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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.

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_{ads} 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_x) 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_x particles. The Pt–SiO_2 particles in ratios of 1:1 and 2:1 showed superior performance towards the oxygen reduction reaction (ORR), and their performance in an H_2-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_x) by incorporating PtRu/C nanoparticles into a silica-based matrix; the PtRu/C-SiO_x glass electrodes improved catalytic activity for methanol oxidation and decreased methanol crossover [12]. Anderson et al. developed highly active Pt_{coll}/C-SiO_x 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_x/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_x/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 $m^2\,g^{-1}$, 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_2 protection. Carbon without silica was also processed at 300 °C for 1.5 h under N_2 protection.

Preparation of Pt/SiO_x/C was similar to that of PtPd@Pt/C reported in our previous publication [15]. Briefly, specific amounts of $H_2PtCl_6{\cdot}6H_2O$ and sodium citrate were dissolved in ethylene glycol, followed by the addition of as-prepared SiO_x/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®-lined autoclave and conditioned at 120 °C for 6 h. After cooling to room temperature, 5% HNO_3 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^{-1} 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®-impregnated catalyst. The catalyst ink was prepared by dispersing 5 mg catalyst in 1 ml Nafion®/ethanol (0.25 wt.% Nafion®) 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_2SO_4 or 0.5 M H_2SO_4 + 0.5 M CH_3OH in the potential range of −0.2 to 1.0 V at 50 mV s^{-1}. 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^{-2}.

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_x/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 (1 1 1) peak at about 40° is clearly observable but notably weak, while the Pt (2 0 0), (2 2 0), and (3 1 1) peaks are broadened and almost unobservable, features that indicate very small Pt particle sizes [16,17]. The flattened diffraction peaks make it impossible to evaluate the Pt particle sizes using the Debye–Scherrer equation.

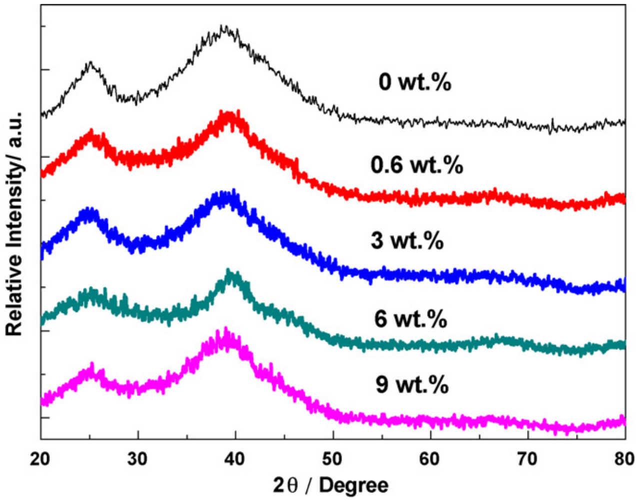

Fig. 1. XRD patterns of Pt/SiO_x/C with different silicon oxide loadings in the catalysts.

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

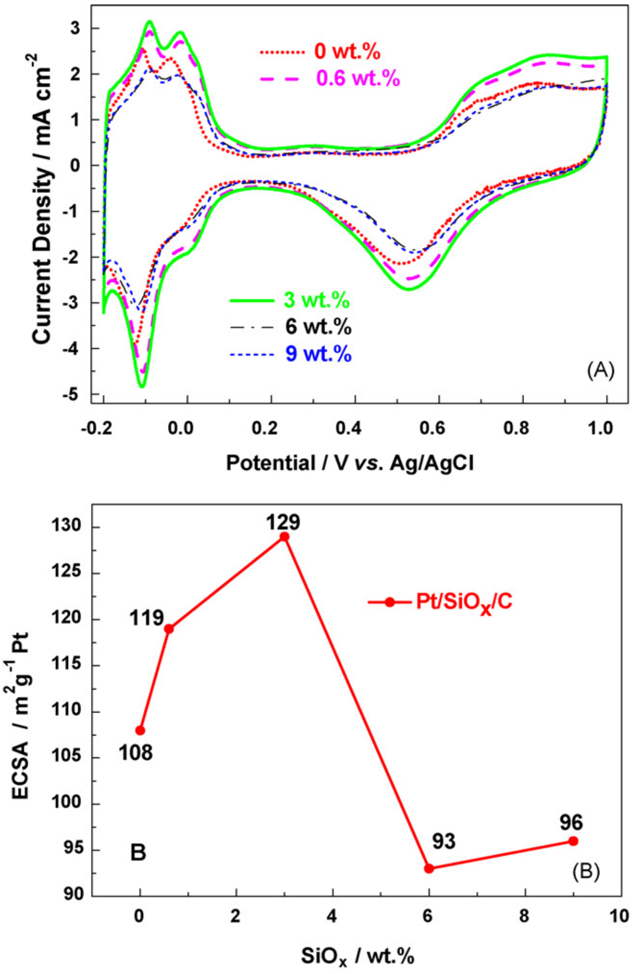

Fig. 2. Cyclic voltammograms of Pt/C and Pt/SiO_x/C catalysts measured at room temperature and in 0.5 M H_2SO_4 solution with a sweep rate of 50 mV s^{-1} (A); the relationship between the electrochemically active surface areas and the silicon oxide load amounts in the catalysts (B).