SnO₂ nanocluster supported Pt catalyst with high stability for proton exchange membrane fuel cells

Meiling Dou a,b, Ming Hou a,∗, Dong Liang c, Wangting Lu a, b, Zhigang Shao a,∗∗, Baolian Yi a

a Fuel Cell System and Engineering Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
b Graduate University of Chinese Academy of Sciences, Beijing 100049, China
c Sunrise Power Co., Ltd, Dalian 116023, China

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A B S T R A C T
Tin oxide nanocluster (SnO₂) with parallel nanorods was synthesized via a hard template method and explored as the anode catalyst support for proton exchange membrane fuel cells (PEMFCs). Single cell test demonstrated that SnO₂ supported Pt catalyst (Pt/SnO₂) exhibited comparable anode performance with conventional Pt/C. Electrochemical measurements showed that Pt/SnO₂ exhibited significantly enhanced electrochemical stability than Pt/C under high potential electro-oxidation and potential cycling. The Pt/SnO₂ catalyst reserved most of its electrochemically active surface area (ECA) under 10 h potential hold at 1.6 V while its ECA degradation rate was one order of magnitude lower than Pt/C under potential cycling between 0.6 and 1.2 V. Therefore, SnO₂ nanocluster can be considered as a promising alternative anode catalyst support for PEMFCs.

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1. Introduction
Durability is currently an important issue in proton exchange membrane fuel cells (PEMFCs) [11]. One of the major challenges lies in the degradation caused by the corrosion of carbon support [2]. Although carbon materials are widely used as electrocatalyst supports because of the high surface area and good electronic conductivity, they are apt to undergo electrochemical oxidation under the practical operation of PEMFCs. Carbon corrosion could weaken the attachment of Pt particles on support, decrease the electronic continuity of the catalyst layer, and consequently result in a rapid degradation of the cell performance. There are intensive works devoted to the research and development of robust cathode catalyst supports [3–5]. Carbon corrosion, however, is also critical at the anode side. When fuel starvation happens, hydrogen is no longer sufficient to be oxidized to maintain the current, raising the anode potential to as high as 1.6 V [6–9]. At such high potentials, carbon oxidation would be initiated and consequently cause the degradation of the cell performance. Therefore, it would be desirable to use more stable carbon-free support to improve the durability of the catalyst.

Tin oxide (SnO₂), with n-type semiconducting property and good electrochemical stability, has been proposed as a potential catalyst support material for fuel cell application [10–18]. Previous studies have shown that SnO₂ can promote the electro-oxidation of CO, methanol, and ethanol due to the formation of OH species at low potentials and the strengthened metal-support interaction [19,20]. There are also works reporting the usage of SnO₂ as a stable catalyst support for the oxygen reduction reaction (ORR). Zhang et al. [16] and Masao et al. [17] investigated the electrochemical stability of SnO₂ nanoparticles as PEMFC cathode catalyst support, and found that SnO₂ had much higher corrosion resistance than carbon. As catalyst support, the stability of SnO₂ as the catalyst support for hydrogen oxidation in PEMFCs also needs to be studied in detail.

Our previous work showed that, using WO₃ nanocatalysts as the Pt support yielded a highly stable and active anode catalyst for PEMFCs [21]. However, the surface areas of the prepared WO₃ nanocatalysts was low (47 m² g⁻¹). In this work, we report a facile synthesis of SnO₂ nanocluster with large surface area (127.7 m² g⁻¹) by using mesoporous silica (SBA-15) as the hard template, and use it as anode catalyst support for PEMFCs. Compared with the commonly used Pt/C, the Pt/SnO₂ catalyst demonstrates excellent stability under both high-potential (1.6 V) hold and potential cycling (0.6–1.2 V), indicating its promising application for PEMFCs.

2. Experimental
2.1. Material synthesis

The SnO₂ nanoclusters were prepared using SBA-15 (described in our previous work [21]) as the template and tin (II) chloride
dihydrate (SnCl₂·2H₂O) as the tin precursor, according to Shon et al. [22]. Typically, 2 g of SBA-15 was activated at 100 °C for 1 h in a single-necked flask, and then 3.06 g of SnCl₂·2H₂O (m. p. 37–38 °C) was poured into the flask. The flask containing the pre-heated silica template and SnCl₂·2H₂O was sealed and shaken vigorously. Subsequently, the flask was heated at 80 °C for 12 h, and then the sample was calcined at 700 °C for 3 h to promote the formation of tin oxide inside the SBA-15 channels. The SBA-15 template was removed by dissolving in HF aqueous solution. After centrifugation and washing with copious distilled water, and vacuum drying at 60 °C, SnO₂ nanocluster was obtained.

