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Electrochimica Acta 52 (2006) 1213–1220
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Synthesis and characterization of Nafion-stabilized Pt nanoparticles for polymer electrolyte fuel cells

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Received 16 April 2006; received in revised form 18 June 2006; accepted 17 July 2006
Available online 22 August 2006

Abstract

Platinum nanoparticles are synthesized by alcohol reduction method using Nafion as a stabilizer under various conditions such as the Nafion/Pt molar ratio and reflux temperature. Nafion–Pt nanoparticles are characterized by agglomeration and the particle size is typically in the range of 2–4 nm. The electrocatalytic activity of Nafion–Pt nanoparticles for polymer electrolyte and direct methanol fuel cells (PEFCs and DMFCs) is investigated in comparison to that of unsupported Pt black and carbon-supported Pt/C electrocatalysts. Nafion–Pt nanoparticles prepared with low Nafion/Pt ratios show higher and/or comparable activities towards O_2 reduction reaction in the absence and presence of methanol in comparison to that of Pt black and Pt/C electrocatalysts. In contrast, the electrocatalytic activity of the Nafion–Pt nanoparticles for the methanol oxidation reaction is very low. The results indicate that Pt nanoparticles embedded in Nafion polyelectrolyte are potential methanol tolerant electrocatalysts for the O_2 reduction reaction in DMFCs.

Keywords: Polymer electrolyte fuel cells; Nafion–Pt nanoparticle; Methanol tolerant catalysts; Polyelectrolyte; Oxygen reduction

1. Introduction

Polymer electrolyte and direct methanol fuel cells (PEFCs and DMFCs) have been attracting enormous research interest as power sources for vehicles and portable electronic devices [1,2]. The performance of a PEFC or DMFC is critically dependent on the electrocatalytic activity of the precious metal catalyst such as platinum and platinum alloys supported on high surface carbon [3]. Pt nanoparticles dispersed on high surface area and electrical conducting supports such as carbon powder, carbon nanotubes and fullerenes are shown to have high elelctrocatalyst activity and the Pt loading has been reduced significantly with improved Pt utilization [4–10].

When the nanosized catalyst is dispersed in high surface carbon black or nanotubes, part of the active sites may be inaccessible to the oxygen reduction or fuel oxidation reactions, thus reducing the utilization of Pt and Pt alloy electrocatalysts. One strategy to improve the Pt utilization is to add or impregnate the protonic conducting polymers such as Nafion into the Pt/C catalyst layer since the ionic and electronic contacts are essential components for the high Pt catalyst utilization [11–14]. Nafion impregnation extends the three phase boundary where electronic collection, ionic collection and reactant gas meet, resulting in the increase of the catalyst utilization. The content and distribution of Nafion in the catalyst layer play an important role on the structure and electrochemical performance of a fuel cell [15–19]. As shown by Uchida et al., the contact between the ionic conducting ionomer and Pt catalyst is related to the particle size and distribution of Pt nanoparticles [20,21]. Thus, the preparation of ionic conducting ionomer impregnated Pt catalysts supported on carbon can also significantly affect the performance and catalytic activity of the catalysts.

Pt and Pt alloy nanoparticles dispersed in polymer matrix show interesting catalytic properties [22–26]. In particular the Pt and Pt alloy nanoparticles embedded in conducting polymer matrix could offer the possibility of a large number of active sites for the electrochemical and catalytic reactions in fuel cells. Sarma et al. prepared Nafion-stabilized PtRu/C catalysts and showed higher catalytic activity than a commercial E-TEK PtRu/C catalyst [27]. A recent report on the Pt nanoparticles embedded in poly(diallyldimethylammonium chloride) (PDDA) show considerable catalytic activity for the methanol

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doi:10.1016/j.electacta.2006.07.027

oxidation reaction in comparison to a commercial Pt/C catalyst [28]. PDDA is a positively charged polymer. This shows that polyelectrolyte may promote the electrocatalytic activity of Pt nanoparticles under certain conditions. This motivated us to investigate the electrocatalytic activity of Nafion-stabilized Pt nanoparticles because Nafion is a negatively charged polymer and is also a good proton conductor. In this report, Pt nanoparticles without carbon support were prepared by alcohol reduction method using Nafion as a stabilizer. The results indicate that Nafion–Pt nanoparticles show considerable activity for the oxygen reduction but very low activity for the methanol oxidation reaction in particularly in comparison to that of a conventional unsupported Pt black electrocatalyst. Nafion stabilizer significantly modifies the electrocatalytic activity of Pt nanoparticles for fuel cells.

2. Experimental

2.1. *Synthesis of Nafion–Pt nanoparticles*

Nafion-stabilized Pt nanoparticles were prepared from Nafion (5 wt.%, DuPont), H_2PtCl_6 (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.

Nafion–Pt nanoparticle colloidal solutions were prepared by alcohol reduction of platinum ions in ethanol/water (4/6, v/v) using Nafion as a stabilizer. Five milliliter H_2PtCl_6 (20 mM Pt) solutions and 40 mL ethanol were added sequentially in a Nafion solution under intensive stirring. The total volume was kept at 55 mL. The mixture was then transferred into a three-neck flask and brought to reflux in an oil bath. The reflux temperature was controlled at 82 °C and the pH of the solution was adjusted to 8.5 by adding NaOH. The effect of Nafion/Pt molar ratio was studied in the range of 1:2–8:1. The effect of the reaction temperature was studied at 82, 75 and 65 °C with Nafion/Pt ratio of 2:1.

