

Short communication

Synthesis of PDDA–Pt nanoparticles for the self-assembly of electrode/Nafion membrane interface of polymer electrolyte fuel cells

Zengcai Liu, San Ping Jiang*

School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore

Available online 30 June 2006

Abstract

PDDA–Pt nanoparticles are synthesized by the alcoholic reduction of the Pt ions in ethanol/water system. The PDDA–Pt nanoparticle size is in the range of 2–4 nm. The electrocatalytic activity of the self-assembled PDDA–Pt nanoparticle/Nafion membrane interface depends strongly on the morphology and agglomeration of the PDDA–Pt nanoparticles, which in turn are related to the PDDA/Pt molar ratio in the ethanol/water solution. The highest activity is obtained on the self-assembled membrane interface with the PDDA–Pt nanoparticles prepared with PDDA:Pt = 1:1. The present study shows that appropriate agglomeration of the PDDA–Pt nanoparticles is beneficial to the electrocatalytic activity of the self-assembled Pt nanoparticle/Nafion membrane interface.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fuel cell; Electrocatalytic activity; Membrane

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been considered as the most promising power sources for portable devices and electric vehicles due to their high power density and low operation temperatures (70–90 °C). In order to make the PEFCs commercially viable, there is an urgent need to increase the catalyst utilization and to improve the performance with reduced loading of precious noble metal catalysts such as Pt. Various efforts and significant progresses have been made to reduce the Pt loading with the increased catalyst utilization [1–5]. Addition of a proton conductor, such as Nafion, into the catalyst layer is known to increase the Pt utilization significantly [6,7]. Due to the morphology, low gas permeability and poor electronic conductivity of Nafion, there is a limit to the Nafion quantity that can be added before adversely affecting cell performance [2,5,8,9]. Typical methods of manufacturing electrode–membrane assembly for PEFCs involve painting, spraying, or printing of catalyst inks that contain a matrix of electrolyte and carbon-supported catalysts. However, the methods are limited on the effective distribution of Pt catalysts in the three-phase interface region of

catalysts, carbon and electrolyte that allows effective proton, electron and gas transport to and from the catalyst sites [10].

We have shown recently that charged Pt nanoparticles can be self-assembled to the surface of the Nafion electrolyte membrane, forming a Pt catalyst monolayer [11,12]. The initial results show that the self-assembled Pt nanoparticle/Nafion electrolyte interface has high electrocatalytic activity for the electrode processes in PEFCs. In this paper, the synthesis of charged PDDA–Pt nanoparticles via alcohol reduction with various PDDA/Pt molar ratios will be reported. The activity of the self-assembled Pt nanoparticle/Nafion electrolyte interface is characterized.

2. Experimental procedures

Positively charged PDDA–Pt nanoparticles were prepared from poly(diallyldimethylammonium chloride) (PDDA, $M_w = 5000–20,000$, Aldrich), H_2PtCl_6 (99.8%, Sigma), absolute ethanol (99.8%, Sigma) and deionized water (Millipore Milli-Q, 18.2 M Ω at 25 °C). PDDA is a polycation. Pt nanoparticle colloidal solutions were prepared by alcohol reduction of platinum ions in ethanol/water (volume ratio: 4/6) with various PDDA/Pt molar ratios. Reflux was carried out at 82 °C and the pH of the solution was 8.5 by adding NaOH. The color of

* Corresponding author. Tel.: +65 6790 5010; fax: +65 6791 1859.
E-mail address: mspjjiang@ntu.edu.sg (S.P. Jiang).

