Enhanced life of proton exchange membrane fuel cell catalysts using perfluorosulfonic acid stabilized carbon support

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ABSTRACT

We report a new and simple solution to increase life of Pt/C catalysts using the proton-conducting polymer (perfluorosulfonic acid, PFSA) stabilized carbon support (denoted these catalysts as Pt/NFC catalysts) as compared to conventional Pt/C catalysts commonly used in PEM fuel cells. A high catalytic activity of the catalyst is observed by both CV (cyclic voltammetry) and ORR (oxygen reduction reaction) measurements. Especially, our own catalysts have a 60% better life as compared to Pt/C under electrochemically accelerated durability test conditions. The loss rate of electrochemical active area (ECA) for Pt/NFC catalysts is only $0.007\,m^2\,g^{-1}\,cycle^{-1}$, compared to a value of $0.011\,m^2\,g^{-1}\,cycle^{-1}$ for Pt/C.

1. Introduction

Proton exchange membrane (PEM) fuel cells have been considered to be one of the most promising candidates for power sources in transportation and stationary applications [1,2]. However, the high price and low life of Pt-based catalysts become a heavy concern for PEM fuel cells [3,4]. The durability of Pt-based catalysts in PEM fuel cells strongly depends on the property of metal particle, the metal–support interaction and the durability of support materials [5,6]. Pt nano-particles on carbon supports will migrate once the interaction between Pt particle and carbon is impaired during fuel cell operation. Thus the Pt particles will detach from carbon supports and agglomerate [7], resulting in the decrease of Pt catalyst activity. Colon-Mercado and Branko [8] have evaluated the catalyst durability using an accelerated durability test (ADT) and believed that the decay in performance of catalysts should be partly attributed to Pt particle migration. And Gu et al. [9] observed Pt nanoparticle migration/coalescence during aging procedure using atomic force microscopy (AFM). Siroma et al. [10] further found that this migration decreases the electrochemical surface area of Pt catalysts.

The porous carbon black (e.g. Vulcan XC-72) has been widely used as the support for Pt-based catalysts in PEM fuel cells because of low cost and high availability. But the durability of Pt/C catalysts needs further be enhanced to meet the application of PEM fuel cells. Recently, different carbon supports have been developed for increasing catalyst performance through surface modification by phenyl sulfonic acid [11], 1-aminopyrene [12] and sulfonated polymers [13–15]. In our previous studies, we used the Nafion as a Pt nanoparticle stabilizer and improved the Pt/C catalyst life [16].

Here we demonstrate a new and simple solution to increase life of Pt/C catalysts using the proton-conducting polymer stabilized carbon support as shown in Fig. 1A. At first, the proton-conducting polymer stabilized surface of carbon may not only enhance the interactions between Pt nanoparticles and carbon support, but also slow down the Pt nanoparticles migration and inhibit the coalescence of Pt nanoparticles in comparison with the Pt catalysts supported on the carbon support without treatment (Fig. 1B). In addition, proton-conducting polymer on the surface of the carbon support will be beneficial to increase the three-phase reaction boundary in electrodes to enhance the performance of fuel cells. The chosen polymer, perfluorosulfonic acid (PFSA) Nafion®, is conventionally impregnated into catalyst layers of PEM fuel cells in a form of recast film to improve the activity of Pt catalyst by both acting as a binder and increasing the proton conductivity [17].

2. Experimental

The 500 mg Valcan XC-72 carbon black (Cabot Corp., BET = $250\,m^2\,g^{-1}$) was suspended in 500 ml ethanol solution

