



## Short communication

## Investigating the addition of silicon oxide to carbon: Effects of amount and heat treatment on anti-aggregation and electrochemical performance of Pt catalysts

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## ABSTRACT

Small nanoparticles offer high surface areas and are certainly desirable for electrocatalytic reactions and fuel cells. However, the drawback of using small nanoparticles is their tendency towards particle aggregation. This paper aims to inhibit platinum agglomeration by adding silicon oxide to a carbon support for enhanced catalytic activity in low-temperature fuel cells. The catalysts are characterized by X-ray diffraction and transmission electron microscopy. Physical characterization and cyclic voltammetry techniques at room temperature are used to assess the effects of silicon oxide amount, post-heating temperature, and holding time on particle size and dispersion of active components, and the catalysts' activity towards the methanol oxidation and oxygen reduction reactions. It is found that using a support of carbon powder with 3 wt.% silicon oxide can enhance the electrochemically active surface area of Pt catalysts and their activity towards the anodic oxidation of methanol and reduction of oxygen. The active components are also more resistant than Pt/C to agglomeration upon heating.

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## 1. Introduction

Low-temperature fuel cells, including proton exchange membrane fuel cells (PEMFCs) and direct alcohol fuel cells (DAFCs) have great potential for application in transportation, communication, and small portable electronic devices such as 3G phones, personal digital assistants, and laptops. However, large-scale application of PEMFCs and DAFCs is heavily dependent on the development of key materials, including Pt-based electrocatalysts [1–3]. Undoubtedly, carbon-supported platinum or platinum-based electrocatalysts have been proven effective for the electrocatalytic oxidation of hydrogen and small alcohol molecules [4–7]. However, the performance of Pt-based catalysts is far from satisfactory: they suffer from severe agglomeration at high temperatures or under the operating conditions of fuel cells. Furthermore, Pt catalysts are easily poisoned by CO<sub>ads</sub> intermediates formed during the alcohol oxidation reaction. As a result, catalytic activity degrades over time, leading to poor cell performance [8,9].

Silicon oxide (SiO<sub>x</sub>) doped Pt/C catalysts are reported to demonstrate improved performance towards the methanol oxidation reaction (MOR) relative to Pt/C counterparts. Seger et al. [10] reported a simple sodium borohydride reduction to prepare platinum nanoparticles supported on pre-formed SiO<sub>x</sub> particles. The Pt–SiO<sub>2</sub> particles in ratios of 1:1 and 2:1 showed superior per-

formance towards the oxygen reduction reaction (ORR), and their performance in an H<sub>2</sub>-fuel cell was comparable to that of a Pt-black catalyst. Takenaka et al. [11] found that aggregation of Pt metal particles in catalysts during ethylene decomposition could be resisted by covering Pt with silica layers a few nanometers thick; these silica-coated Pt catalysts showed high catalytic activity for ethylene decomposition. Kim and Kohl prepared platinum–ruthenium glass electrodes (PtRu/C–SiO<sub>x</sub>) by incorporating PtRu/C nanoparticles into a silica-based matrix; the PtRu/C–SiO<sub>x</sub> glass electrodes improved catalytic activity for methanol oxidation and decreased methanol crossover [12]. Anderson et al. developed highly active Pt<sub>coi</sub>/C–SiO<sub>x</sub> catalysts with three-dimensional nanostructured architectures using carbon–silica composite aerogels; the electrocatalytic activity for methanol oxidation on Pt-modified carbon–silica composite was four times higher than that of Pt/C [13]. Niu and Wang synthesized macroscopic SiC nanowires (SiC-NWs) using a simple solid–vapor reaction of silicon powders and carbon oxides, assisted by ZnS. The novel Pt/SiCNW-supported catalyst showed high electrochemical activity towards methanol oxidation and oxygen reduction [14].

However, the above-mentioned literature has not addressed the addition of silicon oxide to supporting carbon materials, or Pt/C catalyst anti-aggregation during electrochemical reactions. In the present study, we investigate the effects of using silicon oxide loaded carbon as an electrocatalytic support, employing different silicon oxide loadings, heat-treatment temperatures, and heat-treatment times to assess the electrocatalytic activity and aggregation of Pt metal particles in Pt/C catalysts. Aggregation of Pt

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metal particles in catalysts during electrochemical reactions is suppressed by adding silicon oxide to the carbon powder. The silicon oxide loaded Pt/SiO<sub>x</sub>/C catalysts are characterized with TEM, XRD, and electrochemical measurements to understand silicon oxide's anti-aggregation and performance enhancing effects on the electrocatalysts.