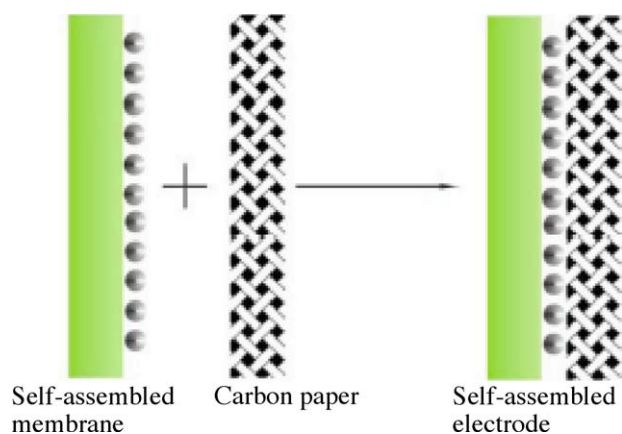


Fig. 1. Schematic diagram of the self-assembled PDDA–Pt nanoparticle/Nafion membrane interface.

the solution changed from yellow to dark brown, indicating the formation of platinum metallic nanoparticles [11,12]. 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) under accelerating voltage of 200 kV.

To prepare the self-assembled Pt nanoparticle/Nafion membrane interface, the pre-treated Nafion 1135 membrane was allowed to float on the surface of the PDDA–Pt colloid solution for 24 h. The self-assembly process would occur between the positively charged PDDA–Pt nanoparticles and the negatively charged sulfonic acid groups, SO_3^- , on the surface of Nafion membrane by the electrostatic interaction. Then the membrane was rinsed with deionized water. As-prepared membrane was hotpressed with one piece of carbon paper as gas diffusion layer at 140°C under 4 MPa for 90 s. Fig. 1 shows the schematic diagram of the membrane electrode with the self-assembled PDDA–Pt nanoparticle/Nafion membrane interface.

The electrochemical characterization of self-assembled Pt nanoparticle/Nafion membrane interface was conducted in a half-cell fixture using an Autolab potentiostat [12]. One molar H_2SO_4 was used as electrolyte. Nafion N-1135 membrane with the self-assembled PDDA–Pt nanoparticles was in contact with the electrolyte. The other compartment was fed with oxygen or nitrogen. Saturated calomel electrode (SCE, 0.241 V versus SHE) was served as reference electrode and platinum foil as the counter electrode. Polarization curves were obtained in 1 M H_2SO_4 at 25°C by scanning the potential from open circuit to 0.1 V versus SHE. Cyclic voltammetry was also carried out in 1 M H_2SO_4 purged with nitrogen. Impedance responses were obtained under dc bias with signal amplitude of 10 mV in the frequency range of 100 kHz to 0.01 Hz. The potentials were reported versus SHE.

3. Results and discussion

Fig. 2 shows UV–vis spectral change during the reduction of Pt ions in ethanol/water (4/6, v/v) with PDDA:Pt=5:1 as

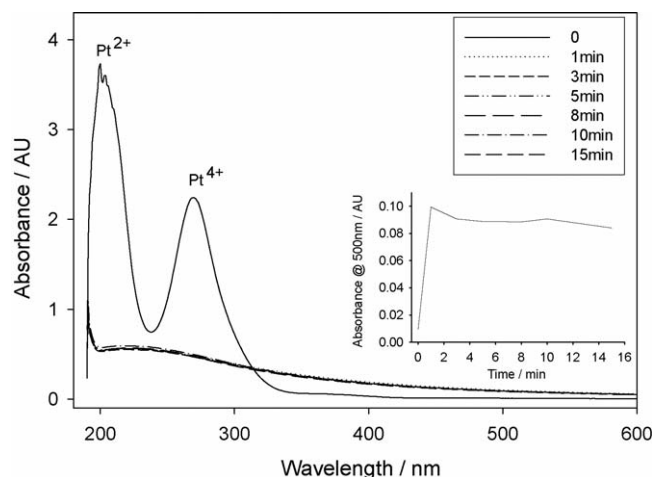


Fig. 2. UV–vis spectra during the alcoholic reduction of Pt ions.

a function of reflux time at 82°C . Before reflux, there are two absorbance peaks at 210 and 260 nm, which are the characteristic absorbance of PtCl_4^{2-} and PtCl_6^{2-} ions, respectively [13,14]. The color of the solution changed suddenly from yellow to dark brown after a very short induction period of less than 1 min. The reduction of PtCl_6^{2-} ions is also indicated by the decrease of the absorbance band at 260 nm. The Pt(0) absorbance was not observed, which was monitored at 500 nm (see inset graph) [15]. The intensity of Pt(0) absorbance at 500 nm increased very rapidly after the induction period, indicating that the reduction of PtCl_6^{2-} ions by ethanol is almost instantaneous.

