Sulfonation of carbon-nanotube supported platinum catalysts for polymer electrolyte fuel cells

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Abstract

Sulfonic acid groups were grafted onto the surface of carbon-nanotube supported platinum (Pt/CNT) catalysts to increase platinum utilization in polymer electrolyte fuel cells (PEFCs) by both thermal decomposition of ammonium sulfate and in situ radical polymerization of 4-styrenesulfonate. The resultant sulfonated Pt/CNT catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectrometry, thermal gravimetric analysis (TGA) and electrochemical methods. The electrodes with the Pt/CNT catalysts sulfonated by the in situ radical polymerization of 4-styrenesulfonate exhibited better performance than did those with the unsulfonated counterparts, mainly because of the easier access with protons and well dispersed distribution of the sulfonated Pt/CNT catalysts, indicating that sulfonation is an efficient approach to improve performance and reduce cost for the Pt/CNT-based PEFCs. The electrodes with the Pt/CNT catalysts sulfonated by the thermal decomposition of ammonium sulfate, however, did not yield the expected performance as in the case of carbon black supported platinum (Pt/C) catalysts, probably due to the significant agglomeration of platinum particles on the CNT surface at high temperatures, indicating that the Pt/CNT catalysts are more sensitive to temperature than the Pt/C catalysts.
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1. Introduction

Polymer electrolyte-based fuel cells (PEFCs), including H_2–O_2 and direct alcohol fuel cells, have been considered as promising power sources for portable, automobile, and stationary applications in terms of the high efficiency, low emission and low-temperature operation [1,2]. The commercialization of PEFCs, however, is still significantly restricted by its high cost, which is mainly caused by the low platinum utilization in the catalytic electrodes [3,4]. The state-of-the-art electrodes are usually made by directly mixing a carbon-supported platinum catalyst with a proton-conducting polymer such as Nafion. In such an electrode, the uniform mixing of the catalyst and Nafion cannot be guaranteed and, thus, a large percentage of platinum is wasted because only the catalyst particles that contact with both electrolyte and reactants are electrochemically active [1,5].

Several studies have been focused on enhancing the catalyst utilization in the PEFC electrodes by extending the so-called triple-phase boundaries [6–15]. Among them, sulfonation of carbon-supported catalysts as mixed electronic and protonic conductors has been proved to be an efficient way to increase the triple-phase boundaries [9–14]. Easton et al. [9] and Xu et al. [10,11] chemically attached sulfonated silanes and sulfonic acid or short-chain sulfonic acid groups onto the surface of the carbon black supported platinum (Pt/C) catalysts and the resulting sulfonated Pt/C catalysts not only showed much better performance than did the unsulfonated counterparts, but also less Nafion was required within the catalyst layers to achieve the best performance. Mizuhata et al. [12] and Kuroki et al. [13] proposed an electrode fabrication method, based on the process of grafting polymerization of a proton-conducting agent (acrylamide tertiary butyl and methyl sulfonic acid groups) onto the Pt/C catalysts before the conventional electrode fabrication process, and a significant increase of the electrochemically active area in the electrode was observed. Kim et al. [14] functionalized the support of Pt/C catalysts with sulfonated polystyrene and the electrodes with such catalysts showed 25% improvement

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in performance compared to the conventional electrodes with unsulfonated Pt/C catalysts.

It is noteworthy that although sulfonation of carbon supported platinum catalysts is a useful approach to improve the platinum utilization by increasing the active triple-phase boundaries, almost all the previous investigations [e.g. 9–14] focused only on the most commonly used carbon black supports, e.g. Vulcan XC-72R, Black Pearls 2000 and Ketjen Black. To the best of our knowledge, no attempt has been done on the carbon-nanotube (CNT) supports so far. Recently, CNTs, as innovative catalyst supports, have drawn a great deal of attention due to their unique surface structures, excellent mechanical and thermal properties, high electric conductivity and large surface areas [16–20]. As compared with the most widely used Vulcan XC-72R carbon support that has an electronic conductivity of $4.0\,S\,cm^{-1}$ and specific surface area of $237\,m^2\,g^{-1}$ [21], CNT has extremely higher electronic conductivities of $10^4\,S\,cm^{-1}$ and significantly high specific surface areas of $200–900\,m^2\,g^{-1}$ [22,23]. Furthermore, Vulcan XC-72R has a large ratio of micropores that are smaller than 2 nm, whereas the CNT has no micropores smaller than 2 nm [21,24]. For the Vulcan XC-72R support, the platinum nanoparticles may sink into the micropores, which will reduce the number of triple-phase-boundary reactive sites, thus reducing the platinum utilization [15]; For the CNT support, however, no platinum particles may sink in the micropores and be wasted [24].

