A Highly Stable Anode, Carbon-Free, Catalyst Support Based on Tungsten Trioxide Nanoclusters for Proton-Exchange Membrane Fuel Cells

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Durability is an important issue in proton-exchange membrane fuel cells (PEMFCs). One of the major challenges lies in the degradation caused by the oxidation of the carbon support under high anode potentials (under fuel starvation conditions). Herein, we report highly stable, carbon-free, WO3 nanoclusters as catalyst supports. The WO3 nanoclusters are synthesized through a hard template method and characterized by means of electron microscopy and electrochemical analysis. The electrochemical studies show that the WO3 nanoclusters have excellent electrochemical stability under a high potential (1.6 V) for 10 h) compared to Vulcan XC-72. Pt nanoparticles supported on these nanoclusters exhibit high and stable electrocatalytic activity for the oxidation of hydrogen. The catalyst shows negligible loss in electrochemically active surface area (ECA) after an accelerated durability test, whereas the ECA of the Pt nanoparticles immobilized on conventional carbon decreases significantly after the same oxidation condition. Therefore, Pt/WO3 could be considered as a promising alternative anode catalyst for PEMFCs.

Introduction

Durability appears to be one of the barriers of PEMFC commercialization.[1] There are several factors that affect the durability of PEMFCs, including Pt particle dissolution and sintering, carbon support corrosion, and membrane thinning.[2] Among these factors, the issue of electrochemical carbon corrosion is considered to be one of the major contributors.[3]

Although carbon materials are widely used in fuel cells as the key electrocatalyst supports due to their high specific surface area and conductivity, such carbon supports are vulnerable to undergo electrochemical oxidation under corrosive conditions used during practical operation. Extensive research has been carried out on the improvement of the material of the cathodic catalyst supports,[4–6] but little attention has been paid to the catalyst support of the anode. Carbon support oxidation, however, also occurs at the anode side. When fuel starvation occurs, hydrogen oxidation is no longer sufficient to maintain the current, and then the anode potential can reach as high as 1.6 V.[7–9] Such a high potential would accelerate the kinetics of electrochemical carbon corrosion at the anode and lead to significant degradation of the fuel cell. In addition, the carbon corrosion at the anode could weaken the attachment of Pt particles to the carbon support and decrease the electronic continuity of the catalyst layer. Moreover, the existence of Pt particles could also accelerate carbon corrosion.[10,11] These effects would result in a rapid degradation of the Pt catalyst and thus shorten the lifetime of the PEMFC. Therefore, more robust, carbon-free support materials, such as conducting metal oxides, have been studied as potential supports with high corrosion-resistant properties.

Tungsten trioxide (WO3) is a widely used material with a variety of potential applications, including electrochromic and photochromic applications, photocatalysis, and gas sensors.[12–14] The advantages of WO3 are that it is resistant to CO poisoning and the hydrogen spillover effect by the formation of hydrogen tungsten bronze.[15–17] The intrinsic conductivity in WO3 arises from its non-stoichiometric composition, giving rise to a donor level formed by oxygen-vacancy defects in the lattice.[18] Furthermore, WO3 can exhibit considerable proton transfer ability because of the formation of WO3 hydrates.[19] Due to these properties, WO3 is a worthy consideration as an alternative anode catalyst support in PEMFCs. Previous studies have shown that Pt and Pt–Ru catalysts supported on WO3 have a high activity towards the electrooxidation of methanol and hydrogen.[20–24] Cui at el.[24] synthesized the meso-structured WO3 as an anode catalyst support and they found that the catalyst showed high electrocatalytic activity for hydrogen electrooxidation and exhibited much improved resistance to...
CO poisoning. However, WO₃ usually undergoes dissolution in acidic medium and thus suffers a reduction in electrocatalytic activity. Chhina et al. [25] found that WO₃ was more thermally and electrochemically stable than carbon supports. As a catalyst support in PEMFCs, the stability of WO₃ needs to be studied in detail.

Herein, we report a simple impregnating route to synthesize WO₃ nanoclusters by using mesoporous silica (SBA-15) as the hard template, with a focus on the durability of the support WO₃ nanoclusters and the anode catalyst Pt/WO₃. The as-prepared WO₃ nanoclusters materials show excellent electrochemical stability under a high potential. The Pt/WO₃ anode catalyst also exhibits high and stable electrocatalytic activity for the oxidation of hydrogen.