## 2. Experimental

The silicon oxide modified carbon support (denoted as SiO<sub>x</sub>/C) was prepared as follows. Ethanol-diluted tetraethoxysilane (1 wt.%) was agitated to form a homogeneous solution; Vulcan XC-72R carbon (Cabot Corp., BET: 237 m<sup>2</sup> g<sup>-1</sup>, denoted as C) was added to the above solution to form a slurry, which was then dried at room temperature under stirring. Remaining ethanol was removed using further vacuum drying at 40 °C for 12 h, followed by baking at 300 °C in a tube furnace for 1.5 h under N<sub>2</sub> protection. Carbon without silica was also processed at 300 °C for 1.5 h under N<sub>2</sub> protection.

Preparation of Pt/SiO<sub>x</sub>/C was similar to that of PtPd@Pt/C reported in our previous publication [15]. Briefly, specific amounts of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and sodium citrate were dissolved in ethylene glycol, followed by the addition of as-prepared SiO<sub>x</sub>/C support and acetone. Under vigorous stirring with KOH/ethylene glycol, the pH value of the mixture was adjusted to above 10. The suspension was then transferred into a Teflon<sup>®</sup>-lined autoclave and conditioned at 120 °C for 6 h. After cooling to room temperature, 5% HNO<sub>3</sub> aqueous solution was used to adjust the pH to less than 3, followed by filtering, washing with de-ionized water, and vacuum drying at 90 °C. The nominal loading of platinum was 20 wt.% in all catalysts.

Information on particle size and shape as well as size distribution was obtained using transmission electron microscopy (TEM; JEOL JEM-2010HR, Japan) operated with an acceleration voltage of 200 kV.

X-ray diffraction (XRD) information was obtained with a Shimadzu XD-3A (Japan) X-ray diffractometer using a filtered Cu-Kα radiation source, operated at 35 kV and 30 mA. Diffraction patterns were collected between 20° and 80° at a scan rate of 4° min<sup>-1</sup> with a step size of 0.01°.

The electrochemical activity of the catalyst was evaluated by cyclic voltammetry (CV) using a three-electrode cell and collected with an IM6e electrochemical work station (Zahner, Germany) at room temperature. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The working electrode was glassy carbon disk (ca. 5 mm in diameter) pipetted with a thin layer of Nafion<sup>®</sup>-impregnated catalyst. The catalyst ink was prepared by dispersing 5 mg catalyst in 1 ml Nafion<sup>®</sup>/ethanol (0.25 wt.% Nafion<sup>®</sup>) using sonication for 20 min, after which 6 μl of the ink was transferred onto the glassy carbon disk using a pipette. CV testing was conducted in a solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> or 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH in the potential range of -0.2 to 1.0 V at 50 mV s<sup>-1</sup>. The results were recorded after a stable response was established. Pt loading of the catalyst on the electrode surface was 0.0031 mg Pt cm<sup>-2</sup>.

## 3. Results and discussion

### 3.1. Effects of silicon oxide loading amount on anti-aggregation and electrochemical performance of the catalysts

XRD patterns of the different Pt/SiO<sub>x</sub>/C are shown in Fig. 1. The diffraction peak at 25° can be attributed to the graphitic nature of the carbon support in all the catalysts. The Pt (111) peak at about 40° is clearly observable but notably weak, while the Pt (200), (220), and (311) peaks are broadened and almost unobservable, features that indicate very small Pt particle sizes [16,17].

