37.45% higher than that of MEA without titanium coating.

Introduction

Fossil fuel has played indispensable and irreplaceable roles in industry development. With the rapid consumption of fossil fuel reserves and increased environmental protection awareness, numerous countries have explored the cutting-edge technology of using new resources as substitute for fossil fuel [1,2]. Among these new resources, hydrogen has been regarded as one of the best candidates and with high potential as fuel resource for the future because of its renewable, clean, and sustainable nature. Hydrogen-fueled proton exchange membrane fuel cells (PEMFCs) are a promising technology to replace fossil fuel and can be broadly commercialized in transportation, residential, and portable device applications in the near future. PEMFCs have high

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http://dx.doi.org/10.1016/j.ijhydene.2014.10.055

energy conversion efficiency, high power density, low operating temperature, and near-zero pollutant emission [3–7] compared with conventional internal combustion systems that use fossil fuels.

The membrane electrode assembly (MEA), a key module of PEMFC, consists of three main components, namely, anode, electrolyte (a Nafion membrane), and cathode. Carbon fiber-based non-woven paper is usually adopted in anodes and cathodes as a gas diffusion layer (GDL), which is embedded between the catalyst layer and the gas flow channel in PEMFCs. The GDL protects the delicate catalyst structure, provides mechanical strength, allows gas access to the catalyst, and enhances electrical conductivity, which plays an important role in PEMFC. Therefore, GDL modification has been paid much attention for the improvement of the physical properties of PEMFCs.

Several approaches have been proposed to improve cell performance. Polytetrafluoroethyene (PTFE) combined with carbon black powder coated on the GDL substrate as a microporous layer (MPL) effectively improves the water management characteristics and also minimizes electric contact resistance with the adjacent catalyst layer, thereby enhancing cell performance [8–12]. Metal compound has also been deposited on GDL as a water adsorbent layer to improve the wettability of the interface between the membrane and GDL at low humidity conditions [13–17]. Thus, coating GDLs is a promising approach to enhance cell performance.

Titanium has been extensively examined as electrode and bipolar plate material to improve the mechanical strength of microstructure in MEA, thereby reducing the mass transport overpotential of fuel cell [18–22]. Titanium has good corrosion resistance, high electrical conductivity, good thermal conductivity, and low production cost [23–25]. Thus, this element is a good candidate for GDL modification.

This study investigates the feasibility of improving PEMFC performance by coating titanium on the anode GDL by sputtering technique. The microstructure and morphology of the titanium coating were characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM). Wettability, electrical resistance, and the thickness of the titanium coating on the GDL are the three critical factors of the titanium-coated GDL. Cell performance was evaluated using a polarization test conducted at operating temperatures of 25 °C, 45 °C, and 65 °C. Polarization measurements were conducted at ambient conditions.

Experimental

Preparation of titanium-coated GDL and Pt/C catalyst

The GDL (SGL-10BA, SIGRACET®) was coated with a titanium thin film by direct current (DC) magnetron sputtering. The sputtering operating parameters are listed in Table 1. Titanium was sputtered on the GDL for 10, 30, and 60 min, and the resulting samples were labeled as titanium-10 m, titanium-30 m, and titanium-60 m, respectively. Pt/C (20 wt.%) catalyst was synthesized by an impregnation method. The natural inorganic mineral, sodium montmorillonite (MMT, Nancor), was first used to disperse carbon black (CB; Vulcan XC-72, Cabot) in distilled water. The mixture was then ultrasonicated for 2 h to obtain a well-dispersed CB mixture. Then, the platinum precursor (H_2PtCl_6 $6H_2O$; Alfa Aesar, 99.95%), 10 mL of 1 M NaOH, and 10 mL of 99.8 methanol (EM-1001, ECHO, Chemical Co., Ltd.) were added to the mixture. The solution was stirred for 4 h at 80 °C to completely disperse the Pt/C catalyst. The as-prepared Pt/C catalyst was filtered and dried in a vacuum oven for 6 h at a pressure of 100 Pa at 80 °C.

Table 1 – Sputtering parameters of the titanium coatings on GDL.

Target	Titanium
Substrate	Carbon paper (SGL-10BA)
Base pressure	1.0×10^{-5}
Working pressure	5.0×10^{-3}
DC power	250 W
Ar	50 sccm
Working distance	5 cm (holder location)
Sputtering time	10, 30, 60 min
Operation temperature	Room temperature

Characterization of titanium coatings

The microstructure of the titanium coatings were characterized using a glancing-incidence (1°) X-ray diffractometer (MAC MXP III) operated at 40 kV and 30 mA, with Cu Kα radiation ($\lambda = 0.154$ nm, at sweeping angle of 2θ from 20° to 50°, and sweeping rate of $2°min^{-1}$). The diffraction peaks were identified using the JCPDS data files. Surface morphology of titanium-coated carbon paper was examined using a field-emission-scanning electron microscope (FESEM, JEOL JEM-6700F). Chemical composition of the titanium-coated GDLs was estimated by inductively coupled plasma-atomic emission spectrometry (ICP-AES) system (ICAP 9000, Jarrell-Ash, USA). The contact angle of water on the titanium-coated GDLs was measured by a Fat 200 contact angle system using the sessile drop method.

Measurement of polarization curves

A 20 wt.% Pt/C catalyst, 5 wt.% Nafion® solution (Dupont®), and alcohol (98%, Aldrich) were mixed using an ultrasonicator for 2 h and then sprayed onto the titanium-10 m, titanium-30 m, and titanium-60 m samples to serve as anodes. The cathode used the as-received GDL substrate without the titanium coating and was prepared using a similar method. A Nafion 112 membrane (Dupont®) was sequentially pretreated with 5% H_2O_2 (Aldrich), deionized water, and 1.0 M H_2SO_4 (Aldrich) for 1 h at 80 °C. The Nafion 112 membrane was sandwiched between the anode and the cathode and then hot-pressed under 20 kgf cm^{-2} for 3 min at 135 °C. Pt loading at both the anode and the cathode was 0.4 mg cm^{-2}, and the effective area of MEA was 5 cm^2. The anodes of the MEA samples with titanium-10 m, titanium-30 m and titanium-60 m GDLs, which were combined with the Nafion membrane and the cathode, were labeled as MEA10, MEA30, and MEA60, respectively. The as-received GDL used for the anode and cathode, along with the membrane, was designated as MEA0.

A fuel-cell test station (Beam 100 from Beam Associate Co., Ltd.) was used to measure the polarization curves of a 5 cm^2

Please cite this article in press as: Fang S-Y, et al., Enhancement of proton exchange membrane fuel cell performance by titanium-coated anode gas diffusion layer, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.10.055