Results and Discussion

Structural characteristics

The XRD profiles of the WO₃ nanoclusters and WO₃-supported Pt nanoparticles are displayed in Figure 1. All of the WO₃ reflections correspond to the expected reflections of single crystalline monoclinic WO₃ (JCPDS card no. 24-0747) with no reflections corresponding to impurity phases, indicating well-crystallized frameworks. The WO₃-supported Pt sample shows a peak around at $\theta = 39.9^\circ$ corresponding to the [111] reflection of Pt in addition to the strong reflections corresponding to WO₃.

![Figure 1. XRD patterns of WO₃ and WO₃-supported Pt.](image)

The nitrogen sorption (adsorption and desorption) isotherms and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution of WO₃ are shown in Figure 2. The WO₃ isotherm (Figure 2a) shows a large hysteresis loop with adsorption and desorption branches at high relative pressures, which is attributed to the presence of mesopores. This is further confirmed by the pore size distribution curve (Figure 2b) showing pore sizes centered in the ranges of 2–4 nm and 9–13 nm for the WO₃ support, indicating a bimodal pore size distribution. The 2–4 nm pores may arise from the removal of the silica wall, and those at 9–13 nm are likely to be related to the structure of the hard template, SBA-15. The Brunauer–Emmett–Teller (BET) surface area of the WO₃ support synthesized in this study is calculated to be 47 m²g⁻¹ with a total pore volume of 0.124 cm³g⁻¹.

The surface compositional information of the prepared WO₃ is collected by means of X-ray photoelectron spectroscopy (XPS). Figure 3a shows the full spectrum of the prepared WO₃; Figure 3b shows the observed W4f spectrum for the WO₃ nanoclusters. The W4f spectrum can be resolved into two peaks.

![Figure 2. a) Nitrogen adsorption/desorption isotherms of WO₃ support and b) corresponding BJH pore size distribution.](image)

![Figure 3. a) Full spectrum and b) the W4f region of the XPS spectra of WO₃.](image)
major peaks; peaks for W 4f\textsubscript{7/2} and W 4f\textsubscript{5/2} are located at 35.6 eV and 37.6 eV, respectively. These results are in accordance with the reported data for W 4f\textsubscript{7/2} and W 4f\textsubscript{5/2} in WO\textsubscript{3}, suggesting the presence of pure WO\textsubscript{3}.

The morphology of WO\textsubscript{3} is studied by means of TEM. SBA-15 is a type of mesoporous silica with uniform channel structure (Figure 4a). The WO\textsubscript{3} nanoclusters inside the channels of SBA-15 are intuitively confirmed by Figure 4b, which clearly displays WO\textsubscript{3} uniformly distributed inside the channels of SBA-15 even after calcination at 600 °C for 4 h. Figure 4c shows the TEM image of the pure WO\textsubscript{3} nanoclusters after removal of the silica template by etching with concentrated aqueous HF. It can be seen that the nanocluster is a bundle of parallel nanorods interconnected through small bridges. The diameter of the nanorod is approximately 8.3 nm, which is consistent with the channel structure (7–9 nm) of pure mesoporous silica (SBA-15). This indicates that the prepared WO\textsubscript{3} has inherited the morphology of the silica template. Hence, the clusters replicate the SBA-15 pore structure including the micropores that interconnect the mesoscale channels and give rise to the short bridges between the nanorods (Figure 4c). Energy-dispersive X-ray spectroscopy (EDS) analysis (Figure 4d) shows a weak silica signal for the template-free WO\textsubscript{3}, implying almost complete removal of the SBA-15 template.

The high-resolution TEM (HRTEM) images of the Pt/WO\textsubscript{3} sample are shown in Figure 5. The data indicates that the Pt particles are well dispersed on the WO\textsubscript{3} nanoclusters and that there are two types of crystal lattice strips. The spacing of the distinct lattice fringes shown in Figure 5 are approximately 0.23 and 0.38 nm, which correspond to Pt [111] and WO\textsubscript{3} [020], respectively. This indicates that the Pt nanoparticles are immobilized on the mesoporous WO\textsubscript{3} nanoclusters. The size of the Pt particles on WO\textsubscript{3} nanoclusters are in the range of 1–3 nm according to HRTEM analysis. In addition, the presence of Pt particles on the WO\textsubscript{3} nanoclusters is also confirmed by means of EDX analysis shown in Figure 6.

The thermal stability of the support is also tested by using a thermal analyzer. WO\textsubscript{3} exhibits considerable stability at high temperatures compared to Vulcan XC-72 (Figure 7). Detailed electrochemical stability data are discussed in the electrochemical testing section. 