In the present study, we extended sulfonation from Pt/C catalysts to the CNT supported platinum (Pt/CNT) catalysts by chemically linking proton-conducting sulfonic acid groups onto the surface of Pt/CNT catalysts. For this purpose, two different sulfonation approaches were employed and compared: treating the Pt/CNT catalysts with thermal decomposition of ammonium sulfate and in situ radical polymerization of 4-styrenesulfonate, which is schematically illustrated in Fig. 1. The resulting sulfonated Pt/CNT catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectrometry, thermal gravimetric analysis (TGA), cyclic voltammetry (CV)

and polarization curves. The effects of sulfonation on the Pt/CNT catalysts were explored and it was found that the electrodes with the Pt/CNT catalyst sulfonated by in situ radical polymerization of 4-styrenesulfonate showed much higher performance, whereas the electrodes with the Pt/CNT catalyst sulfonated by thermal decomposition of ammonium sulfate showed worse performance than did those with the unsulfonated counterparts.

2. Experimental

2.1. Preparation of CNTs and Pt/CNT catalysts

The multiwalled CNTs were prepared by means of the catalytic decomposition of CH_4 over Ni nanoparticles obtained from reducing rare earth nickelate (La_2NiO_4), based on the method reported elsewhere [25]. Further, purification of the CNTs was carried out by refluxing CNTs with 60% HNO_3 at 90 °C for 2 h to remove the metal particles. Afterward, the mixture was diluted, filtered, washed with excess deionized (DI) water, and dried at 50 °C in a vacuum oven for overnight. After the purification process, the surface oxidation of the CNTs was carried out by refluxing CNTs in 4 M H_2SO_4 and 4 M HNO_3 at 90 °C for 5 h. Finally, the treated CNTs were diluted with water, filtered, washed with excess DI water, and dried at 50 °C in a vacuum oven overnight.

The Pt/CNT catalysts at 20 wt.% were prepared by maintaining a constant concentration of H_2PtCl_6 (0.0065 mM) and using $NaBH_4$ as a reducing agent. An appropriate amount of the precursor solutions with the CNTs were taken in tetrahydrofuran (THF) solvent. The resulting suspensions were stirred for 2 h, and then the solvent THF was evaporated at 60 °C. After complete evaporation of the solvent, the dry mixtures were dispersed in diluted methanol and ultrasonicated for 15 min. Subsequently, an excess quantity of 0.15 M $NaBH_4$ was added, drop-by-drop, to the mixtures with vigorous stirring for the complete reduction of platinum from the metal salt. After that, the mixtures were stirred for 2 h at room temperature. Finally, the mixtures were
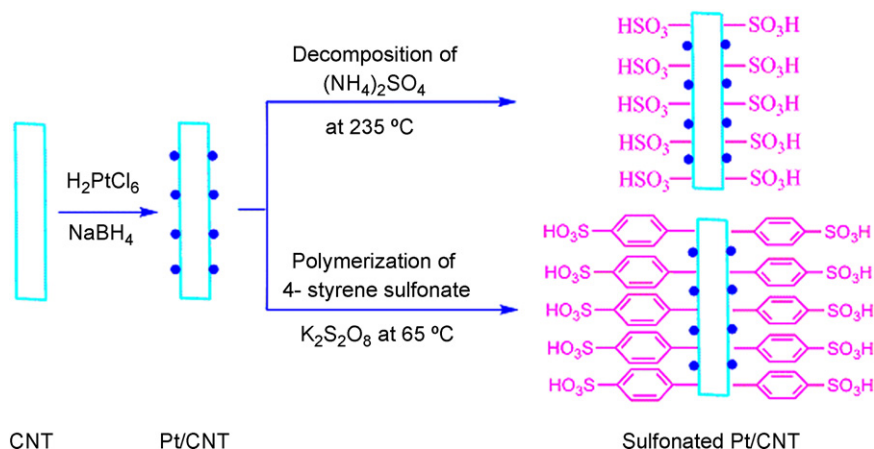

Fig. 1. Schematic illustration of the two sulfonation routes for Pt/CNT catalysts: (a) decomposition of ammonia sulfonate; (b) in situ radical polymerization of 4-styrenesulfonate.

filtered, washed with excess DI water, and dried in a vacuum oven at 70 °C for 2 h.