Fig. 3 shows TEM images of PDDA–Pt nanoparticles prepared with various PDDA to Pt ratio. In the case of the PDDA:Pt=1:1, the formation of agglomeration is clearly observed (Fig. 3a), indicating that the concentration of PDDA is not high enough to prevent the agglomeration of Pt nanoparticles. As the concentration of PDDA increases, the dispersion of the Pt nanoparticles increases substantially. At molar ratio of PDDA:Pt=3:1, there is no agglomeration between Pt nanoparticles (Fig. 3b). This indicates that the separation and dispersion of Pt nanoparticles are critically related to the molar ratio of PDDA and Pt. The Pt particle size was estimated to be in the range of 2–4 nm.

Fig. 4 shows cyclic voltammograms of the membrane electrodes prepared by the self-assembly of PDDA–Pt nanoparticles in 1 M H_2SO_4 saturated with N_2 at 25°C . The hydrogen desorption peak around 0–0.4 V was not observed. The disappearance of the hydrogen desorption peak for the self-assembled PDDA–Pt nanoparticle/Nafion membrane interfaces may be due to the very low platinum loading (less than $2\ \mu\text{g cm}^{-2}$) [12]. However, it was observed that hydrogen evolution current decreased with the increase of molar ratio of PDDA to Pt and highest hydrogen evolution current was observed for the self-assembled interface prepared by the PDDA–Pt nanoparticles with PDDA:Pt=1:1. As shown in Fig. 3, the morphology of the PDDA–Pt nanoparticles prepared with PDDA:Pt=1:1 is characterized by the agglomeration.

Fig. 5 shows the polarization behavior of self-assembled Pt nanoparticle/Nafion membrane interfaces prepared with