The Pt/SnO₂ catalyst was prepared via the polylol method. Typically, 12.58 mg H₂PtCl₆·6H₂O was dissolved in 30 mL ethylene glycol containing 7 mmol NaOH, and stirred for 30 min. The mixture was then heated for 1 min in a microwave oven to promote the reduction of Pt⁴⁺ to Pt nanoparticles. The Pt colloidal thus obtained was added to the SnO₂ nanocluster dispersed in distilled water, followed by the addition of nitric acid. The pH of the final mixture is about 2. After 24 h stirring, the precipitate was washed with water and dried at 60 °C under vacuum. The Pt loading of the prepared Pt/SnO₂ catalysts was measured 14 wt.% according to the measurement of inductively coupled plasma atomic emission spectrometry (ICP-AES). For comparison, Pt/C with the same Pt loading was also prepared.

2.2. Material characterizations

X-ray diffraction (XRD) measurements were carried out using a Cu Kα source (Phillips X’ pert Pro X-ray diffractometer) operated at 40 kV and 30 mA. The Brunauer–Emmet–Teller (BET) area and pore size distribution were estimated using a Micromeritics ASAP 2010 system. Transmission electron microscope (TEM) characterization was performed on a JEOL JEM-2000EX microscope. Elemental analysis was carried out on a JEOL 6360LV scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDX). X-ray photoelectron spectroscopy (XPS) spectra were measured with a VG ESCALAB MK2 spectrometer using an Al Kα source operated at 12.5 kV and 250 W, and the binding energies were referenced to the C 1s peak from adventitious hydrocarbon contamination set at 284.6 eV.

2.3. Electrochemical measurements

All electrochemical measurements were conducted using a CHI730 electrochemical station. Pt sheet and saturated calomel electrode (SCE) were employed as the counter and reference electrode, respectively. All the potentials, however, are given versus the normal hydrogen electrode (NHE). Working electrode was prepared by coating appropriate amount of electrocatalyst and Nafion® on the glassy carbon electrode (d = 4 mm) according to the literature [23,24]. Catalyst ink was obtained by sonicating 5 mg catalyst, 50 μL Nafion® solution (5 wt.%, Alfa Aesar), and 1 mL ethanol into homogeneous slurry. Then, 10 μL of the ink was transferred onto the glassy carbon electrode and the Pt loading was ca. 56 μg cm⁻². Cyclic voltammetry (CV) was profiled in 0.5 M H₂SO₄ solution de-aerated with high purity N₂ in the potential range of 0 and 1.2 V at a scan rate was 50 mV s⁻¹.

A constant potential of 1.6 V and a potential cycling test from 0.6 V to 1.2 V were conducted to examine the electrochemical stability of the catalysts, respectively. The electrochemical surface area (ECA) of catalysts was estimated according to the charge of hydrogen desorption after double-layer correction, assuming monolayer hydrogen adsorption on Pt surface (0.21 mC cm⁻²).

2.4. Single cell test

Commercially available catalyzed gas diffusion layer (0.4 mg Pt cm⁻², JM 40% Pt/C) was used as the cathode for all single cell assembly. The anode (0.2 mg Pt cm⁻²) was prepared by brushing desired amount of Pt/SnO₂ or Pt/C catalyst ink onto the gas diffusion layer. Homogeneous catalyst ink was prepared by sonicating the catalyst with Nafion® solution (5 wt.%, Alfa Aesar) in ethanol for at least 2 h. A Nafion® 212 membrane (DuPont) was sandwiched between the anode and cathode and hot-pressed at 140 °C 0.1 MPa for 1 min to obtain the membrane electrode assembly (MEA). Single cell of 5 cm² active area was operated at 60 °C with fully humidified reactants (flow rates were 20/100 mL min⁻¹.

![Fig. 1. XRD patterns of the SnO₂ and SnO₂-supported Pt.](image)

![Fig. 2. (a) Nitrogen adsorption/desorption isotherms and (b) the corresponding pore size distribution of SnO₂ and Pt/SnO₂ support.](image)
for H\textsubscript{2}/O\textsubscript{2}). The operating pressures were kept at 0.05 MPa for both electrodes.