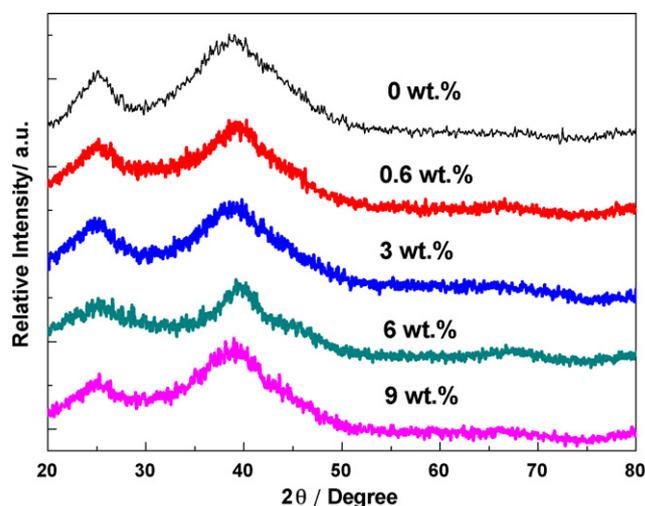


Fig. 1. XRD patterns of Pt/SiO<sub>x</sub>/C with different silicon oxide loadings in the catalysts.

The flattened diffraction peaks make it impossible to evaluate the Pt particle sizes using the Debye–Scherrer equation.

For electrocatalysts, the electrochemically active surface area (ECSA) matters more than the geometric surface area of the work-