2.2. Sulfonation of Pt/CNT catalysts

The first sulfonation approach for the Pt/CNT catalysts was derived from the procedure presented by Xu et al. [11]. First, $(NH_4)_2SO_4$ solution was mixed with a proper amount of Pt/CNT catalysts based on a predetermined weight percentage of $(NH_4)_2SO_4$. The weight percentage was defined as the ratio of the weight of $(NH_4)_2SO_4$ to the total weight of $(NH_4)_2SO_4$ and the Pt/CNT catalysts. Second, after the mixture was well agitated, it was heated at 235 °C for 30 min. It is believed that at 235 °C, $(NH_4)_2SO_4$ decomposes to generate SO_3, and the formed SO_3 reacts with carbon via its surface hydrogen atoms to have $-SO_3H$ groups linked onto it. The resultant Pt/CNT catalyst is called "sulfonated" catalyst, while the original Pt/CNT catalyst is called "unsulfonated" catalyst.

The other sulfonation approach for the Pt/CNT catalysts was based on the in situ radical polymerization of 4-styrenesulfonate. Specifically, a 100 mL flask was charged with a magnetic stirring bar, some DI water and predetermined amount of sodium 4-styrenesulfonate (NaSS) and Pt/CNT catalyst. After vigorous stirring for 10 h at room temperature, $(NH_4)_2S_2O_8$ was added, and then the flask was heated to 65 °C under stirring to start polymerization. After 48 h, the reaction was stopped by cooling to room temperature. The mixture was diluted with DI water, bath sonicated for 1 h and then washed many times with DI water. After that, the mixture was filtered and then mixed with a large amount of 4 M H_2SO_4 and stirred for 24 h at room temperature to transform the sulfonated Pt/CNT catalysts from Na^+ form to H^+ form. Finally, the mixtures were filtered, washed with excess DI water, and dried in a vacuum oven at 60 °C for 12 h.

2.3. Characterization of the sulfonated Pt/CNT catalysts

XRD patterns of the Pt/CNT catalysts were recorded with a Philips Powder Diffraction System (model PW 1830) using a Cu Kα source. TEM images and elemental analysis of the Pt/CNT catalysts were obtained by using a high-resolution JEOL 2010F TEM system. Sulfonation of the Pt/CNT catalysts was confirmed by FTIR spectroscopy using a FTS 6000 (Bio-Rad) spectrophotometer and by TGA using a TGA 7 (Perkin-Elmer).

The electrochemical performance of the sulfonated Pt/CNT catalyst was evaluated by a half-cell method, which was proved to be reliable in our previous investigations [26,27]. In this half-cell, a half-membrane electrode assembly (MEA), consisting of a Nafion membrane with a gas diffusion electrode (GDE) on one side, was held vertically. The GDE, consisting of a catalyst layer and a gas diffusion layer, was in contact with a flow field plate, through which O_2 was supplied and electric current was extracted. The other side of the membrane was exposed to the electrolyte solution, in which a platinum mesh served as a counter electrode. A saturated calomel electrode (SCE) was positioned approximately 4.0 mm away from the membrane via a Luggin capillary to serve as a reference electrode (RE). The underlying consideration of employing the half-cell method is

that the potential of the working electrode can be precisely controlled through a stable RE, and the working electrode was still identical to the normal PEFC electrode that consisted of the catalyst layer, gas diffusion layer and flow field. More importantly, this half-cell configuration can guarantee a fully hydrated Nafion membrane. As such, the effect of the membrane humidity on cell performance was eliminated.

The half-MEA with an active area of 1.0 cm × 1.0 cm was fabricated by employing a Nafion 115 membrane and an in-house CNT-based GDE electrode with platinum loading ca. 0.05 mg cm^{-2} and without Nafion electrolyte. The Nafion 115 membrane was pretreated by boiling the membrane for 1 h in 3 vol.% H_2O_2, 1 h in DI water, 1 h in 0.5 M H_2SO_4 and 1 h in DI water, followed by washing in DI water. The in-house GDE was fabricated by spraying a catalyst ink consisting of the Pt/CNT catalysts and ethanol onto a wet-proofed carbon cloth substrate (E-TEK, Type A). The final half-MEA was formed by hot pressing the GDE and the membrane at 135 °C and 5 MPa for 3 min.