3. Results and discussion

3.1. Structural characteristics

Fig. 1 shows the XRD patterns of synthesized SnO\textsubscript{2} nanocluster and Pt/SnO\textsubscript{2} catalyst. The SnO\textsubscript{2} nanocluster shows well-resolved peaks at 26.8°, 34.2°, 38.3°, and 52.2° which can be respectively indexed to the (1 1 0), (1 0 1), (2 0 0), and (2 1 1) reflections of cassiterite SnO\textsubscript{2}. The presence of metallic Pt for Pt/SnO\textsubscript{2} is also clearly revealed by the peak at 39.9° and 46.2° attributed to the Pt [1 1 1] and [2 0 0] reflection, respectively. The broadening of two peaks indicates the small particle size of Pt.

Fig. 2 displays the nitrogen sorption (adsorption and desorption) isotherms and the corresponding Barrett–Joyner–Halenda (BJH) pore size distributions for SnO\textsubscript{2} and Pt/SnO\textsubscript{2}. As can be observed, SnO\textsubscript{2} and Pt/SnO\textsubscript{2} mainly possess pores in the range of 9–12 nm, which indicates the presence of mesopores. The BET surface area of SnO\textsubscript{2} is 127.7 m\textsuperscript{2} g\textsuperscript{−1} and the total pore volume is 0.35 cm\textsuperscript{3} g\textsuperscript{−1}. These values dropped to 113.6 m\textsuperscript{2} g\textsuperscript{−1} and 0.25 cm\textsuperscript{3} g\textsuperscript{−1} after the Pt loading.

As revealed by TEM characterization, SnO\textsubscript{2} is uniformly distributed inside the channels of SBA-15 after calcination at 600 °C for 4 h (Fig. 3b). After the removal of template, the remaining SnO\textsubscript{2} inversely replicated the structure of SBA-15 (Fig. 3c), resulting with a bundle of parallel nanorods. The diameter of each nanorod is ca. 8.0 nm. This value is consistent with the SBA-15 channel size (7–9 nm) (Fig. 3a). EDX analysis of SnO\textsubscript{2} indicates very weak signal of Si, which implies the relatively complete removal of the template.

Fig. 4a shows typical TEM images of the Pt/SnO\textsubscript{2} sample. It can be seen that the Pt particles are well dispersed on SnO\textsubscript{2} nanocluster. The sizes of Pt particles are in the range of 1–3 nm according to statistical measurement of random chosen areas.

3.2. Electrochemical properties

The catalytic performance of Pt/SnO\textsubscript{2} at PEMFC anode was first demonstrated by single cell test. The Pt loading was controlled at 0.2 mg cm\textsuperscript{−2}. The polarization curves in Fig. 5 indicate a comparable cell performance with Pt/SnO\textsubscript{2} anode and the commonly used Pt/C anode. Even at high current of 1 A cm\textsuperscript{−2}, the voltage of the single cell with Pt/SnO\textsubscript{2} anode remains very close to that with Pt/C. Therefore, the electrode performance of Pt/SnO\textsubscript{2} can qualify the practical PEMFC anode use.

The durability of Pt/SnO\textsubscript{2} was then studied using the electrochemical measurements. Fig. 6 shows the CVs of SnO\textsubscript{2}, Pt/SnO\textsubscript{2}, XC-72 and Pt/C before and after oxidation treatment at an elevated potential (1.6 V for 10 h). It was reported that, under fuel starvation, the anode potential can reach to as high as 1.6 V. At such high potential, the traditionally used carbon supports would corrode severely [6–9]. As shown in Fig. 6a, a significant decrease of the hydrogen

![Fig. 3. TEM images of (a) mesoporous silica SBA-15, (b) SnO\textsubscript{2} nanocluster supported on SBA-15, (c) SnO\textsubscript{2} nanocluster after removal of the SBA-15 silica material using aqueous HF as etching reagent, and (d) EDX spectrum of the SnO\textsubscript{2} nanocluster.](image-url)
Table 1
Durability study results.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Potential hold</th>
<th>Potential cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SnO₂</td>
<td>11.3%</td>
<td>23.0%</td>
</tr>
<tr>
<td>Pt/C</td>
<td>64.7%</td>
<td>99.6%</td>
</tr>
</tbody>
</table>

Fig. 4. Typical TEM image (a) and EDX spectrum (b) of Pt/SnO₂.