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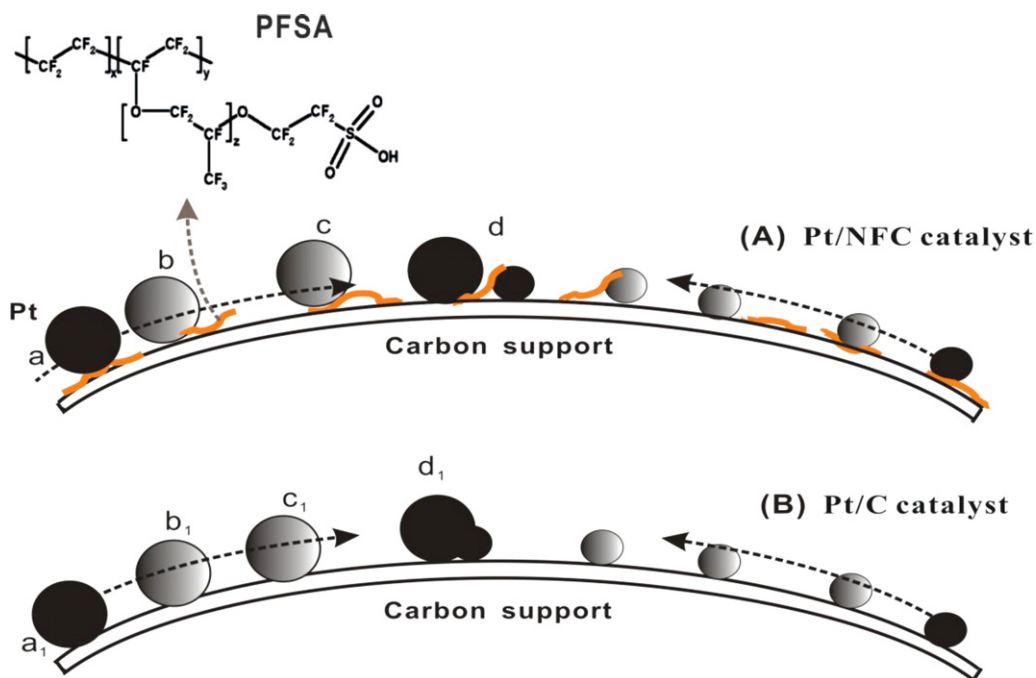E-mail addresses: msc@whut.edu.cn, mushichun@gmail.com (S. Mu).

Fig. 1. Schematic diagram of Pt/ NFC catalysts (A) and Pt/C catalysts (B).

and ultrasonicated for 30 min. The dispersed carbon solution and 1.2 ml Nafion® (5 wt%, Dupont Co.) were mixed and then agitated at room temperature for 5 h. After filtration, washing, and drying at 373 K in a vacuum oven, the Nafion stabilized carbon (denoted as NFC) was prepared and the weight ratio of carbon to Nafion is about to 9:1. The Pt/NFC catalysts were prepared as follows. $H_2PtCl_6 \cdot 6H_2O$ was well mixed with ethylene glycol in an ultrasonic bath. Then NFC was added into the slurry and stirred for 5 h. After the pH of the solution was adjusted to more than 10 by adding $1.0 \, mol \, L^{-1}$ NaOH/EG, the well-dispersed slurry was obtained followed by stirring and ultrasonication for 20 min. Then the slurry was heated to 373 K and stirred for 2 h at 373 K. In order to promote the adsorption of the suspended Pt nanoparticles onto the support, hydrochloric acid was adopted as the sedimentation

promoter. The resulting black solid sample was filtered, washed and dried at 373 K overnight in a vacuum oven.