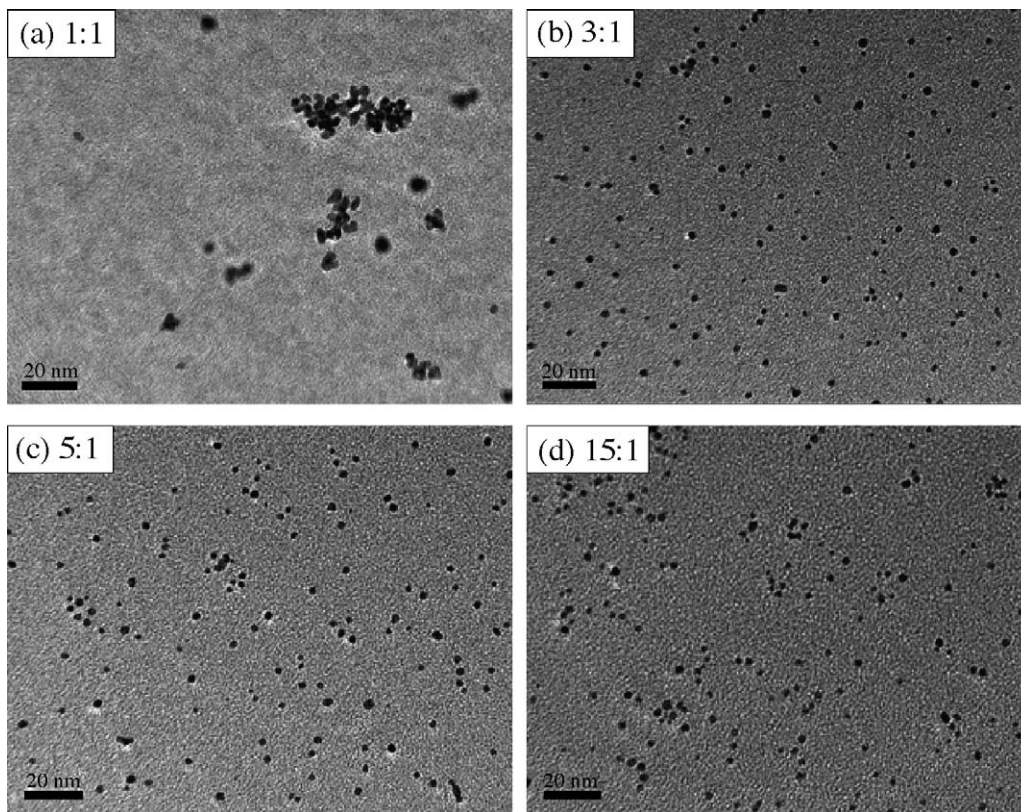


Fig. 3. TEM micrographs of PDDA–Pt nanoparticles prepared with various PDDA/Pt ratios.

different molar ratios of PDDA to Pt. Best performance was obtained for the membrane interface self-assembled in the PDDA–Pt colloid solution prepared with PDDA:Pt = 1:1. At 0.4 V, the polarization current was 3.8 mA cm^{-2} . When the PDDA to Pt molar ratio increased to 3:1, the current density decreased to 1 mA cm^{-2} , a reduction in the current density by 74% as compared to the self-assembled interface

with PDDA:Pt = 1:1. However, with the further increase in the PDDA/Pt ratio, the change in the polarization performance is very small.

Fig. 6 shows the impedance curves for the O_2 reduction on the self-assembled PDDA–Pt nanoparticle/Nafion membrane interfaces prepared with different PDDA/Pt molar ratios. The electrode polarization resistance increased significantly with the

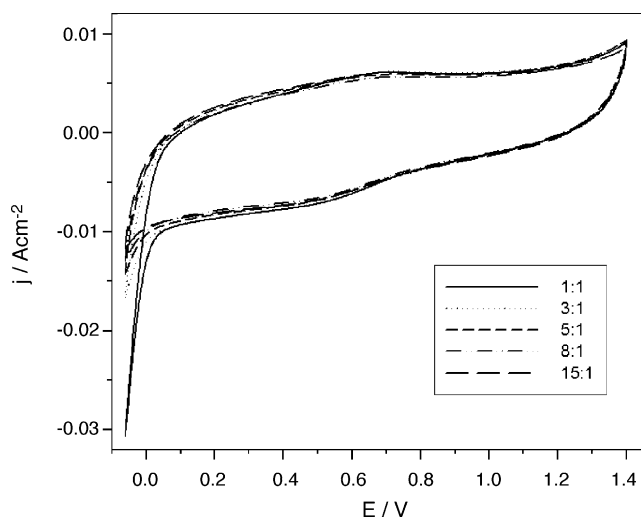


Fig. 4. Cyclic voltammograms of the membrane electrodes prepared by the self-assembly of PDDA–Pt nanoparticles with various PDDA to Pt ratios in 1 M H_2SO_4 saturated with N_2 at 25°C . The scanning rate was 100 mV s^{-1} .