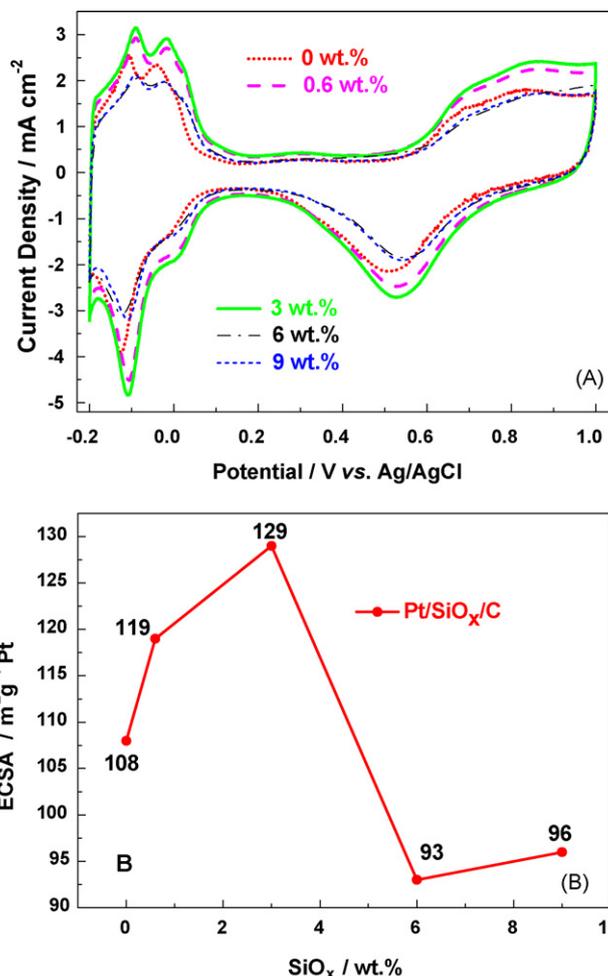
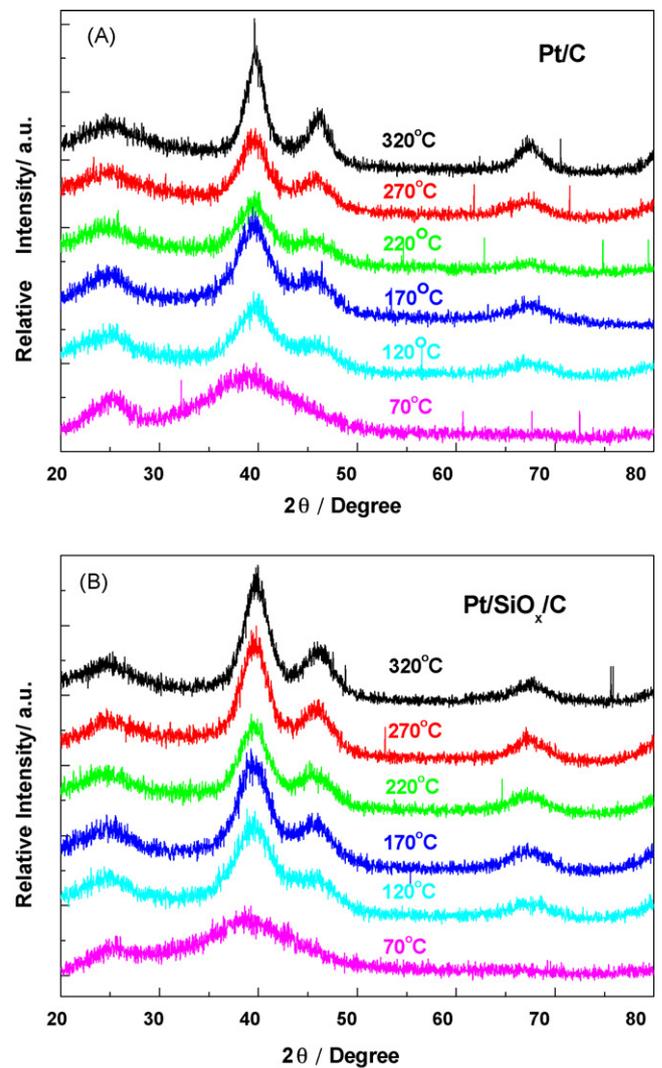
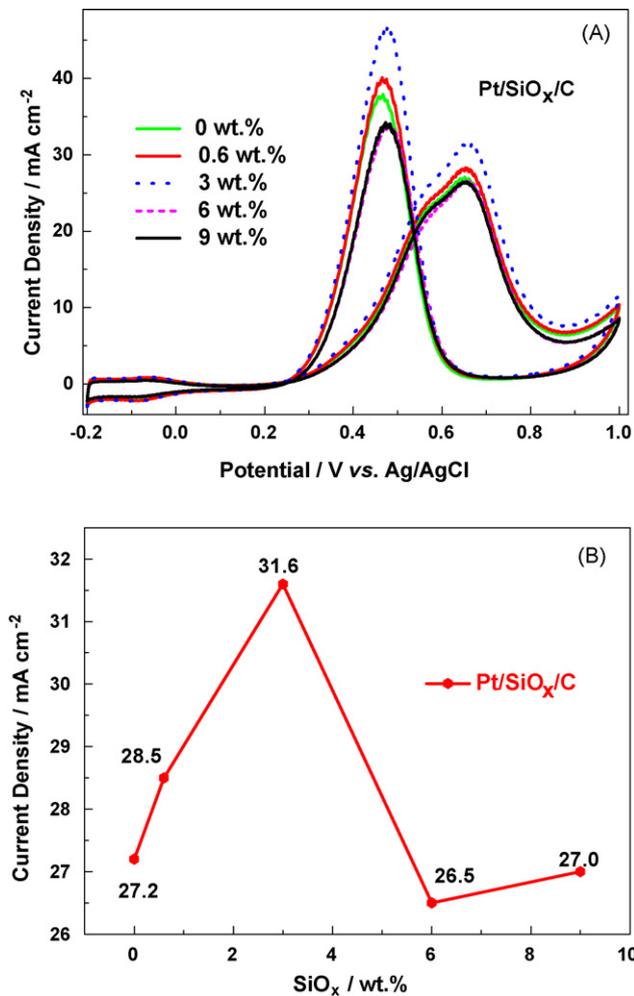
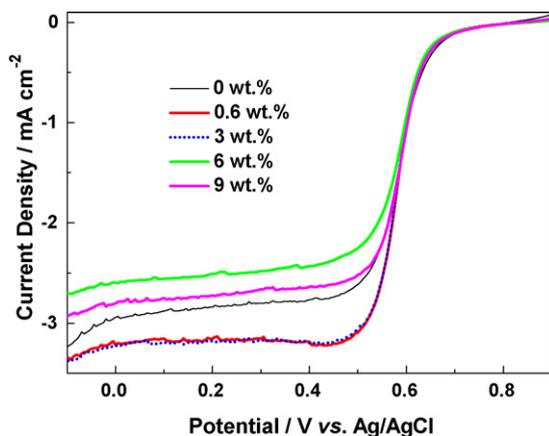


Fig. 2. Cyclic voltammograms of Pt/C and Pt/SiO<sub>x</sub>/C catalysts measured at room temperature and in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with a sweep rate of 50 mV s<sup>-1</sup> (A); the relationship between the electrochemically active surface areas and the silicon oxide load amounts in the catalysts (B).

