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Effects of support particle size and Pt content on catalytic activity and durability of Pt/TiO_2 catalyst for oxygen reduction reaction in proton exchange membrane fuel cells environment

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HIGHLIGHTS

- Support size and Pt content affect ORR activity and stability of Pt/TiO_2 catalyst.
- ORR activity and stability increase with increase in TiO_2 particle size.
- 12 wt%Pt on TiO_2 30 nm support has the best ORR catalytic performance.
- Further increase in Pt content beyond 12 wt% doesn't improve ORR performance.

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ABSTRACT

For proton exchange membrane fuel cells (PEMFCs), instability of Pt-based catalysts due to carbon support corrosion is a critical issue that limits their wide application. Alternative corrosion resistant supports, such as metal oxides, have been investigated in conductive carbon containing matrix and demonstrated improved stability. This study probes systematically the effects of TiO_2 support particle size (5, 18, and 30 nm) and Pt content (6, 12, and 37 wt%) on the oxygen reduction reaction (ORR) activity and stability of the Pt/TiO_2 catalyst in the absence of corrosive carbon. The average Pt nanoparticle size increases with increased TiO_2 support size and Pt content. For 12 wt% Pt loading, with increasing support size the ECSA increases from 4.91 to 7.23 $m^2 g_{Pt}^{-1}$, 6.5%–10.6% of the predicted electrochemical surface area, respectively. This result suggests that there is an increased support contribution with increased TiO_2 support size to improve Pt accessibility. The mass and area specific ORR activities are the highest for the 12 wt% Pt on 30 nm TiO_2, 0.083 $A\ mg_{Pt}^{-1}$ and 1134.56 $\mu A\ cm_{Pt}^{-2}$, respectively. Accelerated stress testing results in only a 5.9% loss in ECSA for the 12 wt% Pt/TiO_2 (30 nm) catalyst.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) offer numerous advantages such as high power output, high-energy conversion efficiency, low noise, and zero to minimal environmental pollution, which make them a promising technology for mobile and stationary power applications [1,2]. Despite inherent advantages of PEMFCs, some economical and technical barriers impede their large-scale commercialization. One of the most active researched area in PEMFCs is associated with cathode catalyst performance, durability and cost; typically, carbon supported platinum (Pt/C) nanoparticles. Carbon supports offer high electrical conductivity and high Pt nanoparticle densities, but have weak interaction with Pt and are susceptible to corrosion in the acidic PEMFCs environment [3]. In order to inhibit the corrosion of the support and enhance the stability of the catalyst during PEMFCs operation, more stable and corrosion resistant catalyst supports are required. Therefore, one of the significant challenges today is to develop and optimize novel catalyst supports that are stable under PEMFC conditions and to improve the durability of the Pt nanoparticles through potential co-catalytic functionalities that can enhance oxygen reduction reaction (ORR) activity and prevent or delay the degradation of the catalysts [4].

Recently, titanium dioxide (TiO_2) nanoparticles have been investigated as a catalyst support in PEMFCs due to their high stability in acidic and oxidative environments, which promotes good corrosion resistance over a wide operating potential range [5,6]. To circumvent

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TiO_2's low electrical conductivity, carbonaceous materials have been incorporated into the catalyst films, thereby partially diminishing their potential corrosive stability. Xiong et al. [7] studied the ORR activity of $Pt/TiO_x/C$ nanocomposites in direct methanol fuel cells (DMFCs) and found that the $Pt/TiO_x/C$ catalysts can show methanol tolerance about three times higher than that of Pt/C. Liu et al. [8] investigated the stability of $Pt/TiO_2/C$ catalyst in PEMFC using accelerated stress test and demonstrated improved stability with only 24.4% loss in the electrochemical surface area (ECSA), as compared to 57.4% loss for Pt/C. Additionally, the apparent exchange current density of ORR for $Pt/TiO_2/C$ catalyst was reduced to 0.37×10^{-9}, from 3×10^{-9} for Pt/C catalyst. Jiang et al. [3] synthesized Pt/TiO_2-C catalyst using the microwave-assisted polyol process and reported higher stability in PEMFC of only 22–35% ECSA loss during accelerated stress testing compared to 49% for Pt/C synthesized by the same process. They also found that the optimized particle size of TiO_2 support was 20 nm and 40% TiO_2 existed in the mixed support was optimal for stability of the Pt/TiO_2-C catalyst. The novelty of this study is to systematically look at the intrinsic stability and ORR activity of TiO_2 supported Pt catalyst (Pt/TiO_2) in the absence of an electrical conductivity enhancer.

In this paper, we present an investigation on the effect of TiO_2 support sizes (5, 18, and 30 nm) and Pt contents (6 wt%, 12 wt%, and 37 wt%) on the ORR activity and stability of the Pt/TiO_2 catalyst. The Pt/TiO_2 catalysts were prepared using a simple and efficient polyol process. The catalyst as prepared were characterized using transmission electron microscopy (TEM), and X-ray diffraction analysis (XRD). The ECSA and catalytic behaviors were assessed via the CO stripping method, ORR activity analysis, and stability test (accelerated stress test (AST) 5000 cycles from 0.6 V to 1.0 V).