The half-MEA was tested at ambient temperature (20 °C), using an Autolab PGSTAT 30. Prior to each measurement, N_2 was fed to the electrode at a flow rate of 50 mL min^{-1}. At the same time, 2 M H_2SO_4 solution was introduced into the cell and the solution was purged by bubbling N_2 for 30 min. The surface of the platinum catalyst in the electrode was then cleaned electrochemically by cycling the potential between 0.0 and 1.2 V (vs. RHE) at a sweep rate of 50 mV s^{-1} until the CV profiles no longer showed changes. A fresh H_2SO_4 solution was then exchanged and N_2 was bubbled through the solution for at least 30 min. At the same time, pure oxygen was fed to the electrode at a flow rate of 100 mL min^{-1}. Finally, the electrode performance was evaluated by CV with a sweep rate of 50 mV s^{-1} and by steady-state potential scanning with stabilizing time for 1 min at each potential.

3. Results and discussion

3.1. Sulfonation by thermal decomposition of ammonium sulfate

The Pt/CNT catalysts, unsulfonated and sulfonated by thermal decomposition of $(NH_4)_2SO_4$, were analyzed by XRD and the results are shown in Fig. 2. The featured peaks of platinum crystal for the unsulfonated Pt/CNT catalyst clearly indicated that the platinum particles were successfully reduced onto the CNT surface, which was consistent with our previous results [25]. It was, however, found that the sulfonated Pt/CNT catalyst by thermal decomposition of $(NH_4)_2SO_4$ showed significantly sharper XRD peaks than did the unsulfonated one, which indicated that the sulfonated Pt/CNT catalyst had larger particles than did the unsulfonated one. The average particle sizes for the Pt/CNT catalysts unsulfonated and sulfonated by thermal decomposition of $(NH_4)_2SO_4$ were calculated to be 2.9 and 12.6 nm, respectively, from the broadening of the (2 2 0) diffraction peaks using Scherrer's equation [28]:

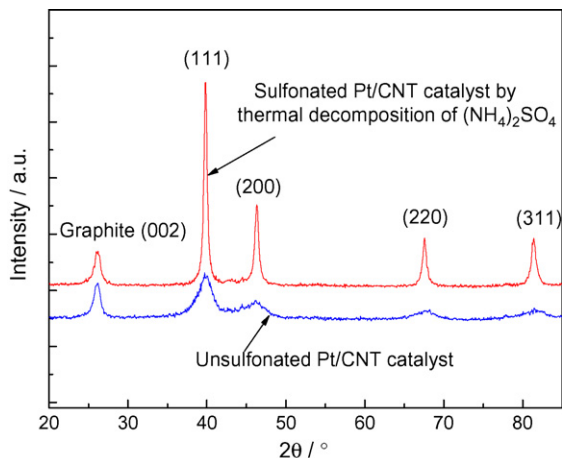$$d = \frac{0.9\lambda}{B_{2\theta} \cos \theta_{\max}} \tag{1}$$

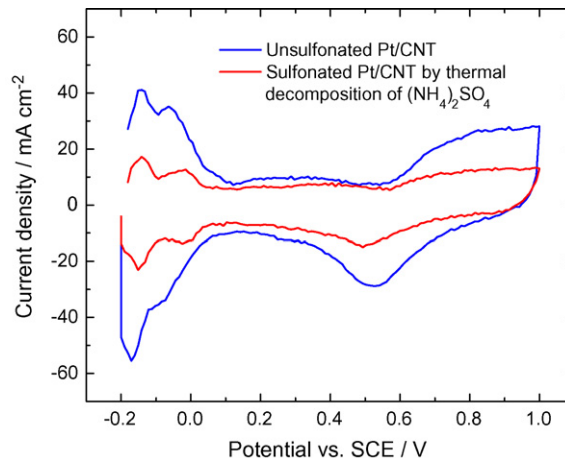Fig. 2. XRD patterns of the Pt/CNT catalysts unsulfonated and sulfonated by thermal decomposition of $(NH_4)_2SO_4$.

Fig. 4. CV curves of the half-cells made with the Pt/CNT catalysts unsulfonated and sulfonated by thermal decomposition of $(NH_4)_2SO_4$.

where d is the average particle size in nm, λ the wavelength of the X-ray (1.54056 Å), θ the angle at the maximum of the peak, and $B_{2\theta}$ is the width of the peak at half-height.