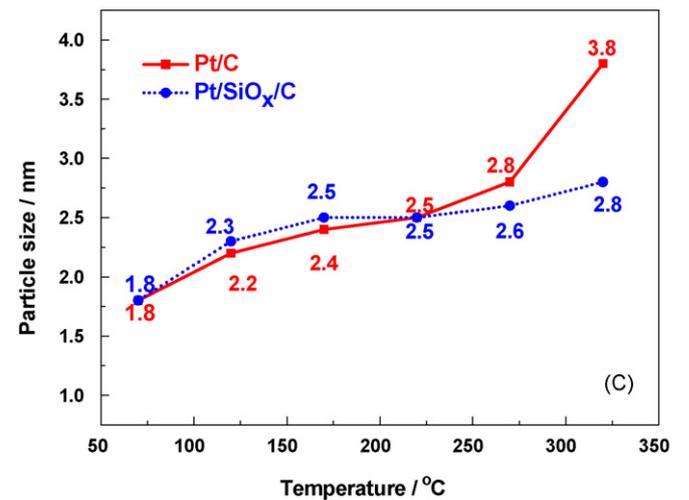


**Fig. 3.** Cyclic voltammograms of Pt/C and Pt/SiO<sub>x</sub>/C catalysts with various silicon oxide loadings, measured at room temperature and in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH solution with a sweep rate of 50 mV s<sup>-1</sup> (A); the relationship between catalytic activities for methanol anodic oxidation and silicon oxide loaded amounts in the catalysts (B).

ing electrode. To evaluate the ECSA, 0.5 M sulfuric acid was used as the electrolyte and purged of oxygen using high-purity nitrogen before reproducible cyclic voltammograms were recorded. Fig. 2A shows the room temperature cyclic voltammograms of the cata-



**Fig. 4.** Polarization curves of oxygen on Pt/C and on Pt/SiO<sub>x</sub>/C with various silicon oxide loadings, at room temperature and in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, with a sweep rate of 5 mV s<sup>-1</sup> and a rotation speed of 1600 rpm.



**Fig. 5.** XRD patterns of Pt/C (A) and 3 wt.% silicon oxide loaded Pt/SiO<sub>x</sub>/C (B) heated at different temperatures; the relationship between particle sizes and heating temperatures (C).

lysts measured in 0.5 M sulfuric acid at a scan rate of 50 mV s<sup>-1</sup>. The relationship between ECSA and the different SiO<sub>x</sub> content in the carbon support is shown in Fig. 2B. It can be seen that addition of 0.6% and 3% SiO<sub>x</sub> to the carbon support increased the ECSA from

