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Electrochemical study of highly durable cathode with Pt supported on ITO-CNT composite for proton exchange membrane fuel cells

Sehkyu Park [a,b,*], Yuyan Shao [a], Vilayanur V. Viswanathan [a], Jun Liu [a], Yong Wang [a,c,**]

[a] Pacific Northwest National Laboratory, Richland 99352, USA
[b] Department of Chemical Engineering, Kwangwoon University, Seoul 01897, Republic of Korea
[c] The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman 99164, USA

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ABSTRACT

In this paper, we describe a highly stable cathode containing a Pt catalyst supported on an indium tin oxide (ITO) and carbon nanotube (CNT) composite. The dependence of cathode performance and durability on the ITO content and the diameter of the CNTs were investigated by electrochemical techniques. The cathode with 30 wt% ITO and CNTs with diameters 10–20 nm in the composite offered preferred locations for Pt stabilization and was very resistant to carbon corrosion (i.e., 82.7% ESA retention and 105.7% mass activity retention after an accelerated stress test for 400 h).

Introduction

PEM fuel cells have garnered interest as alternative, auxiliary, and emergency power sources for both automotive and stationary applications, and they are anticipated to replace fossil fuel power sources, such as the internal combustion engine, and many other types of electrical power sources. PEM fuel cells have been extensively studied in academia and industry, leading to remarkable advances in this technology. However, reaching a state of commercial viability of PEM fuel cells is challenging because they lack long-term stability [1,2].

In PEM fuel cells, the membrane-electrode assembly is the core part controlling the performance and lifetime of the cell. As an electrolyte, the membrane provides a protonic pathway that is connected to both catalytic sites at the anode and the cathode. Typically, Nafion has been used as an electrolyte in PEM fuel cells, and the durability of Nafion 120 is reported to be approximately 60,000 h [3]. However, the degradation of Nafion over time is dependent on the membrane properties (e.g., chemical structure, equivalent weight, and thickness) and operating conditions (e.g., temperature, relative humidity, and load cycle) [2]. The electrode includes a catalyst layer (CL) and a gas diffusion layer (GDL). The GDL is primarily responsible for transport processes for both the reactant and the product during operation and the CL is a layered structure of Pt-based catalysts, providing numerous three-phase boundaries (TPBs) that represent triple junctions of the catalyst, ionomer, and reactant [4].

Pt or a Pt alloy is usually supported on high-surface-area carbon to increase the electrochemical surface area of the catalyst [4,5]. The durability of the carbon-supported catalyst strongly depends on the supporting material because the catalyst support determines the dispersion and stabilization of the supported catalyst nanoparticles [6]. The carbon support, however, is vulnerable to oxidation by the sudden potential increase (>1.0 V vs. the standard hydrogen electrode, SHE) that occur at the cathode during repeated start-up/shut down processes [7–9]. To mitigate carbon corrosion, a variety of alternative carbon supports, such as CNTs, mesoporous carbon, and graphene, have been proposed [6,10–14]. Among these candidates, CNTs have been reported to be very durable compared to carbon black (e.g., Vulcan® XC-72) during long-term stress tests and accelerated stress tests for catalyst supports in single cells [13]. In contrast, metal-based supports, such as titanium oxide with different particle morphologies (spherical, nano-wire, etc.), tin

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[*] Corresponding author at: Department of Chemical Engineering, Kwangwoon University, Seoul 01897, Republic of Korea. Tel.: +82 2 940 8676; fax: +82 2 918 5685.
[**] Corresponding author at: Pacific Northwest National Laboratory, Richland 99352, USA. Tel.: +1 509 371 6273; fax: +1 509 371 6498.
E-mail addresses: vitalspark@kw.ac.kr (S. Park), yong.wang@pnnl.gov (Y. Wang).

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oxide, and tungsten oxide, have also been recently studied in attempts to improve both electrode performance and durability for PEM or direct methanol fuel cell applications [15–20]. However, despite surface modification with metals [21], the relatively poor electrical conductivity and the low specific surface area of metal-based supports still hinders their use as replacements for carbon-based supports in PEM fuel cells [22,23]. Therefore, a different approach to prepare hybrid supports comprised of carbon and metal-based materials, which form metal nanoparticle-decorated carbon scaffold supports [24,25], has been taken. This approach has been adopted by several research groups [25–29], and these hybrid catalyst supports have been shown to be promising. Similarly, Qu et al. synthesized TiO_2-deposited reduced graphene as a Pt nanoparticle support to form a three-phase junction structure for methanol oxidation, [30] and Kim et al. improved catalytic activity for oxygen reduction reaction using Pd-WO_3 on carbon black for use as an electrocatalyst. [31]. Furthermore, we have shown [25] through theoretical calculations and the thin-film disk electrode techniques (TFDE) [32] that a hybrid support increases the stabilization of Pt at the junction of the metal oxide and the carbon support, thereby enhancing the catalyst durability. In this study, based on the assumption that (i) for a single catalyst support, Pt nanoparticles are mainly deposited on a carbon because of its higher surface area, higher electrical conductivity, and more defects than in a metal oxide; (ii) Pt nanoparticles are well dispersed on a carbon in the presence of a metal oxide; and (iii) Pt cluster are preferentially anchored at the junction of carbon and metal oxide for a hybrid catalyst support due to a higher interaction energy than Pt cluster on the metal oxide [25]; we have prepared a new Pt catalyst supported on a composite of indium tin oxide (ITO) and CNTs. In addition, we have characterized the catalytic properties and durability of the supported catalyst in a single PEM fuel cell by cyclic voltammetry, polarization analysis, and electrochemical impedance spectroscopy under accelerated stress testing conditions for the catalyst supports. The effects of the ITO content and the diameter of the CNTs in the composite support on the cathode performance and stability were investigated to explore the potential applications of the composite as an alternative catalyst support in PEM fuel cells.