2.2. *Characterization*

The formation of Nafion–Pt nanoparticles was monitored using UV–vis spectroscopy (HP 8350) as a function of reflux time. Pt nanoparticles were examined by transmission electronic microscope (TEM, JEOL 2010) under accelerating voltage of 200 kV. TEM sample was obtained by immersing copper grid coated with carbon film in the colloid solution and was allowed to dry at room temperature. X-ray diffraction (XRD) patterns of the Nafion–Pt nanoparticles were obtained on a diffractometer (Philips PW1830) using Cu Kα radiation.

Rotating disc electrode (RDE) technique was used to evaluate the electrocatalytic activity of Pt nanoparticles using an Autolab potentiostat (PGSTAT30, The Netherlands). The diameter of the glassy carbon electrode (GCE) was 3 mm. The GCE was pre-coated with a carbon ink mixed with 30% Nafion and dried at 80 °C for 30 min. A certain volume of Pt nanoparticle solution was placed on a GCE using a microsyringe. The Pt loading was 5.6 $\mu g\,cm^{-2}$. The polarization curves for the oxygen reduction were measured in an O_2-saturated 1 M H_2SO_4 solution with and without 0.5 M CH_3OH under a rotating rate of 3000 rpm. The oxygen reduction was also studied in an O_2-saturated 1 M H_2SO_4 solution under various rotating rates from 100 to 5000 rpm. Ag/AgCl (0.207 V versus NHE) electrode and Pt foil electrode were used as the reference and counter electrodes, respectively. The polarization was conducted by scanning the potential from 1.0 to 0.1 V (versus NHE) at a scan rate of 5 $mV\,s^{-1}$. The activity of the Nafion–Pt nanoparticles for the methanol oxidation was measured in a N_2-saturated 1 M H_2SO_4 + 2 M CH_3OH by scanning the potential between 0.2 and 1.2 V (versus NHE) at a scan rate of 100 $mV\,s^{-1}$. The Pt loading was 56 $\mu g\,cm^{-2}$. The GCE was kept static. All potentials in the text are referred to the NHE reference electrode. For comparison, the electrocatalytic activity of a Pt black (E-TEK), Pt/C catalyst (20 wt.%, E-TEK) and poly(diallyldimethylammonium chloride)–Pt nanopparticles with the same Pt loading was also measured under the same experimental conditions. The synthesis and characterization of the PDDA–Pt nanoparticles were given in ref. [28].

3. Results and discussion

3.1. *Synthesis of the Nafion–Pt nanoparticles*

Fig. 1 shows the UV–vis spectra of solutions containing 10^{-3} M Nafion, 10^{-4} M H_2PtCl_6 and 10^{-4} M mixture of Nafion:H_2PtCl_6 = 2:1. For pure Nafion solution, there was a plateau from 200 to 245 nm with a maximum absorption at 235 nm. The absorbance at the wavelength of smaller than 200 nm may be due to CF_2–CF_2 group [29]. For H_2PtCl_6 solution, there were two absorbance peaks at 201 and 260 nm, characteristic absorbance of platinum complex of $PtCl_4{}^{2-}$ and $PtCl_6{}^{2-}$, respectively [30,31]. On the other hand, the absorbance peaks at 201 and 260 nm shifted slightly for the mixture of H_2PtCl_6 and Nafion solution. The small shifting of the absorbance peaks indicates the coordination of S or O from Nafion to Pt^{2+} and Pt^{4+}, which may provide the stabilizing effect of Nafion to Pt nanoparticles [32].

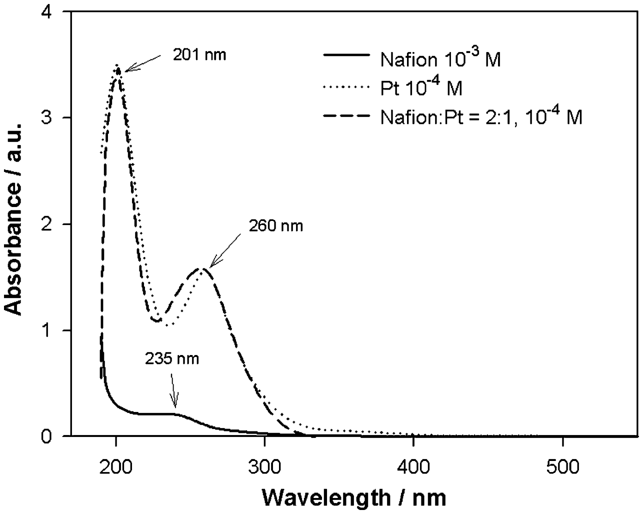

Fig. 1. UV–vis absorption spectra of Nafion (10^{-3} M), H_2PtCl_6 (10^{-4} M) and Nafion:H_2PtCl_6 = 2:1 mixture (10^{-4} M) solutions.