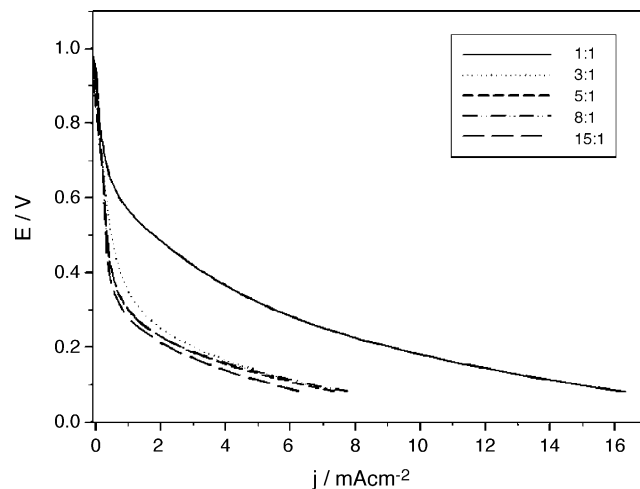


Fig. 5. Polarization curves of self-assembled PDDA–Pt nanoparticles membrane electrodes prepared in the presence of various molar ratios of PDDA to Pt. The curves were measured in 1 M H_2SO_4 saturated with O_2 at 25°C under scanning rate of 5 mV s^{-1} .

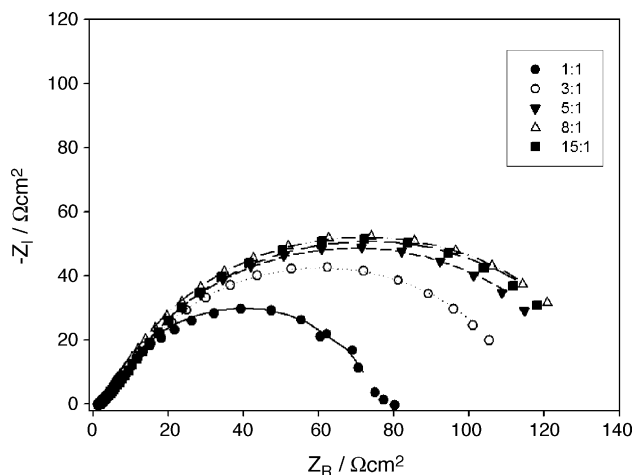


Fig. 6. Impedance behavior for the O_2 reduction on the self-assembled PDDA–Pt nanoparticle/Nafion membrane interface prepared with various PDDA/Pt molar ratios. The curves were measured in 1 M H_2SO_4 saturated with O_2 under dc bias of 0.6 V.

increase of the PDDA to Pt molar ratio. With the PDDA/Pt molar ratio higher than 3:1, the change in the impedance arcs is relatively small. The impedance responses for the O_2 reduction in H_2SO_4 is characterized by an almost perfect semicircle and thus was fitted using a simple $R(R_E C)$ circuit. The fitting between the experimental data and fitted one is quite reasonable. Table 1 summarizes the fitting results. The electrode polarization resistance (R_E) for the O_2 reduction at the Pt nanoparticle/Nafion membrane interface prepared with PDDA:Pt = 1:1 was $70 \Omega \text{ cm}^2$, significantly lower than those prepared with higher PDDA/Pt ratios. This is consistent with that of the cyclic voltammetry and polarization results.

The self-assembled Pt nanoparticle/Nafion membrane interface shows significant electrocatalytic activity for the O_2 reduction reaction and the electrocatalytic activity of the self-assembled interface depends strongly on the morphology of the PDDA–Pt nanoparticles assembled. This in turn is related to the PDDA/Pt ratio during the alcoholic reduction of the Pt ions. As shown in this study, the self-assembled Pt nanoparticle/Nafion membrane interface prepared with PDDA/Pt molar ratio of 1:1 shows the low electrode polarization resistance and high polarization performance. On the other hand, the PDDA–Pt nanoparticles prepared with the PDDA/Pt molar ratio of 1:1 are characterized by the distinct agglomeration of nanoparticles while with the increase of the molar ratios, the agglomeration decreases significantly (Fig. 3). This indicates that appropriate

Table 1
Fitted impedance results for the O_2 reduction on Pt nanoparticle/Nafion membrane interface prepared with various PDDA/Pt molar ratios under dc bias of 0.6 V at 25 °C