Experimental

Synthesis of the Pt on ITO-CNT composite

To form ITO nanoparticles with 10 wt% SnO_2, $In(acac)_3$ (0.2672 g) and $Sn(OtBu)_4$ (0.02729 g) were mixed with benzyl alcohol (20 mL) with continuous stirring and transferred to an autoclave. The first step in the preparation of the ITO-CNT composites was to disperse the as-received CNTs (Cheap Tubes, Inc.) in benzyl alcohol at a concentration of 0.0045 g mL^{-1}. The CNTs used in this study had been graphitized and COOH-functionalized (3.86 wt%) by the manufacturer. Then, a designated amount of the CNT/benzyl alcohol mixture was added to the $In(acac)_3$ and $Sn(OtBu)_4$ solution, stirred overnight, and heat-treated in an autoclave at 200 °C for 17 h. The resultant material was thoroughly washed with ethyl alcohol and chloroform and dried in air. A chemical reduction method was used to load 20 wt% of Pt nanoparticles on the different composite supports: H_2PtCl_6 (0.0525 g) was first dissolved in ethylene glycol (40 mL, EG), and the pH was adjusted to 12 with a 2 M NaOH/EG solution. To prepare the Pt on ITO-CNT composite (Pt/ITO-CNT), the ITO-CNT (0.1 g) composite was added to the chloroplatinic acid solution, and the mixture was ultrasonically blended for 5 min and heat-treated at 140 °C for 4 h. The products were washed with a large amount of water and dried in air.

Electrochemical measurements in solution

The electrochemical measurements were made in a standard three-electrode cell using a Pt wire counter electrode and an Hg/Hg_2SO_4 reference electrode at room temperature. To prepare the working electrodes, the catalyst (10 mg) was first added to a solution of 2-propanol (10 mL) and 5.0 wt% Nafion® (45 μL), and the solution was ultrasonically mixed to form a homogeneous catalyst ink. Then, the well-dispersed catalyst ink (15.0 μL) was applied to a polished glassy carbon disk to fabricate thin-film disk electrodes. After drying at room temperature, a 0.05 wt% Nafion solution (10 μL) was applied to the surface of the CL to bind the catalyst particles. Cyclic voltammetry (CV) was performed on the TFDEs between 0 and 1.1 V at 50 mV s^{-1} in an N_2-saturated 0.1 M $HClO_4$ solution until a steady voltammogram was obtained. The accelerated stress tests (AST) for the supported catalyst were performed using the potential step method with an upper potential of 1.4 V for 150 s and a lower potential of 0.85 V for 30 s in each period [33]. The voltammograms were recorded before and after 44 h of AST for each catalyst.

Preparation of the membrane-electrode assembly

The catalyst ink for the cathode was prepared by mixing 20 wt% Pt/ITO-CNT catalyst with a 5 wt% Nafion solution (Ion Power, Inc.), deionized water, and methanol for 1 h. The catalyst ink was applied to hydrophobized carbon paper with microporous layers (SGL 10CC, SGL group), followed by drying at 80 °C for 10 min. This process was repeated until a total Pt loading of 0.2 mg cm^{-2} was achieved. The catalyst ink for the anode was prepared using commercially available Pt/C (20 wt% Pt, Electrochem, Inc) and was sprayed on the carbon paper in the same manner. A thin layer of Nafion (0.4 mg cm^{-2}) was applied to both the anode and the cathode surface to enhance the adhesion between the electrode and the membrane. Two gas diffusion electrodes were hot-pressed with a Nafion 117 membrane at 140 °C for 3 min. The geometric area of the MEA used for all of the single cell tests was 8 cm^2.

Electrochemical measurements in single cells

Polarization curves were obtained at an automated fuel cell test station (Arbin Instrument, Inc.). CV and electrochemical impedance spectroscopy (EIS) measurements were performed with a potentiostat (VersaStat, AMETEK, Inc.). To obtain the CV curves, the cathode was cycled as a working electrode at 50 mV s^{-1} between 0.02 and 1.1 V vs. SHE. The electrochemical surface area (ESA) of the cathode fabricated in this study was determined with the total charge corresponding to the hydrogen atoms desorption peak in the CV, the total charge related to a monolayer of hydrogen atoms (210 μC cm^{-2}), and Pt loading on the cathode (0.2 mg cm^{-2}). The EIS experiments were carried out under H_2/O_2 by applying an AC amplitude of 10 mV over a frequency range from 50 mHz to 10 kHz. The impedance data in H_2/O_2 were obtained at 0.9 V and $\upsilon_{H_2} = \upsilon_{O_2} = 100\ cm^3\ min^{-1}$. The AST for the catalyst support [2] in this study was conducted in a single-cell fixture by holding the potential at 1.2 V using fully humidified H_2/N_2 at 80 °C and 150 kPa for a defined period.

Results and discussion

Fig. 1 displays the initial ESA for the Pt/ITO-CNT with CNT diameters ranging from 10 to 20 nm (d_{CNT} = 10–20 nm) and the ESA retention values after a 44 h AST at various ITO contents using the ITO-CNT composite as the catalyst support. The experiments were performed in a 0.1 M perchloric acid solution with N_2 bubbled through the solution at room temperature. The ESA