Thermogravimetric analysis (TGA7, PerkinElmer, Norwalk, CT, USA) was used to determine the Nafion content of NFC support under air flowing at $10 \, ml \, min^{-1}$. The temperature ranged from room temperature to 1273 K at a heating rate of $278 \, K \, min^{-1}$. The samples were heated at 373 K for 8 h in a vacuum oven before the test. Energy dispersive X-ray (EDX) analysis was used to determine the element contents in the samples. Transmission electron microscopy (TEM) images of catalysts were performed by JEOL 2010 high-resolution transmission electron microscopy (HRTEM). X-ray diffraction (XRD) patterns for the catalysts were obtained on a D/MAX-IIIA using Cu K radiation with a Ni filter. The samples were also analyzed by X-ray
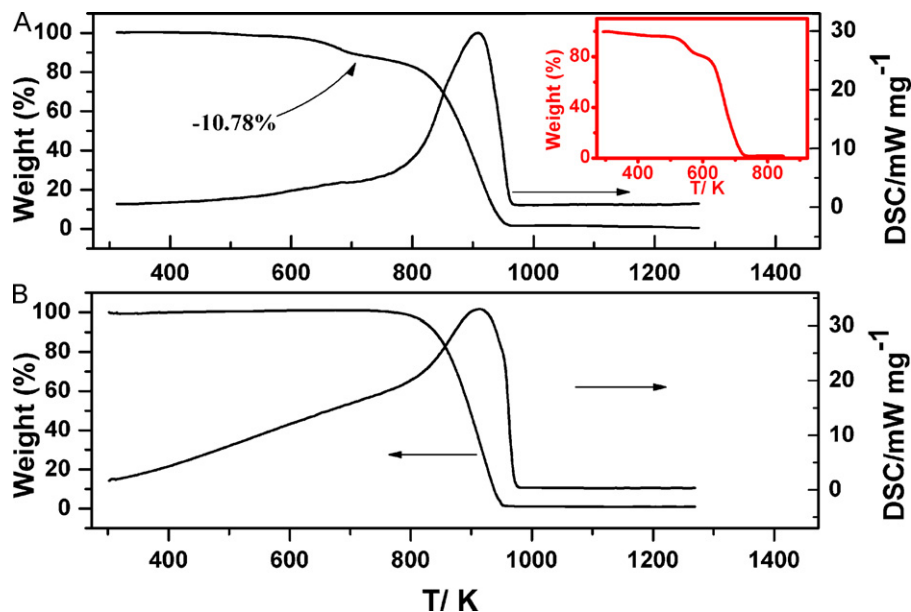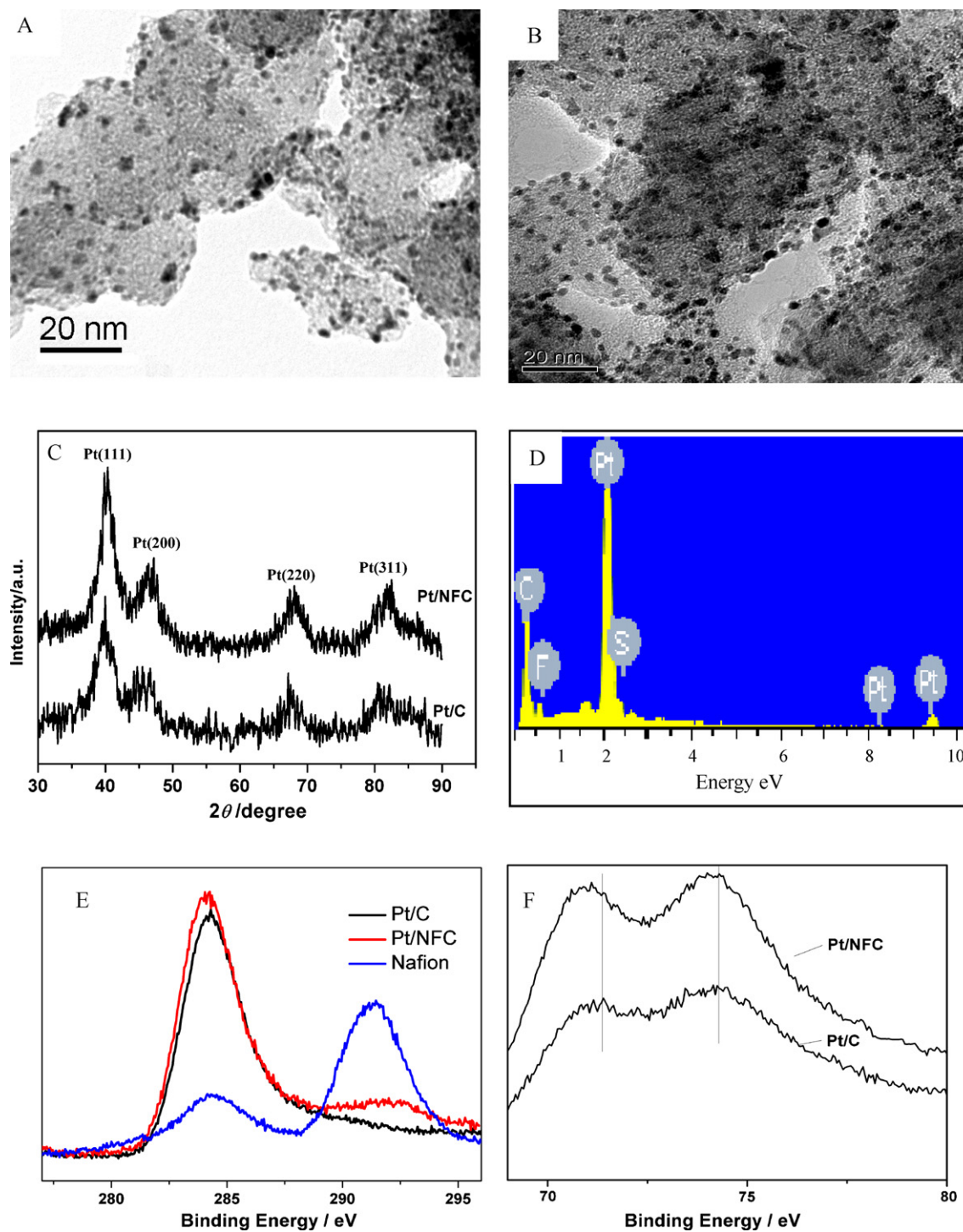