The significant increase in platinum particle size was probably due to the facile agglomeration of nano-platinum particles on the CNT surface at high thermal decomposition temperature. Fig. 3 presents TEM images of the Pt/CNT catalysts unsulfonated and sulfonated by thermal decomposition of $(NH_4)_2SO_4$. The platinum particle size for the unsulfonated Pt/CNT catalyst was found to be small, around 3.0 nm, and highly uniform. As expected, the platinum particle size for the Pt/CNT catalyst sulfonated by thermal decomposition of $(NH_4)_2SO_4$ was significantly larger. This observation was consistent with the XRD results, indicating that the treatment of the Pt/CNT catalyst by thermal decomposition of $(NH_4)_2SO_4$ at 235 °C can cause significant agglomeration of platinum particles.

Fig. 4 presents the CV curves of the half-cells with the Pt/CNT catalysts unsulfonated and sulfonated by thermal decomposition of $(NH_4)_2SO_4$, respectively. Clearly, the Pt/CNT catalyst sulfonated by thermal treatment at 235 °C showed significantly smaller electrochemical active surface area than did the unsulfonated Pt/CNT catalyst, which was in good agreement with the XRD and TEM results in Figs. 2 and 3, mainly due to the platinum agglomeration on the CNT surface at high temperature, in spite of the expected increase in platinum utilization, after the sulfonation procedure. This result for the Pt/CNT catalyst seems to be contrary to the case for the Pt/C catalyst as observed by Xu et al. [11], where the electrodes with the Pt/C catalyst sulfonated by thermal decomposition of $(NH_4)_2SO_4$ at 235 °C performed much better than did those with the unsulfonated counterpart. The discrepancy for the Pt/CNT and Pt/C catalysts can be explained by different natures of the CNT and carbon black supports. Generally, as mentioned in Section 1, the CNT surface is almost smooth except a few defective sites or
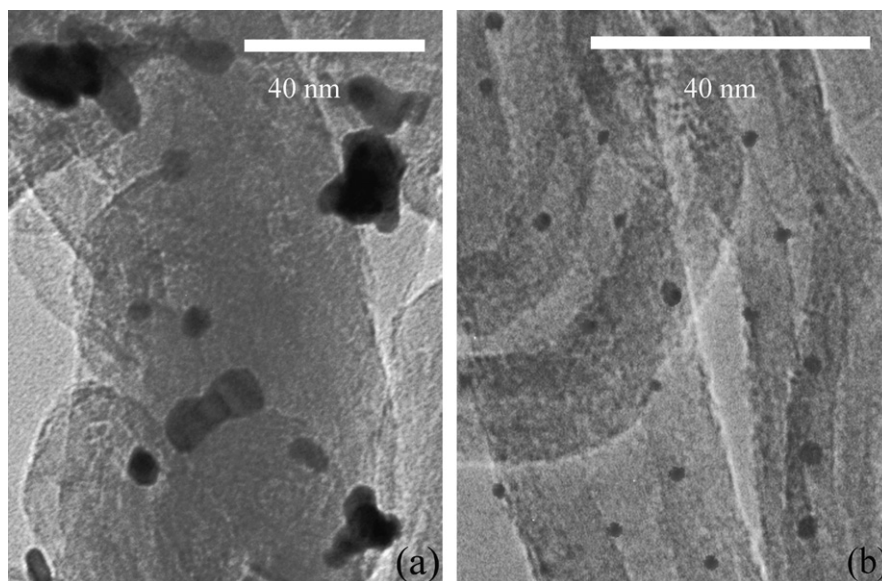

Fig. 3. TEM images of the Pt/CNT catalysts sulfonated by thermal decomposition of $(NH_4)_2SO_4$ at 235 °C (a) and unsulfonated (b) (scale bar: 40 nm).

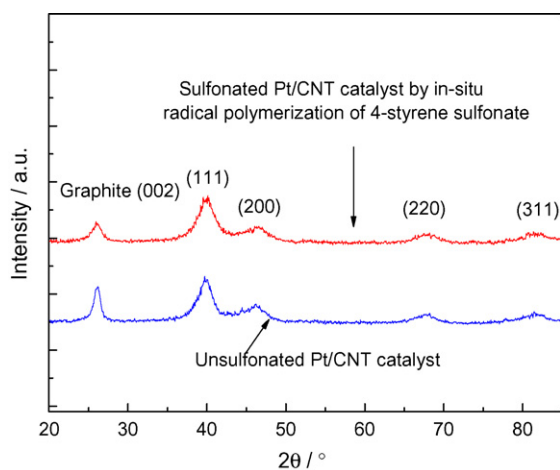Fig. 5. XRD patterns of the Pt/CNT catalysts unsulfonated and sulfonated by in situ radical polymerization of 4-styrenesulfonate.

