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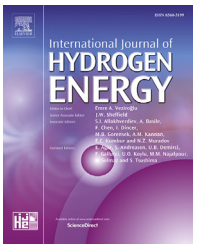

Direct formation of Pt catalyst on gas diffusion layer using sonochemical deposition method for the application in polymer electrolyte membrane fuel cell

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ABSTRACT

In this study, the facile and direct formation of platinum catalyst on a carbon paper (gas diffusion layer) via the sonochemical deposition method is demonstrated. An ultrasound irradiation with a carbon paper substrate in a platinum precursor solution formed interconnected platinum grains on the carbon paper surface. The surface morphology and deposition amount of platinum were strong functions of both ultrasound parameters (power and time) and solution composition. The platinum-deposited carbon paper was then directly used as a gas diffusion electrode in PEMFC without adding the ionomer. This exhibited high stability in the accelerated stress test in a single cell operation. The interconnected grains of platinum on carbon paper had high resistance to dissolution in an oxidizing environment and the absence of carbon support also enhanced resistance to carbon oxidation. Although the overall performance did not exceed that of the commercial Pt/C, this approach may be an option to form a stable platinum catalyst for PEMFCs.

Introduction

Hydrogen is attracting attention as an alternative energy carrier to fossil fuels due to its environmental friendliness. Proton exchange membrane fuel cells (PEMFCs), which use hydrogen as their energy source instead of fossil fuel, have undergone considerable technological advances according to studies in recent years. However, the high cost and poor stability of platinum catalysts still hinder the wider propagation

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of fuel cells; although recent studies have shown remarkable performance improvements in both oxygen reduction reaction (ORR) and single cell operation [1–7]. Platinum catalysts lose their catalytic activity under continuous fuel cell operations via dissolution, aggregation, redeposition, and falling-off [8,9].

For these reasons, many researchers have proposed various types of catalysts like alloy catalysts, core-shell catalysts, and ultra thin catalyst layers (UTCL) in order to maximize their utilization and to improve the stability. In recent years, UTCLs of various structures have been extensively studied including nanostructured thin film (NSTF) catalyst, an inverse-opal structure catalyst, and a wheat ear-like catalyst layer [10–13]. UTCLs have the advantage of achieving high catalyst utilization through thickness control [14–16]. Furthermore, as they are in form of interconnected grains of catalyst material, the stability can be improved compared to the conventional catalyst consisting of discrete catalyst nanoparticles. UTCLs are generally formed directly on the gas diffusion layer (GDL) rather than the membrane, which is so-called catalyst-coated substrate (CCS) method. The CCS method can avoid the damage of the membrane by the chemical or physical process for the fabrication of UTCLs. Debe et al. reported that a 0.27-μm-thick NSTF catalyst deposited on polymer whiskers exhibited superior performance and stability compared to a conventional Pt/C catalyst with 10 μm thickness [10]. Kim et al. formed a platinum electrode of an inverse opal structure on GDL by electrodeposition using a polystyrene opal as a negative template [11]. The inverse-opal-structure electrode is beneficial for mass transfer and water management due to its high porosity. Zhang et al. synthesized a wheat ear-like catalyst layer on a Nafion membrane via Co–OH–CO_3–Pt (and/or Pd) nanowire transfers [12]. The common benefit of UTCLs is that they can demonstrate improved platinum utilization and stability with a relatively small amount of platinum loading.

In this study, we suggest a sonochemical deposition method to form a platinum catalyst layer on GDL directly. The adoption of ultrasound is known as an effective approach in synthesizing nanostructured materials and supporting them on various substrates [17–24]. The ultrasound irradiation affects the processes both chemically and physically. When the ultrasound is irradiated in an aqueous solution, the irradiation makes a number of bubbles that grow and collapse in a very short period of time. At the moment a bubble explodes, the temperature instantly rises (~5000 K) and falls with very fast heating and cooling rates of 10^{10} K s^{-1} and a pressure reaching up to 1000 bar. This harsh condition makes some H· and OH· radicals having tremendous chemical activity, and these radicals can be used for chemical reactions like reduction of metal precursors and synthesis of metal oxides. In addition, the generation of shock waves and micro jets at the liquid-solid interface can be used to support synthesized particles on a substrate. When bubbles explode next to the substrate surface, the solvent containing particles is forced to move to the substrate and the particles get stuck in the substrate by the strong solvent stream [18]. It has already been reported that ultrasounds can form intimate contacts between nanoparticles and support materials like polymers and silica spheres [20–22]. Pollet et al. reported sonoelectrodeposition of platinum on GDL [23,24]. The ultrasound irradiation during electrodeposition facilitates mass transfer by cavitational and acoustic streaming effects, thereby decreasing overpotential for platinum ion reduction. However, the direct sonochemical deposition of platinum on GDL has rarely reported.

Herein we demonstrate that a platinum ion can be reduced and coated on GDL simultaneously via simple ultrasound irradiation. The membrane electrode assembly (MEA) prepared by this method was also applied to PEMFC and its performance was evaluated.

Experimental

Reaction monitoring

The effect of ultrasound irradiation on Pt ion reduction was investigated by UV–Vis (ultraviolet–visible) spectroscopy (Thermo Scientific, Genesys 10S). The ultrasound was irradiated to 60 ml of a solution containing 0.5 mM $H_2PtCl_6{\cdot}6H_2O$ and 0.5 mM ascorbic acid at different power density and time using ultrasound generator (BRANSON, Digital Sonifier 450, 60 kHz). The change of the solution during the irradiation was then monitored by UV–visible spectroscopy. The concentration of ascorbic acid (0.5 mM) was the highest level at which reliable UV–Vis absorption spectra could be obtained. If the concentration of ascorbic acid is higher than 0.5 mM, the absorbance becomes too strong and exceeds the detection limit of UV–vis spectroscopy. The absorption spectra ranging from 200 nm to 500 nm were obtained every 5 min during the ultrasound irradiation.

Catalyst formation

A carbon paper with a microporous layer (SIGRACET® 35BC GDL) was used as a substrate. The thickness of the carbon paper was 325 (±25) μm and the polytetrafluoroethylene (PTFE) content was 5%. The substrate was mounted in an acrylic frame and then immersed in the mixture of $H_2PtCl_6{\cdot}6H_2O$ and ascorbic acid. The exposed area of the substrate was 2.5 cm × 2.5 cm. After positioning a sonifier tip at 1 cm above the substrate, the ultrasound was irradiated with different power density: 8 W, 12 W, and 16 W. The scheme of the experimental set-up is shown in Fig. S1. To investigate the effect of solution composition on the formation of catalyst, the solutions with different concentration ratios of $H_2PtCl_6{\cdot}6H_2O$ and ascorbic acid were prepared; the ratios of the platinum precursor to ascorbic acid were 0.5 mM:0.5 M, 0.5 mM:1.0 M, 1.0 mM:0.5 M and 1.0 mM:1.0 M.

MEA fabrication

Pt-deposited carbon paper prepared by ultrasound irradiation was used as the cathode. The loading amount of platinum on the cathode was 0.28 mg_{Pt} cm^{-2}, which was measured using thermogravimetric analyser (TGA; Sinco, TGA-N1000). The anode was prepared by spraying 40 wt% Pt/C (Alfa Aesar) on GDL. The platinum loading amount of the anode was 0.2 mg_{Pt} cm^{-2} for every MEA investigated in this study. The Pt/C ink slurry consisted of 6.25 mg Pt/C, 0.625 mL isopropyl alcohol

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