2. Experimental methods

2.1. Catalyst preparation

Platinum (II) chloride ($PtCl_2$) with purity of ≥99.9% was purchased from Sigma-Aldrich. Anatase TiO_2 nanoparticles supports with particle sizes of 5, 18 and 30 nm were utilized in this study (purity of 99.50%–99.98%, US Research Nanomaterials, Inc). The Pt/TiO_2 catalysts were synthesized by a simple polyol process involving a single step chemical reduction of the $PtCl_2$ with Pt contents of 6 wt%, 12 wt% and 37 wt%. A brief overview of preparation: 50 mg of TiO_2 nanoparticles were stirred in a solution containing 20 ml of Ethylene Glycol (EG, Sigma-Aldrich) and 50 mg of polyvinylpyrrolidone (PVP MW = 55,000, Sigma-Aldrich, capping/stabilizing agent) in 50 ml beaker for 30 min. The suspension was then ultrasonicated (Branson 200 Ultrasonic Cleaner) for 1 h to ensure all of the PVP-capped TiO_2 nanoparticles were well dispersed in the solution. Then a calculated amount of $PtCl_2$ was dissolved and dispersed into a solution containing 20 ml of EG and 50 mg of PVP for 1 h to form a brownish color solution. This solution was then poured into the TiO_2 suspension that was already prepared in the previous step. The mixture was magnetically stirred and slowly heated to 130 ± 1 °C to reflux with a heating rate of ~10 °C/min. After refluxing in 130 °C for 10 h, the heating source was removed and the solution was allowed to cool down in the air. The synthesized Pt/TiO_2 nanoparticles were then washed and precipitated repeatedly by deionized water (18 MΩ cm, Millipore) and centrifugation at 10000 rpm. The obtained Pt/TiO_2 catalysts were dried at 80 °C in oven for 8 h and then stored in the vials with an inert atmosphere.

2.2. Microstructural characterizations

Microstructural characterizations of the synthesized Pt/TiO_2 nanoparticles were performed by transmission electron microscopy (TEM, Zeiss Libra 200 MC), and X-ray diffraction analysis (XRD, Rigaku Ultima IV Diffractometer). The Pt particle size distribution and average Pt particle size were investigated using imaging software (Image J) measuring the diameter of the Pt particles shown in TEM images. Pt particles were approximately spherical, the diameter measurements were performed randomly for 50–60 particles. For XRD, a normal line focus Cu K_α radiation tube was used with power settings of 40 kV, 44 mA and 1.76 kW. Measurements were made using a D/teX Ultra High Speed Detector with the detector discriminator set in a fluorescent reduction mode. All samples were loaded into an automatic rotary sample changer, and diffraction patterns were recorded using scan speed of 1.00 deg min^{-1} and scan range of 20–80° in 2θ. The raw data was imported into the PDXL software package for phase analysis and compared with the standard patterns in the ICDD database. Pt contents of the synthesized catalysts were measured by Energy Dispersive Spectroscopy (EDS).

2.3. Electrochemical characterizations

Electrochemical measurements were performed using a three electrode cell, an interchangeable rotating disk electrode (RDE, glassy carbon disk, Pine Research Instruments, MSR rotator), and a Solartron Analytical potentiostat model 1470E at room temperature. For the working electrode, a thin film was deposited onto the RDE as follows: 12.5 mg of catalyst was mixed with 3 ml isopropanol (IPA-99.9%, Sigma-Aldrich), 7 mL Millipore deionized water and 40 μL of Nafion ionomer solution (LQ-1105, 1100 EW, 5 wt%, Ion Power) and ultrasonicated for 30 min to make a uniform suspension. A 10 μL droplet of the suspension was pipetted onto the glassy carbon (Tokai Carbon) disk with a 5 mm diameter (0.196 cm^2) embedded in a Teflon holder using a micropipette (Transferpette® S, 20 μL, accuracy: 0.49%). A uniformed thin catalyst film was then formed by drying the electrode for 3 h in an IPA environment. A Pt gauze was used as the counter electrode and a Hydroflex® reversible hydrogen electrode (RHE) was used as the reference electrode. An aqueous solution of 0.1 M $HClO_4$ (70% ACS Reagent, Sigma-Aldrich), purged with either argon, oxygen or 10% carbon monoxide (CO) in a nitrogen balance (Airgas, Ultra High Purity), was used as the electrolyte in all electrochemical experiments.

In order to remove the remaining PVP from the surface of catalyst and activate the RDE working electrode, it was first electrochemically cleaned by potential cycling 200 times in the range of 0.05–0.8 V vs. RHE with scan rate of 200 mV s^{-1} [9]. In addition, a single potential square wave profile between 0.6 V and 1.2 V vs. RHE was applied for 120 s. After the electrochemical cleaning process, a fresh electrolyte was used and the RDE was rinsed with deionized water to eliminate any impurities from the solution that were desorbed from the electrode which might be formed during electrochemical cleaning (e.g. decomposition of electrolyte or PVP). Cyclic voltammetry (CV) analysis was performed by sweeping the potential between 0.05 V and 1.0 V vs. RHE with scan rate of 20 mV s^{-1}. The initial ECSA was measured by carbon monoxide (CO) stripping by adsorbing at 0.1 V vs. RHE in saturated CO electrolyte (10% CO in a Ar balance) for 15 min and then purging with Ar for 30 min, followed by CVs. ORR polarization measurements were carried out in O_2 saturated electrolyte analyzing the anodic sweep the potential from 0.025 V to 1.0 V vs. RHE at 20 mV s^{-1} at a rotation speed of 1600 rpm. In order to study the catalysts stability, the accelerated stability test (AST) was conducted by cycling the working electrode between 0.6 V and 1.0 V vs. RHE at 500 mV s^{-1} in Ar saturated electrolyte for 5000 cycles to simulate peak power to idle transients in an automotive drive cycle. ORR and CV were investigated again after 5000 cycles [10]. All results were repeated three times to ensure reproducibility. The relative differences in the ECSAs after AST were determined via hydrogen desorption (210 μC cm^{-2}) charges from the CVs.

3. Results and discussion

The effects of 12 wt% Pt/TiO_2 support particle sizes (5, 18, and 30 nm) and the effect of Pt/TiO_2 catalyst loading (6 wt%, 12 wt%, and 37 wt%) on 30 nm TiO_2 support particles are presented herein.