Fig. 6. FTIR spectrum for the Pt/CNT catalysts substracted before from after in situ radical polymerization of 4-stryrene sulfonate.

amorphous carbon, whereas the surface of carbon black, such as Vulcan XC-72R, has a large ratio of micropores, which are in the range of several nanometers [21,24]. As we know, the highly dispersed nano-platinum particles have extremely high energy and tend to agglomerate thermodynamically. For the smooth CNT support, platinum particles can agglomerate very easily, especially at elevated temperatures; for the porous carbon black support, however, platinum particles have to get over the barriers of the micropores to agglomerate. Therefore, the platinum particles supported on CNTs are more likely to agglomerate than those supported on carbon blacks. In conclusion, sulfonation of the Pt/CNT catalyst by thermal decomposition of $(NH_4)_2SO_4$ at 235 °C seems not to be feasible, although it had been proven effective for the Pt/C catalyst. This analysis also suggests that the Pt/CNT catalysts seem not applicable to the high temperature PEFCs, in spite of higher catalytic activity verified by many researchers [24,29], as compared to the Pt/C catalysts.

3.2. Sulfonation by in situ radical polymerization of 4-styrenesulfonate

In view of the high sensitivity of Pt/CNT catalysts to the sulfonation temperature, a low-temperature sulfonation route for Pt/CNT catalysts is desirable. Here, we applied in situ polymerization of 4-styrenesulfonate at 65 °C as an alternative sulfonation approach to the Pt/CNT catalysts. Fig. 5 presents the XRD patterns of the Pt/CNT catalysts unsulfonated and sulfonated by in situ radical polymerization of 4-styrenesulfonate. Both Pt/CNT catalysts showed similar featured peaks of platinum in terms of peak position and intensity, which, in contrast to the case of sulfonation by thermal decomposition of $(NH_4)_2SO_4$, indicated that the platinum particles did not change significantly after the in situ radical polymerization procedure. The average particle size of the Pt/CNT catalyst sulfonated by in situ radical polymerization of 4-styrenesulfonate was calculated to be 3.1 nm using the Scherrer equation, which was almost equal to the average particle size of unsulfonated Pt/CNT catalyst (2.9 nm). TEM images of the Pt/CNT catalyst sulfonated by the in situ radical polymerization, which were taken and not
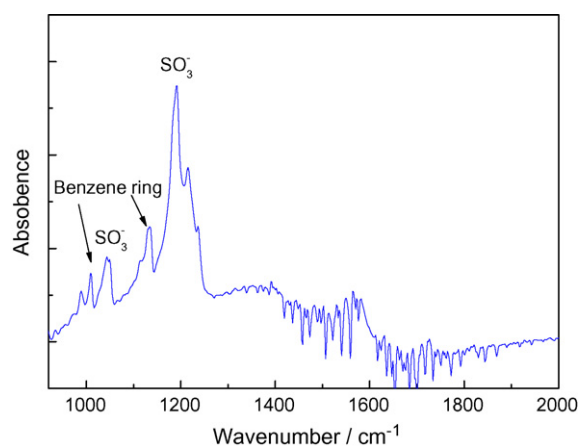
shown in the present paper, also implied no observable increase of platinum particle size after the 65 °C sulfonation process. All these results indicated that sulfonation by in situ radical polymerization of 4-styrenesulfonate seemed applicable to the Pt/CNT catalysts. It is noteworthy that the peaks at 2θ of ca. 26°, which is ascribed to the carbon-nanotube (0 0 2) surface, showed some variation in peak intensity for the two Pt/CNT catalysts. The similar phenomenon was also observed for pure CNT when CNT was treated by strong acids [30] or some coating polymers [31], which might suggest that the CNT supports of the Pt/CNT catalysts were successfully coated by polystyrene sulfonic acid (PSSA).