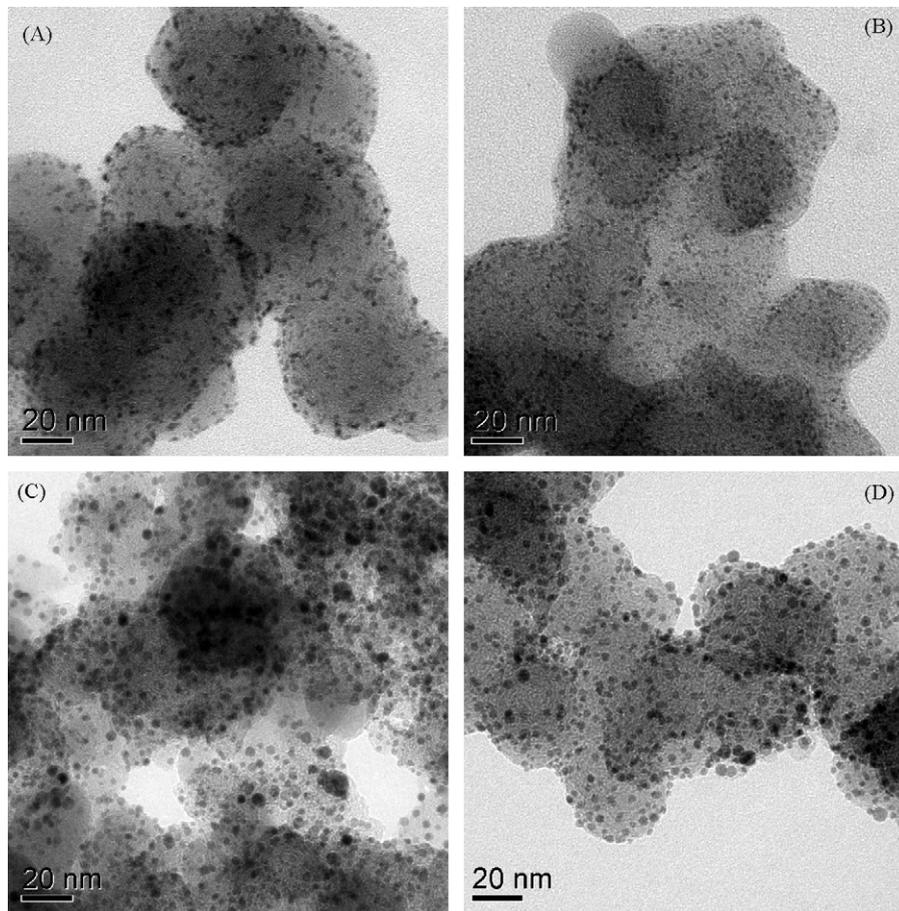


Fig. 6. TEM images of Pt/C heated at 70 °C (A) and 320 °C (C); 3 wt.% silicon loaded Pt/SiO<sub>x</sub>/C catalyst heated at 70 °C (B) and 320 °C (D).

108 m<sup>2</sup> g<sup>-1</sup> to 119 and 129 m<sup>2</sup> g<sup>-1</sup> Pt, respectively. Greater ECSA means better proton accessibility to the Pt sites. Further addition of silicon oxide to the carbon support led to decreased ECSA, possibly because the silicon oxide blocked Pt sites.

Fig. 3A shows room temperature cyclic voltammograms of the catalysts measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH at room temperature, while Fig. 3B presents the relationship between silicon oxide content and surface area normalized mass activity. It is clear that compared with Pt/C (27.2 mA cm<sup>-2</sup>), the addition of 0.6 and 3 wt.% silicon oxide into the carbon support significantly increased the catalysts' mass activity, with a maximum current density of

31.6 mA cm<sup>-2</sup> for Pt/SiO<sub>x</sub>/C containing 3 wt.% silicon oxide. Positive effects were only achieved with low silicon oxide content; further addition (higher than 3 wt.%) led to decreased activity. At the optimized silicon oxide content (3 wt.%), a balance was achieved between silicon oxide's positive anti-aggregating effects and negative electronic channel interruption effects. Above 3 wt.%, the loss of electronic channels led to decreased ECSA and consequently decreased mass activity for the MOR. It should be noted that the carbon supports for all the catalysts were treated at 300 °C; therefore, the treatment effects of temperature on carbon can be excluded.

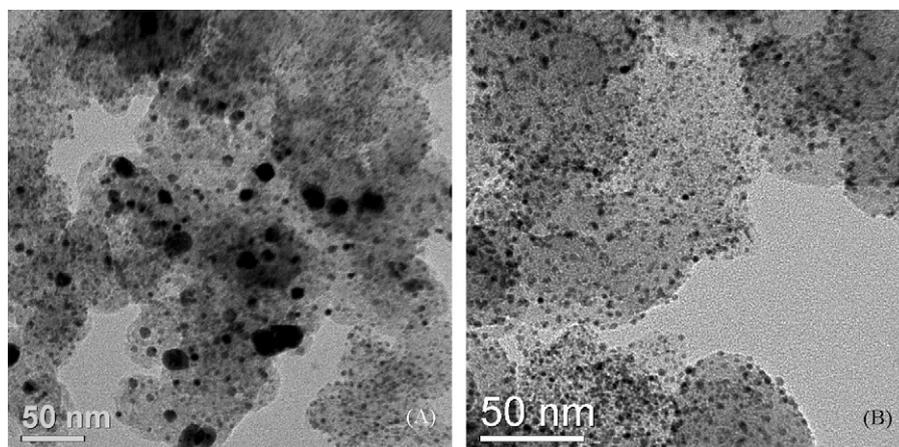


Fig. 7. TEM images of Pt/C (A) and 3 wt.% silicon oxide loaded Pt/SiO<sub>x</sub>/C (B) heated at 320 °C for 15 h.

