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Development of advanced catalytic layer based on vertically aligned conductive polymer arrays for thin-film fuel cell electrodes

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HIGHLIGHTS

- Vertically aligned PPy NWs were employed as the ordered catalyst supports.
- PtPd-PPy electrode without additional proton conducting ionomer.
- PtPd-PPy show better mass-transfer than that of commercial Pt/C based electrode.

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ABSTRACT

The degradation of carbon supports significantly influences the performance of proton exchange membrane fuel cells (PEMFCs), particularly in the cathode, which must be overcome for the wide application of fuel cells. In this study, advanced catalytic layer with electronic conductive polymer −polypyrrole (PPy) nanowire as ordered catalyst supports for PEMFCs is prepared. A platinum −palladium (PtPd) catalyst thin layer with whiskerette shapes forms along the long axis of the PPy nanowires. The resulting arrays are hot-pressed on both sides of a Nafion® membrane to construct a membrane electrode assembly (without additional ionomer). The ordered thin catalyst layer (approximately 1.1 μm) is applied in a single cell as the anode and the cathode without additional Nafion® ionomer. The single cell yields a maximum performance of 762.1 mW cm^{-2} with a low Pt loading (0.241 mg Pt cm^{-2}, anode + cathode). The advanced catalyst layer indicates better mass transfer in high current density than that of commercial Pt/C-based electrode. The mass activity is 1.08-fold greater than that of DOE 2017 target. Thus, the as-prepared electrodes have the potential for application in fuel cells.
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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are one of the most promising alternative energy sources for stationary and transportation applications because of their high power density, quick start-up, zero or low emission, and low operating temperature [1,2]. However, the cost of the PEMFCs must be reduced for wide adoption. Over the past decades, significant research has been devoted to decrease the cost of cell components without sacrificing their performance and durability and to decrease the amount of platinum (Pt) [3]. Many studies have focused on (1) the development of non-Pt-group metal catalysts and (2) the utilization of other metals (Pd, Fe, Co, Ni, and Cu) with Pt to form a core−shell structure or alloy, or the improvement of Pt utilization efficiency with an ordered electrode structure [4–11]. Of these efforts, the development of advanced catalytic layer architecture is of importance to obtain an efficient membrane electrode assembly (MEA), which is the core part of PEMFCs and has significantly influenced the performance and durability of fuel cells.

The ordered electrode structure has been proposed by Middelman in 2002 [12]. Several approaches have proven the concept of the ordered electrode structure since then. One successful approach is the nanostructured thin film (NSTF) electrode that was developed by 3 M Company. 3 M's NSTF electrode is an ultrathin electrode covered with continuous thin Pt or Pt alloy catalyst,

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which provides a novel means to lower Pt cost in low-temperature fuel cells with high performance and long-term durability [13]. Another significant method designed to construct advanced electrode structure with ultralow Pt loading and high performance involves employing vertically aligned carbon nanotubes or nanofibers as the supports for Pt nanoparticles. In addition to these supports, conducting metal dioxides [6,14,15] (e.g., TiO_2 and SnO_2) and conductive polymers [16] are employed as ordered catalyst supports for PEMFCs. These three-dimensional (3D) electrode structures are assumed to enhance Pt utilization and improve the mass transport of reactants/products. The traditional electrode shows low platinum utilization and poor durability of carbon-supported Pt-based catalysts and Nafion® ionomer [1,17–20]. Several studies have reported that the Nafion® ionomer binder in the traditional catalytic layer surrounds the carbon-supported Pt/Pt alloy catalysts, which definitely increase the resistance when oxygen gets through the ionomer film into the catalysts [3].

The physical and chemical properties of PPy polymers are well known, and considerable research has focused on conductive polymer for electrocatalyst dispersion. We designed an ordered catalytic layer structure with vertically aligned PPy nanowires as catalyst support, instead of conventional carbon powder support.

In this study, a novel method of synthesizing advanced catalytic layer in MEA for PEMFCs is presented with vertically aligned PPy nanowire arrays as PtPd catalyst supports. PtPd alloy catalysts with various Pt loadings formed on PPy nanowire arrays in the anode or cathode (PtPd-PPy) are investigated. Two different PtPd-PPy samples (with different Pt loadings) are hot-pressed onto two sides of a Nafion® membrane, namely, the anode and the cathode (called MEA-1), to evaluate the electrochemical performance of PtPd-PPy. Since there is no additional ionomer on the catalyst layer of the proposed electrode, the water film acts as the proton-conducting pathway. Several studies that were based on RDE studies in perchloric acid showed improvement in ORR activity in the absence of Nafion ionomer and numerous protons available in liquid electrolyte [8]. Thus, the proposed benefits of this approach are as follows: (1) removal of ionomers or binders for better gas transport; (2) elimination of carbon supports; (3) thin-film, extended-surface PtPd catalysts; and (4) low tortuosity pathways for transportation [11]. For comparison, a commercial Pt/C-based MEA with the same Pt loading is prepared (MEA-2).