The successful grafting of polystyrene sulfonic acid groups onto the Pt/CNT catalysts was further confirmed by using FTIR spectra and TGA. The FTIR spectrum obtained by subtracting before from after in situ radical polymerization of 4-styrenesulfonate, for the Pt/CNT catalysts, is shown in Fig. 6. There were several absorption peaks observed near 1011, 1044, 1130 and 1190 cm^{-1}. The peaks at 1190 and 1044 cm^{-1} can be assigned to the SO$_3$ group asymmetric and symmetric vibrational adsorption, respectively. The peaks at 1011 and 1130 cm^{-1} can be assigned to the in-plane skeleton vibration of benzene ring and in-plane bending vibration of benzene ring [32]. These absorption peaks can be ascribed to the functional groups of sulfonated polystyrene, which therefore verified that the PSSA, as a proton-conductor, was successfully grafted onto the Pt/CNT catalysts by our method. Based on the increase in the sulfur content for the Pt/CNT catalysts after the in situ radical polymerization of 4-styrenesulfonate, the weight percentage of PSSA in the sulfonated Pt/CNT catalysts can be obtained, which was dependent on the experimental conditions, such as the polymerization time and the concentration of 4-styrenesulfonate monomer.

Fig. 7 shows the results of the TGA analysis for the Pt/CNT catalysts unsulfonated and sulfonated by in situ radical polymerization of 4-styrenesulfonate. The unsulfonated Pt/CNT catalyst had a steady weight loss at the temperature lower than 600 °C, which could be ascribed to the loss of terminal groups such as –OH, =CO and –COOH at the defective sites of the CNT
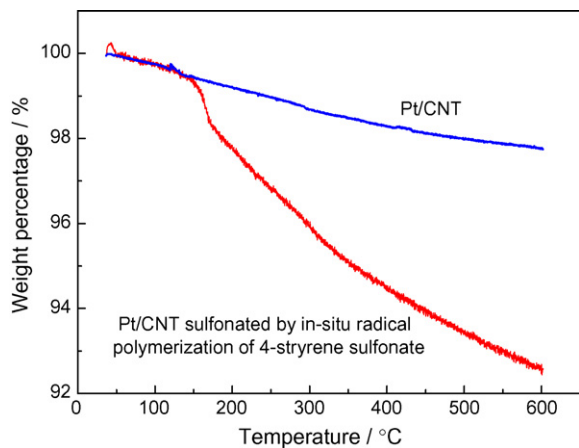
Fig. 7. TGA results for the Pt/CNT catalysts unsulfonated and sulfonated by in situ radical polymerization of 4-stryrene sulfonate at a heating rate of 10 °C/min in nitrogen.

sidewalls, or water absorbed inside the CNTs [33]. In comparison with the unsulfonated Pt/CNT catalyst, the sulfonated Pt/CNT catalyst showed a more significant weight loss, which, in good agreement with the FTIR results, should result from the decomposition of the grafted PSSA and confirmed the successful introduction of PSSA groups onto the surfaces of Pt/CNT catalysts. It was noteworthy that around 150 °C a sharp weight loss was observed for the sulfonated Pt/CNT, which was probably due to the beginning of the PSSA decomposition and indicated that the sulfonated Pt/CNT catalyst by in situ radical polymerization of 4-styrenesulfonate was stable up to around 150 °C.

After the confirmation of the successful polymerization of 4-styrenesulfonate on the Pt/CNT catalysts, electrochemical performance of the resultant sulfonated Pt/CNT catalysts were characterized to examine the sulfonation effects. Fig. 8 shows the polarization curves for the half-cells made of the Pt/CNT catalysts grafted with 0, 8.2 and 21.3 wt.% PSSA, respectively, which was determined from the increase in the sulfur content due to the grafting process. Because of the low working temperature, low platinum loading and zero Nafion content, the overall polarization performance was not high. However, the half-cell

Fig. 8. Half-cell polarization performance of the Pt/CNT catalysts sulfonated by in situ radical polymerization of 4-stryrene sulfonate.