	Molar ratio				
	1:1	3:1	5:1	8:1	15:1
$R_E (\Omega \text{ cm}^2)$	70	110	129	135	135
$C (\text{F cm}^{-2})$	0.0183	0.0147	0.0140	0.0142	0.0135

agglomeration of PDDA–Pt nanoparticles can be beneficial for the electrocatalytic activity of the self-assembled Pt nanoparticle/Nafion membrane interface. As the number of the sulfonic acid groups on the Nafion membrane surface are related to the molecular weight of the polymer and would be limited, appropriate agglomeration could increase the loading and coverage of the Pt nanoparticles on the Nafion membrane surface. This probably explains the high performance and activity of the Pt nanoparticle/Nafion membrane interface self-assembled from the agglomerated PDDA–Pt nanoparticles prepared with PDDA/Pt ratio of 1:1. With the increase of the molar ratio, well-dispersed and distributed PDDA–Pt nanoparticles were obtained. This demonstrates that dispersion of PDDA–Pt nanoparticles can be conveniently controlled by the PDDA to Pt molar ratio.

4. Conclusion

Positively charged PDDA–Pt nanoparticles can be self-assembled onto the surface of Nafion membrane to form electrocatalytic active membrane interface. The activity of the self-assembled PDDA–Pt nanoparticle/Nafion membrane interface depends on the morphology and agglomeration of the PDDA–Pt nanoparticles, which in turn are related to the molar ratio of PDDA to Pt during the reduction of the Pt ions in the ethanol/water solution. The highest activity of the self-assembled membrane interface was obtained on agglomerated PDDA–Pt nanoparticles which was prepared with PDDA to Pt molar ratio of 1:1. Increase of the molar ratio increases the dispersion and distribution of the PDDA–Pt nanoparticles, but decreases the electrochemical activity of the self-assembled interface. This shows that appropriate agglomeration of the PDDA–Pt nanoparticles is beneficial to the self-assembled Pt nanoparticle/Nafion membrane interface.

References

- [1] M. Uchida, Y. Fukuoka, Y. Sugawara, H. Ohara, A. Ohta, J. Electrochem. Soc. 145 (1998) 3708.
- [2] X. Cheng, B. Yi, M. Han, J. Zhang, Y. Qian, J. Yu, J. Power Sources 79 (1999) 75.
- [3] T.R. Ralph, G.A. Hards, J.E. Keating, S.A. Campbell, D.P. Wilkinson, M. Davis, J. St-Pierre, M.C. Johnson, J. Electrochem. Soc. 144 (1997) 3845.
- [4] Z. Qi, A. Kaufman, J. Power Sources 113 (2003) 37.
- [5] S.J. Lee, S. Mukerjee, J. McBreen, Y.W. Rho, Y.T. Kho, T.H. Lee, Electrochim. Acta 43 (1998) 3693.
- [6] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
- [7] M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 139 (1992) L28.
- [8] J.M. Soon, S.Y. Cha, W.M. Lee, J. Power Sources 94 (2001) 78.
- [9] G. Sasikumar, J.W. Ihm, H. Ryu, J. Power Sources 132 (2004) 11.
- [10] S.D. Thompson, L.R. Jordan, M. Forsyth, Electrochim. Acta 46 (2001) 1657.
- [11] M. Pan, H.L. Tang, S.P. Jiang, Z. Liu, Electrochem. Commun. 7 (2005) 119.
- [12] M. Pan, H. Tang, S.P. Jiang, Z. Liu, J. Electrochem. Soc. 152 (2005) A1081.
- [13] J.F. Rivadulla, M.C. Vergara, M.C. Blanco, M.A. López-Quintela, J. Rivas, J. Phys. Chem. B 101 (1997) 8997.
- [14] A. Henglein, B.G. Ershov, M. Malow, J. Phys. Chem. 99 (1995) 14129.
- [15] C.W. Chen, T. Takezako, K. Yamamoto, T. Serizawa, M. Akashi, Colloids Surf. A: Physicochem. Eng. Aspects 169 (2000) 107.