Fig. 2. (A) TGA data of the Nafion-stabilized carbon. Inset: TGA data of the perfluorosulfonic acid (PFSA) Nafion®. (B) TGA data of the Xc-72.

Fig. 3. TEM image of 20% Pt/NFC catalyst (A) and Pt/C catalyst (B). (C) The XRD pattern of 20% Pt/NFC and Pt/C catalyst. (D) Energy dispersive X-ray (EDX) patterns of Pt/NFC catalyst. (E) XPS of spectrum of C1s of Pt/C, Pt/NFC and Nafion polymer. (F) XPS of spectrum of Pt4f of Pt/C and Pt/NFC.

photoelectron spectroscopy (XPS) on a VG ESCALAB MKII spectrometer.

The electrochemical performance and durability of the catalysts were carried out in a conventional three-electrode electrochemical cell using AUTO LAB Electrochemical System (Eco Chemie Corp.). The catalyst powders were mixed with deionized water and 5 wt% Nafion solution, and then coated on a mirror-polished glassy carbon disk electrode ($f = 3$ mm) as the working electrode by using Finnpipette Digital Micropipette (Thermo Electron Corp.). The addition amount of Nafion in Pt/NFC electrode is less than that in Pt/C

electrode to keep identical with Nafion content in both electrodes (the weight ratio of Pt/C to Nafion is 3:1). The electrochemical performance was carried out in 0.5 mol dm^{-3} H$_2$SO$_4$ solution using a platinum wire and a saturated calomel electrode (SCE) as the reference electrode and the counter electrode respectively at room temperature. All the CV is carried out firstly by sweeping anodically and then cathodically.

The electrochemically accelerated durability test (ADT) was used for investigating the life of Pt/C and Pt/NFC catalysts. To avoid the influence of Cl$^-$, Hg/Hg$_2$SO$_4$ was used as the reference elec-

trode. The ADT was carried out by continuously applying linear potential sweeps from 0.6 to 1.2 V vs. RHE at the rate of 20 mV S^{-1}.

A glassy carbon rotating disk electrode (GCRDE) was used to evaluate the electrocatalytic ORR activity of our catalysts. The polarization curves of the ORR were carried out by applying linear potential sweeps from 1.04 to 0.26 V vs. RHE at rotation rate 2500 rpm and scan rate of 5 mV S^{-1} in 0.5 mol dm^{-3} H$_2$SO$_4$ solution (saturated with O$_2$). The LSV was carried out by sweeping cathodically. To evaluate the activity of catalysts, the kinetic current was calculated from the ORR polarization curve by using the Koutecky–Levich equation as follows [18].

