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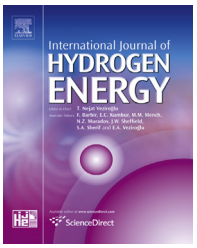

Fabrication of TiN inverse opal structure and Pt nanoparticles by atomic layer deposition for proton exchange membrane fuel cell

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ABSTRACT

A titanium nitride (TiN) inverse opal structure was fabricated on carbon paper as a support of Pt for application in proton exchange membrane fuel cell (PEMFC). Polystyrene spheres with different diameters were coated on carbon paper by spin coating in multilayers as a template. Titanium dioxide (TiO_2) thin film was then deposited on the template by atomic layer deposition (ALD). The TiN inverse opal structure was fabricated by direct nitridation of TiO_2 in flowing ammonia atmosphere at above 800 °C. Platinum nanoparticles were then deposited uniformly on TiN by ALD. The performances of PEMFC using Pt@TiN@carbon paper composite as electrodes were examined. The homemade electrodes showed at least 13 times higher platinum specific power density than commercial E-Tek electrodes.

Introduction

In recent years, PEMFC has drawn a lot of attention for commercialization. However, how to reduce the cost and increase the durability is still a big challenge for commercialization of PEMFCs. Carbon-supported platinum is commonly used as the catalyst in the electrode. Carbon black, such as Vulcan XC-72, has been most widely used as the support for catalyst because of its good electrical conductivity, large surface area, and reasonable cost [1]. In addition, many nanostructured carbon materials with graphitic structure, such as mesoporous carbon [2], nanotubes [3–5], nanofibers [6], and graphene [7], have also been investigated as catalyst support in fuel cells. However, the performance of fuel cells deteriorates when the carbon support gets oxidized or corroded during long-term operation [8,9]. In order to solve this issue, i.e., improving the durability of support and in the meantime enhancing the utilization efficiency of Pt catalyst, it is desirable to search for alternative catalyst supports and the associated method to deposit catalyst.

Titanium nitride, one of the most popular transition-metal nitrides, has been universally accepted as an excellent thermal coating due to its high melting point, extremely high hardness, and high chemical stability. Its special metallic characteristic is ascribed to the single unpaired electron entering into a localized sp hybrid orbital in Ti,

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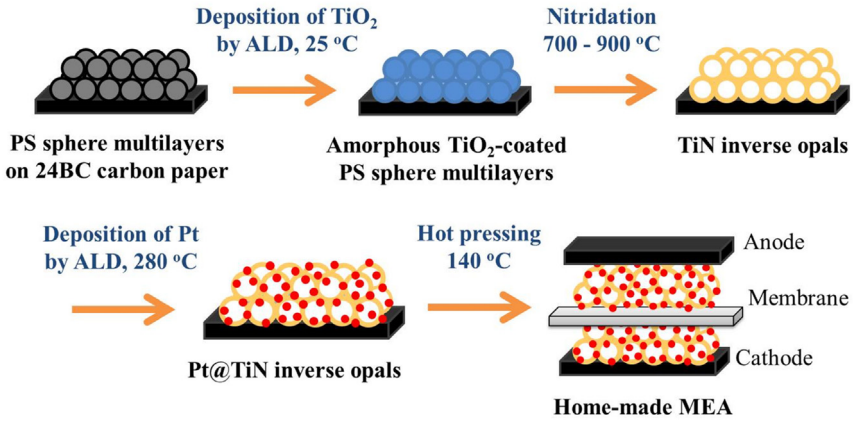

Fig. 1 – Schematic of fabricating Pt@TiN@CP to form MEA for PEMFC.

resulting in non-zero electron density at the Fermi level that contributes to its relatively high electrical conductivity [10–12]. There are several methods for preparation of TiN, including the conventional method of nitridation of Ti-containing compounds with various nitrogen sources, such as ammonia or nitrogen [13,14]. TiN thin film can also be fabricated by sputtering, chemical vapor deposition (CVD), and ALD [15–17].

