

Synthesis and characterization of PDDA-stabilized Pt nanoparticles for direct methanol fuel cells

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Abstract

Pt nanoparticles are synthesized by the alcoholic reduction of H_2PtCl_6 in the presence of a polycation, poly(diallyldimethylammonium chloride) (PDDA). The size of the PDDA–Pt nanoparticle colloids is in the range of 2–4 nm, depending on the PDDA to Pt ratio in the solution. The PDDA–Pt nanoparticles can be self-assembled to the sulfonic acid group, SO_3^- , at the Nafion membrane surface by the electrostatic interaction, forming a self-assembled monolayer (SAM). The study shows that such SAM reduced the methanol crossover and enhanced the power output of direct methanol fuel cells (DMFC) by as much as 34% as compared to the cell based on an un-modified Nafion membrane. In addition, PDDA–Pt nanoparticles synthesized with low PDDA/Pt ratios show considerable catalytic activity for the methanol oxidation reaction (MOR) in comparison to a commercial Pt/C catalyst. However, the electrocatalytic activity of PDDA–Pt nanoparticles decreased significantly with the increase in the PDDA/Pt molar ratio, indicating that the excess PDDA inhibits the MOR.

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1. Introduction

One of the factors limiting the practical development of direct methanol fuel cells (DMFCs) is the significant methanol crossover from anode to cathode through the polymer membrane. Perfluorosulfonic polymers such as Nafion developed by DuPont are the most common electrolyte membranes in polymer electrolyte and direct methanol fuel cells due to the good thermal and chemical stability and high proton conductivity. However, methanol readily migrates from the anode, through the Nafion membrane, to the cathode, causing the significant losses of fuel, reducing open circuit potential by as much as 0.15–0.2 V due to the existence of mixed potentials and poisoning the electrocatalysts on the cathode side.

There is a continuing effort in the modification of Nafion-based membranes in addition to the development of alternative electrolyte membranes with aims to achieve low methanol

permeability and high conductivity [1,2]. One of the most common approaches is to sandwich or deposit an additional methanol-blocking thin film to Nafion membrane. Pu et al. showed that using Pd thin films sandwiched between Nafion membranes reduced the methanol crossover [3]. Unfortunately, the Pd film increased the overall cell resistance. Deposition of Pd nanoparticles through ion exchange and chemical reduction was also shown to decrease the methanol crossover [4]. The dispersed Pd particles through ion-exchange and reduction alter the microstructure of the Nafion membrane, reducing cell performance and stability. Kim et al. [5] reported the performance of the Nafion/PVdF/Nafion laminated membrane for DMFC. The middle PVdF layer blocks the methanol crossover but at the same time reduces the conductivity significantly due to the non-conducting properties of PVdF. Casting non-conducting polymers such polyvinyl alcohol (PVA) onto Nafion membrane can also reduce the methanol crossover [6]. However, casting an additional film causes the significant decrease of the proton conductivity of the Nafion membrane, similar to that of the sandwiched Nafion/PVdF/Nafion approach.

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Self-assembly is a well-known technique in the preparation of well-ordered nano-structures [7]. We have shown recently that Pt nanoparticles can be prepared by alcoholic reduction in the presence of a polycation, poly(diallyldimethylammonium chloride) (PDDA). Due to the fact that PDDA is a positively charged ionic polymer, the PDDA-stabilized Pt nanoparticles can be self-assembled onto the Nafion electrolyte membrane, forming an electrochemically active monolayer on the Nafion membrane surface [8,9]. Preliminary results showed that PDDA-stabilized Pt nanoparticles can also block the methanol crossover through the Nafion electrolyte membrane and enhance the performance of the direct methanol fuel cells [10].

On the other hand, polymer-stabilized metal nanoparticles or nanoclusters often act as an excellent homogeneous catalyst and show interesting catalytic properties [11–13]. They not only provide access to a large number of catalytic sites but also offer the possibility of synergetic effect between the polymer matrix and the metal nanoparticles. For DMFC applications, the polymer matrix might provide an efficient pathway for electron and preferably for protonic species. Niu et al. studied the electrocatalytic behavior of Pt-modified polyaniline electrode and found that Pt dispersed in polyaniline film is a better catalyst than bulk Pt for methanol oxidation [14]. Bensebaa et al. synthesized polypyrrol di(2-ethylhexyl) sulfosuccinate (PPyDEHS) stabilized PtRu catalysts for DMFC [15]. The activity of the polymer-embedded PtRu catalyst for the methanol oxidation is not particularly high probably due to the high concentration of polymer or the presence of a sulfur-containing dopant. Choi et al. showed that PtRu nanoparticles dispersed in poly(*N*-vinyl carbazole) and poly(9-(4-vinylphenyl)carbazole) have some potential for DMFC applications [16]. However, the activity is lower than that of a carbon-supported catalyst probably due to low conductivity of these two polymers.