3. Results and discussion

Fig. 2 shows the TG and DSC data of both carbon support and Nafion stabilized carbon. There is almost no weight loss below 470 K. For Nafion stabilized carbon support (Fig. 2A), it begins to lose its weight at 473 K and there is 10.8% loss of total weight until 691 K, and this loss should be due to the decomposition of Nafion on the surface of carbon, which is consistent with the TG data of Nafion. As shown in Fig. 2A inset, Nafion begins to lose its weight at about 480 K and almost no weight loss above 720 K. However, in the case of pure carbon support, there is almost no weight loss below 793 K and it drops sharply above 793 K (Fig. 2B), which is attributed to the oxidation of carbon. As the result, the weight ratio of carbon to Nafion is about 9:1 from the TG analysis. The thickness of coated Nafion on the surface of carbon support was about 0.5 nm based on the weight percentage and the density of Nafion polymer. DSC analysis (Fig. 2A) showed that there was a peak around 688 K resulted from the decomposition of Nafion on the surface of carbon.

The Pt nanoparticles of 20% Pt/NFC catalyst are spherical in shape and are monodispersed on the surface of NFC with an average size of 3.2 nm (Fig. 3A), which is very similar to the size (3.3 nm) of commercial 20% Pt/C catalyst (Johnson Matthey) obtained from the TEM (Fig. 3B). These nanoparticles have a face-centered cubic (fcc) crystal structure and the average particle size of Pt is 3.05 nm for Pt/NFC and 3.09 nm from XRD (Fig. 3C), which is consistent with the result from TEM images. EDX studies reveal that the presence of elements C, F and S on the Pt/NFC catalyst (Fig. 3D), which approve the existence of Nafion on the carbon support for Pt/NFC catalysts. Fig. 3E shows the XPS C1s spectra of the Pt/C, Pt/NFC and Nafion film. Pt/C has only one peak observed at 285.1 eV and there are two peaks at 285.16 eV and 291.35 eV for both Pt/NFC and Nafion film. The peak at 291.35 eV should be attributed to C–F bonds(C–F, CF$_2$ and CF$_3$) [19], which further confirms the existence of Nafion on the carbon support for Pt/NFC catalysts. Fig. 3F shows the XPS Pt 4f spectra of the Pt/C and Pt/NFC catalysts. For the Pt/C, the binding energies of Pt (4f$_{7/2,5/2}$) are observed at 71.35 eV and 74.35 eV, respectively. And the binding energies of Pt (4f$_{7/2,5/2}$) of Pt/NFC catalyst are 71.15 eV and 74.10 eV, respectively. A slight shift of the Pt (4f) peak towards lower angles was observed for the Pt/NFC catalyst compared to Pt/C catalyst. This is in agreement with the result of Shukla et al. [11], which observed a slight shift of the Pt (4f) peak of the phenyl-sulfonic acid stabilized catalyst towards lower angles as compared to unstabilized catalyst. This shift indicates the change of the electronic structure of Pt surfaces [20], which should be attributed to enhanced interactions of Pt particles and Nafion-stabilized supports for Pt/NFC catalyst.

Fig. 4A shows the cyclic voltammetry (CV) curves of catalysts in the deaerated 0.5 mol dm^{-3} H$_2$SO$_4$ by glass carbon electrode with 0.28 mg cm^{-2} catalyst loading. The electrochemical active area (ECA) was calculated from the hydrogen adsorption peak area in CVs [21]. The Pt/NFC catalyst has an ECA of 68 m^2 g^{-1}, which is higher than the commercial 20% Pt/C catalyst (60 m^2 g^{-1}) (John-