Recently, TiN in various forms of structure has been investigated as catalyst support for direct methonal fuel cell (DMFC) and PEMFC [18–26]. However, most of the reports were basically focused on the study of cyclic voltammetry (CV) and oxygen reduction reaction to validate electrode performance of Pt@TiN. The membrane electrode assembly (MEA) performance of single cells utilizing the TiN support has been seldom demonstrated. Ottakam Thotiyl et al. reported that a maximum power density of 13.5 mW/cm^2 at 70 °C was obtained for DMFC by using 1.33 mg/cm^2 and 2 mg/cm^2 Pt@TiN as the anode and cathode, respectively [19]. Jiang et al. reported that a maximum power density of 390.5 mW/cm^2 for PEMFC was achieved by using 0.2 mg/cm^2 Pt@C and 0.1038 mg/cm^2 Pt-Pd-Co@TiN nanorods as the anode and cathode, respectively [25].

A variety of methods for synthesizing Pt catalyst have been extensively explored, including CVD, physical vapor deposition (PVD) [27], and wet chemical methods [28]. However, one of the major limitations of these traditional processes is that it is difficult to control the uniformity and size of the catalyst particles. ALD is considered as a promising thin film deposition technique because of the self-limiting gas-solid reactions. It is able to produce thin films with excellent thickness control, uniformity, and conformality even on highly complex nanostructures [29–33]. In addition, ALD can also be adopted to prepare Pt nanoparticles with uniform coverage [34–37].

In this study, a titanium nitride inverse opal structure was chosen as an alternative material to replace conventional carbon support for Pt catalyst. It was fabricated by deposition of a TiO_2 inverse opal structure by ALD on multilayered polystyrene (PS) spheres that were coated on carbon paper (CP) as a template and followed by nitridation. Platinum nanoparticles were then deposited on the TiN support, also by ALD. The size and loading of Pt were directly controlled by the cycle number of ALD. The performance of the Pt@TiN@CP electrode was examined and compared with that of commercial E-Tek electrode.

Experimental

A schematic of fabricating Pt@TiN@CP electrode to form MEA is illustrated in Fig. 1. PS spheres (Bangs Laboratories, Inc™) with 200, 500, and 800 nm in diameter were coated in multilayers on carbon paper (SIGRACT® GDL 24 BC) as a template by spin coating. The spin coating was conducted with 1 wt % PS sphere suspension diluted in ethanol at a rate of 600 rpm. The thickness of the PS sphere multilayers could be controlled by the number of times of spin coating. A TiO_2 thin film was then deposited on the PS spheres by 100 cycles of ALD at room temperature. In the ALD of TiO_2, titanium chloride ($TiCl_4$) and deionized water were used as precursors for the sources of Ti and oxygen, respectively. The precursors were vaporized in a stainless bubbler at 34 °C and the pipe temperature was kept at 90 °C to prevent condensation of the precursors. The durations of pulse time for both $TiCl_4$ and H_2O were 0.08 s. After each pulse of precursor, a purge of nitrogen for 7 s was performed. The working pressure was set at 1 torr during the ALD process. The equipment and process for ALD have been reported previously [29–33].

The TiO_2-coated PS spheres on carbon paper were then nitridized to form TiN by heating in a continuous flow of ammonia (working pressure 20 torr) at 700 °C–900 °C for 1, 2, or 5 h. For the ALD of Pt, (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) and oxygen were used as the precursors [5,36,37]. The Pt precursor was held in a stainless steel bubbler at 46 °C, and oxygen was maintained at room temperature. The durations of pulse time of $MeCpPtMe_3$ and O_2 were 0.5 s and 1.5 s, respectively. After each pulse of precursor, a purge with nitrogen for 15 s was performed. The ALD of Pt was conducted at 280 °C.

The formation and crystallinity of samples were examined by X-ray diffraction (XRD, Rigaku TTRAFIII) using Cu K_α radiation at 50 kV and 300 mA. The surface morphologies

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