containing 8.2 wt.% PSSA sulfonated Pt/CNT catalysts exhibited higher cell performance than did the half-cell containing the unsulfonated Pt/CNT catalysts, especially at higher current densities. For example, using the 8.2 wt.% PSSA sulfonated Pt/CNT catalyst, a highest power density of 47.1 mW cm^{-2} was achieved, and this power density is almost 10 times higher than that achieved with the unsulfonated catalyst (5.2 mW cm^{-2}). This result, similar to the case of Pt/C catalysts [10–13], verified the beneficial effect of sulfonation for the Pt/CNT catalysts and indicated that sulfonation was also an efficient approach to improve the performance of electrodes using Pt/CNT catalysts. Noteworthy, however, was that the half-cell containing 21.3 wt.% PSSA sulfonated Pt/CNT catalysts showed lower performance than that containing 8.2 wt.% PSSA sulfonated Pt/CNT catalysts, which suggested that excessive sulfonation of the Pt/CNT catalysts resulted in even adverse effects and there existed an optimal sulfonation degree for the Pt/CNT catalysts. This phenomenon can be explained as follows. Sulfonation of Pt/CNT catalysts would increase the number of platinum particles effectively used in the electrode reaction and thus, cell performance, because the sulfonated Pt/CNT catalysts not only functionalized as both electronic and protonic conductors but also could be well dispersed in solvents, such as isopropyl alcohol, ethylene glycol, *n*-butyl alcohol, etc. [34], which meant that the sulfonated Pt/CNT catalysts in the slurry for electrodes fabrication could be well controlled and homogeneously distributed. In contrast, for the unsulfonated Pt/CNT catalyst, the platinum utilization was limited because the mechanical mixing of the Pt/CNT catalysts and Nafion polymers resulted in inhomogeneous distribution of the proton-transport paths due to the aggregation of Nafion polymers in electrode fabrication processes [35]. However, if too much PSSA were tethered onto the Pt/CNT catalysts, the excess polymer electrolyte would cover the platinum surface, which not only led to an increase in the electron-transfer resistance, but also increased the mass transport resistance either by retarding the access of reactant gas to the active sites or by flooding the electrode. As a result, the cell performance would be deteriorated, especially at high current densities. The above analysis indicated that the sulfonation of Pt/CNT catalysts by in situ radical polymerization of 4-styrenesulfonate increased the reactive platinum area; however, an optimal sulfonation degree existed because of a trade-off among the oxygen transport to the polymer-covered platinum catalysts, electron transfer and proton access to the platinum catalysts.

4. Conclusions

To improve the utilization of noble platinum catalysts in PEFCs, we have modified Pt/CNT catalysts by tethering sulfonic acid groups onto the surface of CNT supports via thermal decomposition of $(NH_4)_2SO_4$ and in situ radical polymerization of 4-styrenesulfonate. The Pt/CNT catalysts can be successfully sulfonated by in situ radical polymerization of 4-styrenesulfonate, and the electrodes with the resultant sulfonated Pt/CNT catalyst exhibited better performance than did those with the unsulfonated counterpart, suggesting that sul-
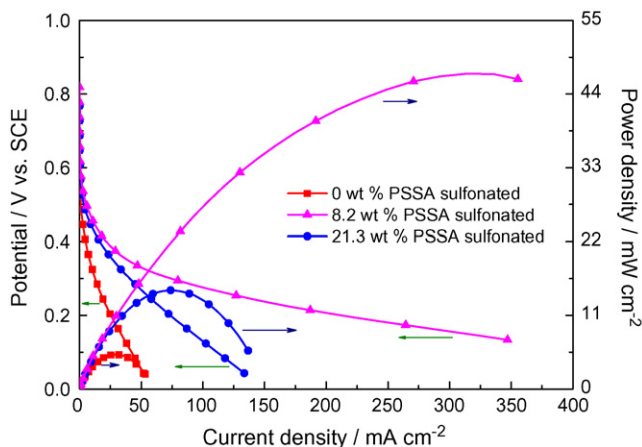
fonation is an efficient way to increase the utilization of Pt/CNT catalysts and thus improve the performance of Pt/CNT-based electrodes. As to this in situ radical polymerization method, there is an optimal sulfonation degree due to the trade-off among the oxygen, electron and proton transport, and the grafted styrene sulfonic acid groups on the Pt/CNT catalyst maintains stable up to ca. 150 °C. The electrodes with Pt/CNT catalysts sulfonated by thermal decomposition of $(NH_4)_2SO_4$ at 235 °C, however, does not present the improved performance as in the case of Pt/C catalysts, which is mainly due to the serious agglomeration of platinum particles at high temperatures. The discrepancy between the two sulfonation approaches indicates that the Pt/CNT catalysts are more sensitive to temperature than Pt/C catalysts and therefore, suitable sulfonation route is critical to the Pt/CNT catalysts.

Acknowledgement

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