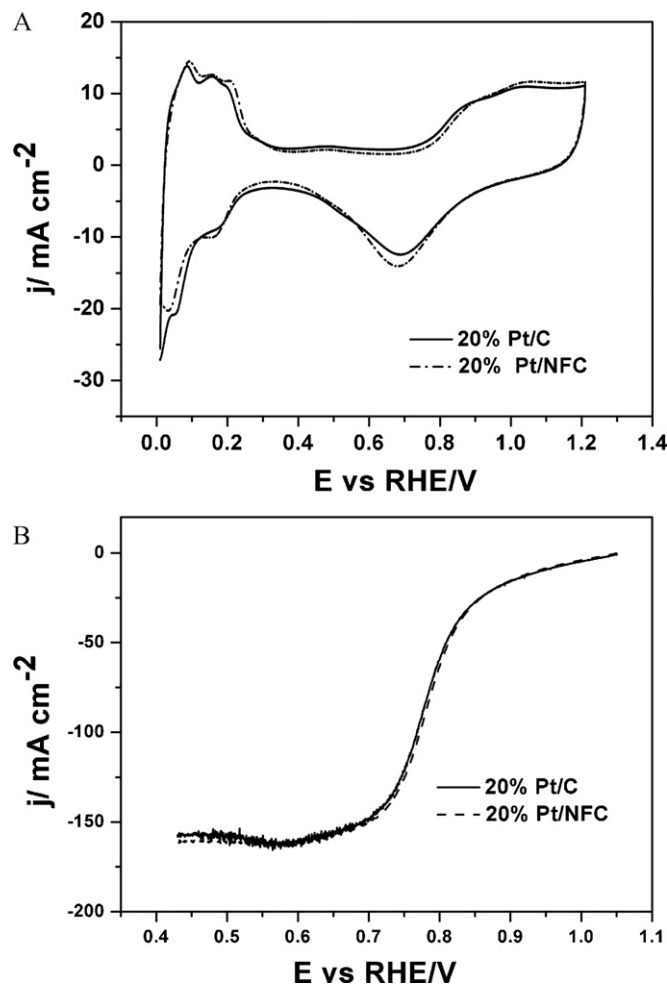**Fig. 4.** (A) Electrochemically cyclic voltammetry (CV) curves of the 20% Pt/NFC and 20% commercial Pt/C in 0.5 mol dm^{-3} H$_2$SO$_4$ at the scan rate of 50 mV/s in a potential window of 0–1.2 V vs. RHE. (B) Comparison of ORR (oxygen reduction reaction) activities of Pt/NFC and Pt/C in 0.5 mol dm^{-3} H$_2$SO$_4$ for ORR reduction at 2500 rpm, sweep rate of 5 mV/s and at room temperature.

son Matthey). Fig. 4B shows the polarization curves for the oxygen reduction reaction of both Pt/NFC and Pt/C catalysts in O$_2$-saturated 0.5 mol dm^{-3} H$_2$SO$_4$ using rotating disk electrode (RDE). The kinetic current was calculated from the ORR polarization curve by using the Koutecky–Levich equation [18] to obtain the activities of catalysts. The Pt/NFC exhibits a slightly higher mass activity of 0.32 mA ug^{-1}$_{Pt}$ at 0.8 V vs. RHE than 0.29 mA ug^{-1}$_{Pt}$ of Pt/C. The comparable activity of Pt/NFC could be attributed to the higher ECA and the effect of SO$_3$$^-$ end group of Nafion [22] on the surface of NFC.