The catalytic behavior of the Pt/SiO<sub>x</sub>/C electrodes towards the ORR is demonstrated in Fig. 4. It is unsurprising that the electrode prepared with catalyst Pt/SiO<sub>x</sub>/C (3 wt.% silicon oxide), which has the largest ECSA, exhibited the best catalytic behavior for the ORR. When the silicon oxide load was increased to 6 wt.%, no obvious increase in ORR activity was observed. However, both activities were higher than that of Pt/C. The enhanced catalytic activity towards the MOR and ORR on optimized Pt/SiO<sub>x</sub>/C (3 wt.%), as indicated above, was possibly due to improved mass transportation of fuel or oxygen at the electrode surface. As a combined result, Pt/SiO<sub>x</sub>/C catalyst with 3 wt.% silicon oxide loading showed the highest ECSA and consequently the best mass activity towards the MOR and ORR [18].

### 3.2. The effects of heat-treatment temperature on anti-aggregating and electrochemical performance

To investigate the anti-aggregation effect of silicon oxide on the catalysts' active components, the consequences of heat-treatment for the catalytic activity of Pt/C and 3 wt.% silicon oxide loaded Pt/SiO<sub>x</sub>/C were investigated in detail. Both catalysts were heated in a nitrogen atmosphere at different temperatures, in 50° intervals. Fig. 5 presents XRD patterns for Pt/C and Pt/SiO<sub>x</sub>/C catalysts with and without heat treatment at different temperatures. Compared with the as-prepared catalysts, the diffraction peak corresponding to Pt (200) for the as-heated catalysts is more distinct in the temperature range 120–320°C due to increased platinum particle size, caused by the sintering effects of heat treatment. Generally, the intensity increased with temperature. However, the Pt/SiO<sub>x</sub>/C catalyst showed a weak and flattened Pt (200) peak compared with that of Pt/C without silicon oxide when subjected to the same heating temperature. This means that the particle sizes in Pt/SiO<sub>x</sub>/C are more resistant to sintering than in Pt/C. This experimental result is presented in Fig. 5C: the Pt particle size in the Pt/SiO<sub>x</sub>/C catalyst, read from Jade software, was 1.8, 2.3, 2.5, 2.5, 2.6, and 2.8 nm for the as-prepared catalyst heated at 120, 170, 220, 270, and 320°C, respectively. For comparison, the particle size of Pt/C increased to 3.8 nm when heated at 320°C.

Fig. 6 compares the TEM images of as-prepared and as-heated (320°C) Pt/C and Pt/SiO<sub>x</sub>/C with 3 wt.% silicon oxide. It can be seen that Pt nanoparticles were well dispersed on the support and showed quite a uniform size distribution. Both the as-prepared Pt/C and Pt/SiO<sub>x</sub>/C catalysts had similar particle sizes, confirmed by the XRD observations presented in Fig. 1. But after heat treatment, the aggregation of platinum particles in the Pt/SiO<sub>x</sub>/C catalyst was less severe than in Pt/C heated at the same temperature, confirming that adding silicon oxide prevents the growth, migration, and aggregation of platinum nanoparticles in catalysts at high temperatures.

To further investigate the thermal stability of Pt/C and Pt/SiO<sub>x</sub>/C over prolonged time, the catalysts were thermally treated at 320°C for 15 h. Fig. 7 shows TEM images of treated Pt/C and Pt/SiO<sub>x</sub>/C. Observable particle size differences occurred for both catalysts: Pt/C thermally treated for 15 h shows obvious particle aggregation, and several particles up to ca. 30 nm are clearly visible; however, for Pt/SiO<sub>x</sub>/C the particle sizes remain at just several nanometers, and quite good particle dispersion is observable.

To evaluate the effects of heat-treatment temperature on electrochemical activity, the catalysts were tested for methanol anodic oxidation; the resulting cyclic voltammograms at room temperature are shown in Fig. 8. Pt/SiO<sub>x</sub>/C exhibited higher activity towards the anodic oxidation of methanol than did Pt/C for the same temperature, possibly due to the interconnected particle network that maximized the ECSA of Pt/SiO<sub>x</sub>/C. For Pt/C, activity towards the MOR decreased from 22.0 to 14.9 mA cm<sup>-2</sup> (a decrease of 32.3%) as