PDDA is not an electronic conducting polymer but is a strong ionic polymer [17]. The strong ionic polymer matrix could influence the electrocatalytic properties of Pt-based nanoparticles. This motivated us to investigate the feasibility of incorporating ionic polymer support into Pt-based catalyst for DMFC applications. In this paper, we will report in detail the synthesis of PDDA-stabilized Pt nanoparticles via alcoholic reduction with different molar ratios of PDDA to Pt and the electrocatalytic activity of the PDDA-stabilized or PDDA-embedded Pt nanoparticles for the methanol oxidation reaction. Finally the effect of the self-assembled monolayer by the PDDA–Pt nanoparticles on the methanol crossover and the performance of DMFC are presented.

2. Experimental

2.1. Synthesis of PDDA–Pt nanoparticles

PDDA-stabilized Pt nanoparticles were prepared from poly(diallyldimethylammonium chloride) (PDDA, 35 wt.% in water, MW = 5000–20,000, Aldrich), H₂PtCl₆ (99.8%, Sigma) and absolute ethanol (99.8%, Sigma). Deionized water (Millipore Milli-Q, 18.2 MΩ at 25 °C) was used in the experiments. The molecular structure of PDDA is shown in Fig. 1.

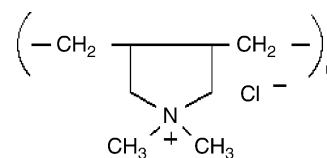


Fig. 1. Molecular structure of PDDA.

Pt nanoparticle colloidal solutions were prepared by alcohol reduction of platinum ions in ethanol/water (4:6, v:v) and the PDDA/Pt molar ratio was varied from 1:1 to 15:1. An appropriate amount of H₂PtCl₆ solutions and ethanol were added sequentially to the PDDA solutions under intensive stirring. The mixture was then transferred into a three-neck flask and brought to reflux at 82 °C in an oil bath. The pH of the solution was adjusted to 8.5 by adding NaOH. The color of the solution changed from yellowish to dark brown, indicating the reduction of Pt ions and the formation of metallic Pt nanoparticles.

2.2. Characterization of PDDA–Pt nanoparticles

The formation of PDDA–Pt nanoparticles was monitored using UV–vis spectroscopy (HP 8350) as a function of reflux time. PDDA–Pt nanoparticles were examined by transmission electronic microscope (TEM, JEOL 2010) using acceleration voltage of 200 kV. TEM samples were prepared by placing a drop of the PDDA–Pt nanoparticle colloidal solution on a Cu grid coated with a carbon film, followed by drying under ambient conditions. To observe the distribution of PDDA–Pt nanoparticles self-assembled on the surface of Nafion membrane, TEM sample was prepared as follows: copper grid with carbon film was first cast with a thin Nafion film by floating on the surface of Nafion solution for 5 min, and dried at room temperature. Then, the Nafion film-cast copper grid was floated on the surface of a PDDA–Pt colloidal solution, with the Nafion film side facing the solution, for 1 h. After the self-assembly process, the copper grid was rinsed thoroughly with deionized water, and dried at room temperature. PDDA–Pt nanoparticles were also collected and characterized by XRD (Philips PW1830) using Cu Kα radiation.

The electrochemical activity of the PDDA-stabilized Pt nanoparticles for the methanol oxidation reaction (MOR) was characterized using a glassy carbon disc electrode in a N₂-saturated 1 M H₂SO₄ + 2 M CH₃OH solution at 25 °C. Tests were conducted in static conditions. The diameter of the glassy carbon electrode was 3 mm. The disc electrode was pre-coated with a carbon ink mixed with 30% Nafion and dried at 80 °C for 30 min. Then, PDDA–Pt solution was placed on the surface of the disc electrode using a microsyringe. The Pt loading was kept to be 5.6 and 56 μg cm⁻². For comparison, the electrocatalytic activity of a Pt/C catalyst (20 wt.%, E-TEK) with the same Pt loading was also measured under the same experimental conditions. Ag/AgCl electrode (0.207 V versus NHE) was used as the reference electrode and Pt foil as the counter electrode. The potential was scanned from 1.0 to 0.1 V (versus NHE) at a scan rate of 5 mV s⁻¹. All potentials in the text are referred to the NHE reference electrode.

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