The electrochemically accelerated durability test (ADT) [18,23] is available to investigate the life of Pt/C and Pt/NFC catalysts. The average Pt particle size of Pt/NFC catalyst increases from ca. 3.2 nm (Fig. 3A) to 6.2 nm (Fig. 5A) after 5800 cycles (Fig. 5B), which is very similar to that of Pt/C (from 3.3 nm to 6.5 nm, Fig. 5C, D) after only 3500 cycles. Fig. 6A shows cyclic voltammograms of both Pt/NFC and Pt/C catalysts before and after ADT and indicates that the catalytic activity of catalysts decreases with the cycles. Fig. 6B presents the ECA loss of catalysts (defined as S_{loss}) is as a function of the electrochemical oxidation cycle number (N_{cycle}) under ADT condition, namely the S_{loss} increases with the N_{cycles}. The S_{loss} reaches ca. 62% and the S_{loss} rate is 0.007 m^2 g^{-1} cycle^{-1} for the Pt/NFC in the range of 5800 cycles, which is a factor of 1.6 lower than that of Pt/C (0.011 m^2 g^{-1} cycle^{-1}) in the range of 3500 cycles. This clearly illustrates that Pt/NFC catalyst has more than 1.6 times higher
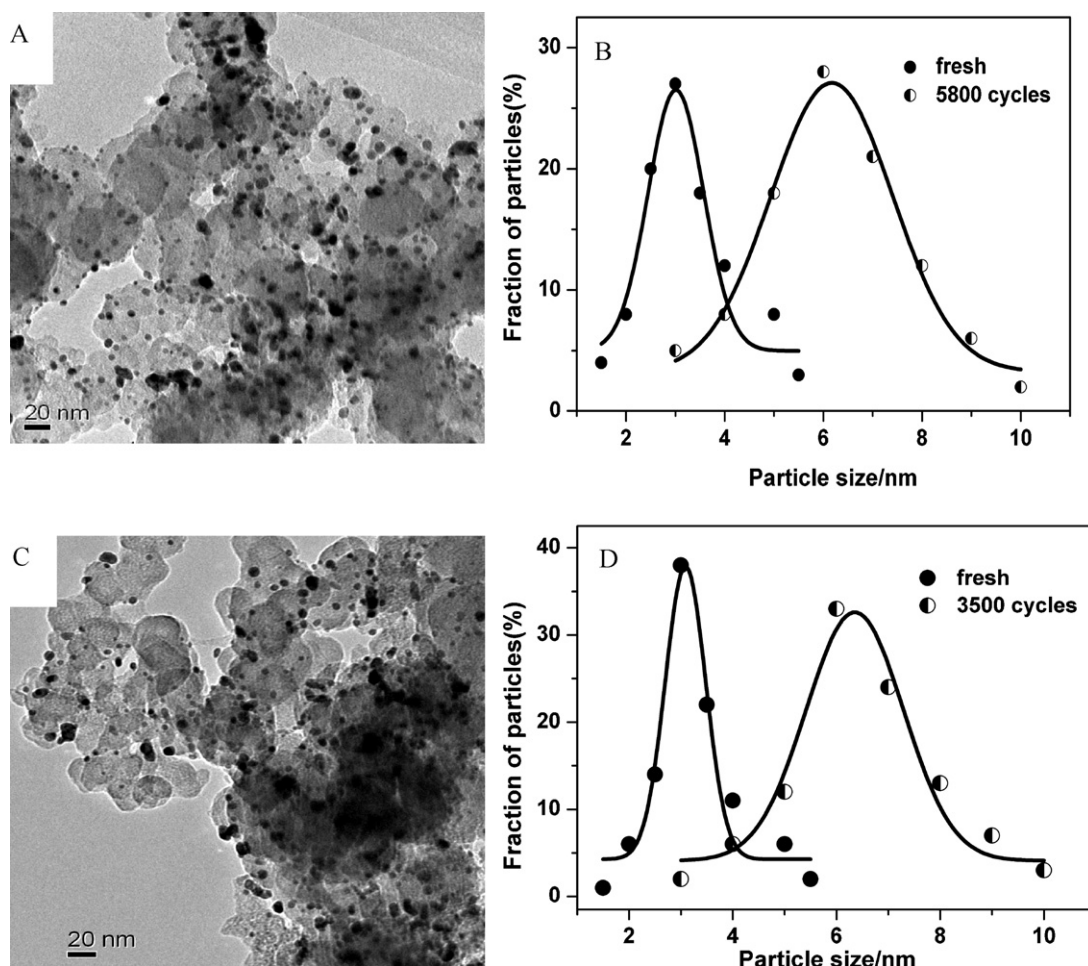
Fig. 5. (A) TEM image of 20% Pt/NFC after ADT and (B) Pt particle size before and after ADT; (C) TEM image of 20% commercial Pt/C after ADT and (D) Pt nanoparticle diameters of 20% commercial Pt/C before and after ADT.

electrochemical durability than Pt/C catalyst under the same ADT conditions. The mechanism of the improved durability of Pt/NFC was explained from mechanic schematic diagram (Fig. 1) as follows. (i) At first, the Pt/NFC catalyst has enhanced interaction between Pt nanoparticle and carbon support stabilized with Nafion polymer (position a) compared with Pt/C catalyst (position a_1). (ii) The