Fig. 5. Polarization and power density curves of the PEM fuel cells with the different anode electrocatalysts (Pt/SnO₂ and Pt/C). Measurements were taken at 60 °C with fully humidified reactants (flow rate was 20/100 mL min⁻¹ for H₂/O₂) and at 0.05 MPa. Pt loading was controlled at 0.2 mg cm⁻² on the anode side and 0.4 mg cm⁻² on the cathode side.

desorption current (at 0−0.4 V) occurs for the Pt/C catalyst. The ECA diminished to its initial 35.3% (see Table 1). This effect is attributed to the detachment and agglomeration of Pt nanoparticles caused by the carbon corrosion. The high potential oxidation also results in the increase of surface functionalized groups (i.e., −OH, −COOH) on carbon, which is evident by the broadened double layer and the redox couple at ca. 0.6 V for XC-72, indicating that severe carbon corrosion has occurred.

While for the Pt/SnO₂, it is observed that only a negligible change of CV is observed, indicating its good resistance against oxidation when subjected to high potentials. After the high potential oxidation, the Pt/SnO₂ reserved as much as 89.7% of its initial ECA and the CV of SnO₂ seldom changed, indicating that the use of SnO₂ as a catalyst support significantly improved the catalyst resistance against high potential. According to the literature [16,17], SnO₂ is the most stable compound in the Sn−H₂O system at 80 °C which is similar to typical PEMFC operation conditions.

It is noted that the response corresponding to the Pt oxidation/reduction for the Pt/SnO₂ catalyst is not obviously seen. In fact, the peaks corresponding to Pt oxidation/reduction could be observed after magnifying the CV curve in the high potential region. The small peak value may be partially ascribed to the low conductivity of the SnO₂ support and the electrons cannot be supplied
sufficiently [18]. On the other hand, this effect has also been attributed to the strong interaction between the Pt and the oxide support [25–28]. A further XPS characterization is carried out to detect the interaction between Pt and the SnO₂ support. As shown in Fig. 7, the Pt4f7/2 binding energy for the Pt/SnO₂ catalyst was lowered by 0.9 eV compared with the Pt/C catalyst, indicating the electron transfer between Pt and SnO₂. Therefore, it is inferred that the origin of the absence of the Pt oxidation and oxide reduction is due to the poor conductivity of the SnO₂ as well as the strong interaction between Pt and SnO₂, which inhibits the formation of PtO.

Fig. 8 shows the chronoamperometric curves of Pt/SnO₂ and Pt/C under constant potential (1.6 V for 2 h). As seen, the corrosion current of Pt/SnO₂ is approximately 0.0031 mA cm⁻², which is 94.7% less than that of Pt/C (ca. 0.059 mA cm⁻²). These results indicate that the SnO₂ nanocluster has higher electrochemical stability than the carbon support. The durability of Pt/SnO₂ was also evaluated by an accelerated stress test based on CV cycling. Fig. 9 shows the CV curves of Pt/C and Pt/SnO₂ during the programmed CV cycle between 0.6 and 1.2 V. The normalized ECAs versus the cycle numbers are calculated in Fig. 10. It can be seen that the ECA of Pt/C decreases rapidly during CV cycling, and only 0.4% of the initial ECA was reserved after 1800 cycles. As for Pt/SnO₂, however, the ECA exhibited a very slow decrease and reserved 77% after the same CV cycles. Further tested to as high as 12,000 cycles, Pt/SnO₂ still has 27% retention of its initial ECA. The ECA degradation during CV cycling can be simulated using an exponent function:

$$y = e^{-At}$$

(1)

where y is the normalized ECA, A is the ECA degradation rate (percentage per cycle), and t represents the cycle number. The calculated degradation rate of Pt/C was 0.29%, which is 24.5 fold higher than that of Pt/SnO₂ (see Table 1). Hence, Pt/SnO₂ also possesses excellent stability under potential cycling.

4. Conclusions

To summarize, we have synthesized the SnO₂ nanocluster structured by parallel nanorods via a hard template method and used it as anode catalyst support for PEMFCs. The Pt/SnO₂ catalyst demonstrated comparable performance to Pt/C and exhibited superior
electrochemical stability. Pt/SnO₂ reserved most of its ECA under 10h potential hold at 1.6 V while its ECA degradation rate was one order of magnitude lower than conventional Pt/C under potential cycling. Hence, the SnO₂ nanocluster can be considered as a robust anode catalyst support for PEMFCs.

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References