2. Experimental

2.1. Preparation of PPy nanowire arrays

PPy nanowire arrays were synthesized using a typical electrochemical polymerization method and were conducted through a workstation. The synthesis process was modified according to previous reports [16,21]. A Pd nanoparticle layer was deposited on a steel stainless plate through physical vapor deposition (PVD) and was used as the working electrode. A Pt plate (5 cm × 5 cm) was used as the counter electrode and a saturated calomel electrode (SCE) was applied as the reference electrode. The electrolyte contained a phosphate buffer solution (pH = 6.86), 0.1 M pyrrole, and 0.1 M *p*-toluenesulfonate acid. The experiment was conducted at room temperature. The PPy nanowire nanoarrays were prepared at a constant potential of 0.7 V (vs. SCE) for 25 min. The as-synthesized samples were cleaned by deionized water before further experimentation.

2.2. Preparation of PtPd-PPy electrode

The Pd nanoparticles were sputtered on the PPy nanowire arrays by PVD, and the entire deposition process was maintained for 8 min at argon atmosphere with working pressure of 8.9×10^{-1} Pa (denoted as Pd-PPy). Then, the Pd-PPy nanowire arrays (3×3 cm^2) were immersed in an ethanol solution that contained 20 or 40 mg K_2PtCl_4 and were saturated with high-purity hydrogen at a flow rate of 30 mL min^{-1} for 1 h. For investigation in a single cell, two kinds of samples with different Pt loadings were prepared (denoted as PtPd-PPy-203 and PtPd-PPy-402). For example, PtPd-PPy-203 means that three as-prepared Pd-PPy nanowire arrays samples (the same scales) were immersed in an ethanol solution that contains 20 mg K_2PtCl_4.

2.3. MEA preparation and single-cell test

A PtPd-PPy-203 sample and a PtPd-PPy-402 sample were hot-pressed onto a Nafion® 211 membrane and were then applied as the anode and the cathode of a single cell, respectively (denoted as MEA-1). MEA-1 was hot-pressed at 140 °C and 0.2 MPa (gauge) for 2 min. For comparison, a commercial Pt/C-based (Johnson Matthey, 20% Pt/C) MEA-2 is prepared for comparison with Pt loading of anode (0.1 mg cm^{-2}) and cathode (0.15 mg cm^{-2}). The experimental areas of MEAs are measured as 4 cm^2.

During the performance test, the cell operating temperature of the single cell was maintained at 70 °C. Fully humidified hydrogen and oxygen at the corresponding flow rates of 50 and 100 mL min^{-1} at 0.05 MPa (backpressure) were supplied to the anode and the cathode, respectively, in either the activation test or the polarization test. For H_2–air condition, humidified hydrogen and air at the corresponding flow rates of 100 and 800 mL min^{-1} at 0.05 MPa were supplied to the anode and cathode, respectively. After full activation, the KFM-2030 impedance meter (Kikusui, Yokohama, Japan) was used for the *i*–*V* curve test. The electrochemical impedance spectroscopy (EIS) test was conducted by Solartron 1287 Electrochemical Interface in conjunction with Solartron 1260 Frequency Response Analyzer in frequencies of 0.1 Hz–10 kHz.

Cyclic voltammetry (CV) was conducted to calculate the electrochemical active surface area (ECSA). After the *i*–*V* curve test, the anode and cathode were purged with humidified N_2 gas to remove reactant gases. After the open circuit voltage decreased to less than 0.05 V, humidified H_2 and N_2 were supplied to the anode and cathode, respectively. The voltage sweep range was 0 V–1.2 V (vs. NHE) with the scan rate of 50 mV s^{-1}, and the cell temperature was maintained at 30 °C. After the CV curve was obtained, ECSA was calculated by integrating the areas of hydrogen adsorption after subtracting the double-layer region [22].

3. Results and discussion

Thin-film and oriented PPy nanowire arrays were fabricated via a conventional electrochemical polymerization method [16,21]. Typically, a clean stainless steel plate was employed as a substrate for growing PPy nanowire arrays. A thin layer of Pd nanoparticles (Pd loading = 0.107 mg cm^{-2}) were sputtered on the stainless plate by PVD and provided sufficient nucleation sites for growing PPy nanowires. After sputtering the Pd catalysts on the vertically aligned PPy nanowire arrays, the sample was immersed in an ethanol solution that contains varying K_2PtCl_4 contents (20 or 40 mg), and the Pt catalysts were in situ reduced on the surface of the Pd catalysts through high-purity hydrogen gas. The PtPd-PPy nanowire film was transferred almost completely from the stainless steel substrate onto Nafion® membrane via hot-press process, and MEAs were fabricated for single-cell test.

The morphology and structure of the PPy nanowires were characterized by FESEM and TEM, as shown in Fig. 1a–d, respectively. The detailed results showed that the nanowire exhibited a

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