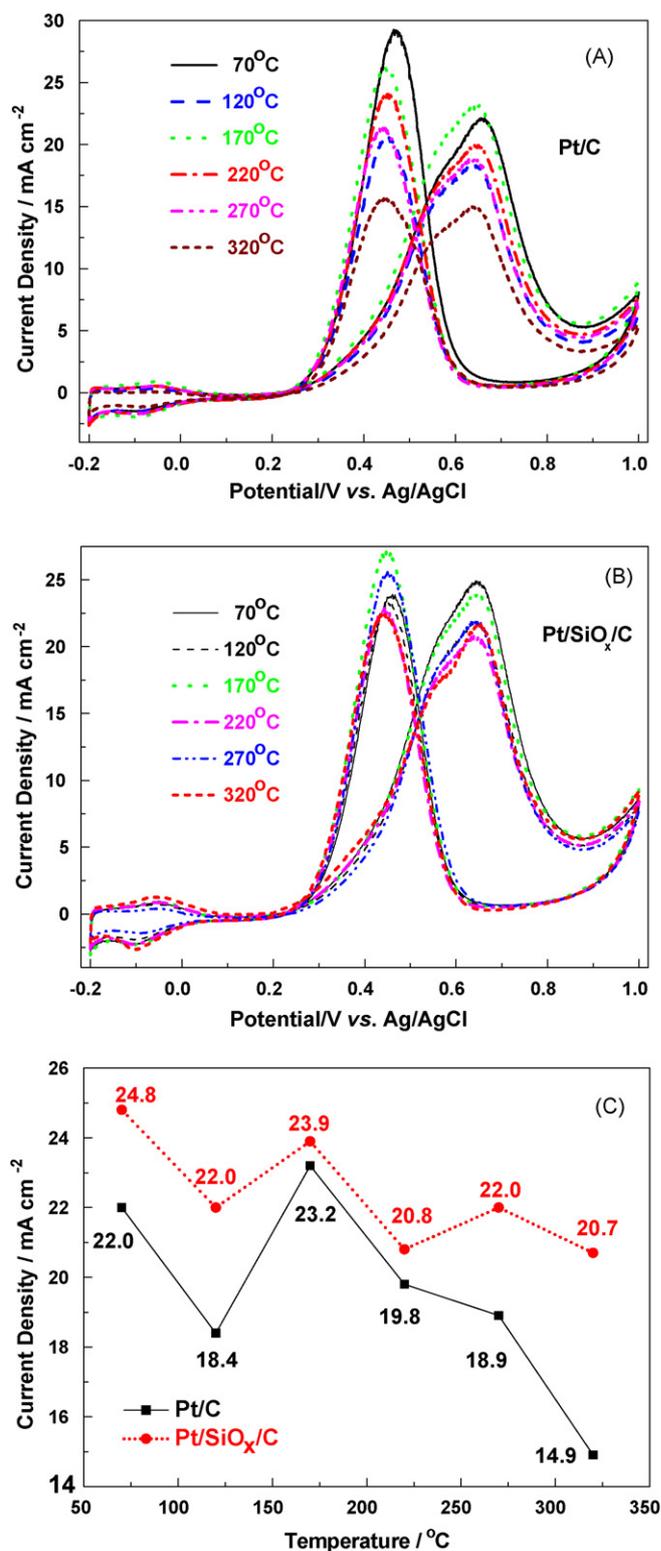


Fig. 8. Cyclic voltammograms of heated Pt/C (A) and Pt/SiO<sub>x</sub>/C (B) measured at room temperature and in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH solution, with a sweep rate of 50 mV s<sup>-1</sup>; (C) relationship between the peak current densities and heating temperatures.

the treating temperature increased to 320°C. Although a drop in mass activity also took place for Pt/SiO<sub>x</sub>/C, the decrease was more moderate, from 24.8 to 20.7 mA cm<sup>-2</sup> (only 16.5%). Pt/SiO<sub>x</sub>/C thus demonstrated better stability towards thermal treatment, implying that appropriate amounts of silicon oxide in the carbon supports of

platinum catalysts will effectively prevent the aggregation of active components, and result in better long-term performance for fuel cells.

#### 4. Conclusions

Pt/C and Pt/SiO<sub>x</sub>/C catalysts were prepared by a colloidal method using carbon and silicon oxide doped carbon as supports, respectively. The catalysts were subjected to post-heat treatment at different temperatures and for various holding times. The MOR and ORR were used as probe reactions to test the catalytic activity at room temperature. It was found that the optimum silicon oxide load amount in carbon was about 3 wt.%, which led to enhanced ECSA and consequently improved mass activity. The improved activity for Pt/SiO<sub>x</sub>/C with 3 wt.% silicon oxide was attributable to anti-aggregation effects upon active components.

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