Nafion on the NFC support can effectively mitigate the Pt nanoparticle migration on the carbon support (positions b and c) once the interaction between Pt nanoparticle and carbon is impaired. (iii) The migration and gathering of Pt nanoparticles take place, the gathering nanoparticles easily coalesce to bigger particles (position d_1) resulting in loss of Pt ECA. But for Pt/NFC catalyst, the aggrega-
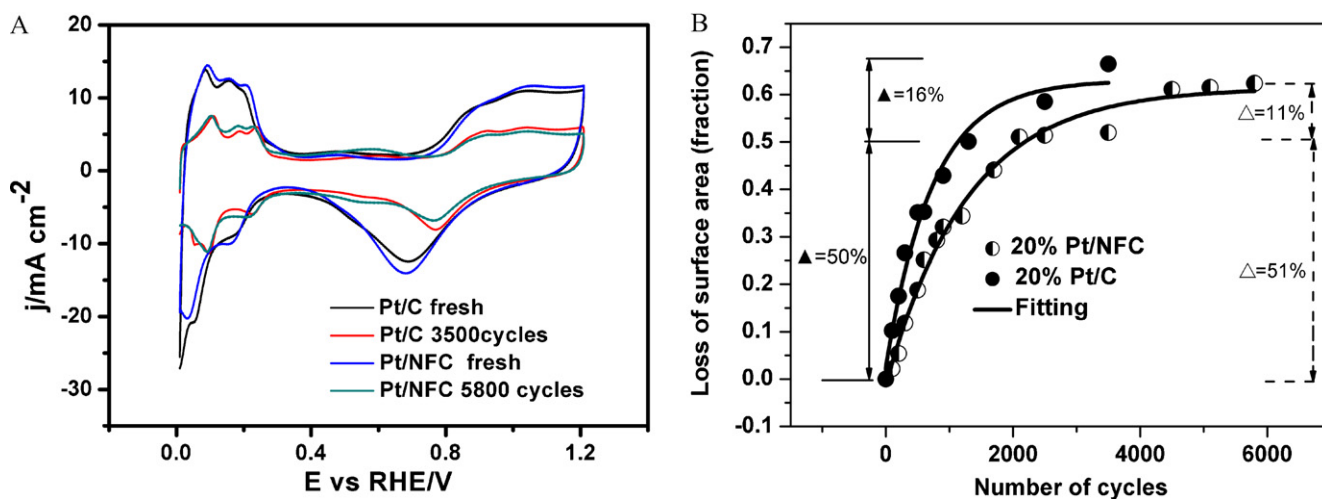
Fig. 6. (A) Cyclic voltammograms of both Pt/C and Pt/NFC before and after ADT and (B) electrochemical active area (ECA) loss of catalysts under the increased ADT cycle numbers, loss of surface area is defined as 1-Pt operating surface area/Pt initial surface area. ECA is calculated from hydrogen adsorption peak area in CVs.

tion is possibly hindered by Nafion polymer on the NFC support (position d).

In addition, a very interesting thing is that the ECA loss of catalysts (Fig. 6B) has two different linear loss values during the ADT, which is also found in the literature [4]. The S_{loss} rate for Pt/NFC catalyst is 0.016 m^2 g^{-1} cycle^{-1} from 0 to 2100 cycles, and 0.0020 m^2 g^{-1} cycle^{-1} from 2100 to 5800 cycles. For Pt/C catalyst, the S_{loss} rate is 0.023 m^2 g^{-1} cycle^{-1} (ranging from 0 to 1300 cycles) and 0.004 m^2 g^{-1} cycle^{-1} from 1300 to 3500 cycles, respectively. This difference indicates that the loss of catalyst surface area over the first stage occurs at a faster rate (6–8 times) than over the second stage. The main reason for this phenomenon is the high surface tension of the nanoparticles. The nano-particles have a fundamental weakness of tending towards agglomeration and/or growth in a variety of environments [4]. The smaller the particle in the first stage, the higher the particle surface tension is. Therefore, the smaller catalyst particles will tend to assemble themselves into/onto larger particles to reduce the overall surface energy of the total catalyst mass. During the ADT, the driving force for particle for particle growth decreases due to the increased average particle size and reduced associated surface energy.

4. Conclusions

We have synthesized the Pt/NFC catalyst using Nafion stabilized carbon and this catalyst shows a slightly higher electrocatalytical activity than that of commercial Pt/C catalyst commonly used in PEM fuel cells. Especially, the Pt/NFC catalyst has a 60% better life than commercial Pt/C, which can be attributed to the stability mechanism of the introduction of Nafion on carbon support. Nevertheless, there are remains to learn about the optimum weight ratio of carbon to Nafion and performance of single cell using the Pt/NFC catalysts.

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