**Electrochemical properties**

The stabilities of Vulcan XC-72 and WO\textsubscript{3} are studied by using a rotating disk electrode (RDE) in 0.5 m H\textsubscript{2}SO\textsubscript{4}. Figure 8 shows the cyclic voltammetry (CV) of Vulcan XC-72 and WO\textsubscript{3} before and after oxidation treatment (potential hold at 1.6 V for 10 h).
The chosen oxidation potential of 1.6 V is close to the anode potential under the condition of fuel starvation. Under such a high potential, the carbon supports would severely corrode.[7–9] As seen in Figure 8 a, the carbon support shows a significant increase in the oxidation current after a potential hold at 1.6 V for 10 h. In addition, the large redox couple at 0.6 V strongly suggests that severe carbon corrosion has occurred. In contrast, only a negligible change in the CV is observed for WO3 (Figure 8 b), indicating good resistance towards oxidation when subjected to high potentials. Figure 9 shows the chronoamperometric curves of Vulcan XC-72 and WO3 under constant potential (1.6 V for 10 h). As seen, the corrosion current of WO3 is approximately 2.6 μA cm\(^{-2}\), 71% less than that of Vulcan XC-72 (ca. 8.9 μA cm\(^{-2}\)). These results clearly indicate that the WO3 support is more electrochemically stable than the conventional carbon supports.

To simulate the fuel starvation conditions, an accelerated corrosion method is also applied to test the durability of the catalyst materials. Figure 10 shows the CV of 6.8 wt % Pt/XC-72 and 6.8 wt % Pt/WO3 before and after oxidation treatment (potential hold at 1.6 V for 10 h). It is observed that Pt/WO3 shows similar electrochemical behavior to the WO3 support, but Pt/ WO3 exhibits a better electrocatalytic activity. It may be attributed to the fact that the mesostructured Pt/WO3 catalyst is more mesoporous WO3-like rather than Pt-like.[24] In addition, the low conductivity resulting from the non-stoichiometric composition of WO3 and low Pt content may make some contribution to the absence of Pt characteristic peaks.

As seen in Figure 10 a, the electrochemically active surface area (ECA) of Pt/WO3 might be derived from a cooperative effect between Pt and WO3. It can be attributed to the formation of H\(_x\)WO3 by hydrogen intercalation/de-intercalation into/out of WO3. Hydrogen on the Pt surface spills over onto the WO3 surfaces. The H-spillover effects from Pt to WO3 leave more Pt active sites free to accelerate the kinetics of hydrogen electrooxidation. The reactions are shown in Equations (1) and (2):

\[
\text{WO}_3 + x \text{Pt-H} \rightarrow \text{H}_x\text{WO}_3 + x \text{Pt} \quad (1)
\]

\[
\text{H}_x\text{WO}_3 \rightarrow \text{WO}_3 + x \text{H}^+ + x \text{e}^- \quad (2)
\]

According to the method reported by Cui et al.[24] we estimated the ECA of Pt/WO3 by measuring the integral charge of
the hydrogen desorption area in the Hupd region (0–0.4 V) after double-layer correction, and using 0.21 mC cm$^{-2}$ Pt as the conversion factor assuming a hydrogen monolayer is adsorbed on Pt surfaces. It can be observed that Pt/WO$_3$ shows good resistance towards oxidation, with the ECA remaining almost unchanged after oxidation at 1.6 V for 10 h. However, the ECA of Pt/XC-72 significantly decreases after oxidation due to the increased double layer current. Serious carbon corrosion takes place under higher potential, indicated by the increased current density of the redox couple at 0.6 V.

The stability of the catalysts is also tested by measuring the electrochemical surface area after oxidation for 2000 cycles between 0.6 and 1.2 V. Figure 11 shows the CV curves of 6.8 wt % Pt/WO$_3$ and 6.8 wt % Pt/XC-72 with a potential cycling. The calculated result reveals that the ECA of the Pt/XC-72 reaches 22% of the initial value after oxidation for 2000 cycles between 0.6 and 1.2 V. As for Pt/WO$_3$, the initial ECA value is almost preserved after 2000 cycles between 0.6 and 1.2 V, indicating excellent resistance to oxidation.

Polarization and power density plots for H$_2$/O$_2$ fuel cells, employing different anode electrocatalysts (Pt/WO$_3$, Pt/XC-72), are shown in Figure 12. The Pt loading is controlled at 0.07 mg cm$^{-2}$ on the anode side and 0.4 mg cm$^{-2}$ on the cathode side. It can be seen that the current density at 0.6 V is 1.2 A cm$^{-2}$, and the maximum peak power density is 0.79 W cm$^{-2}$ when employing the Pt/WO$_3$ as the anode electrocatalysts. The polarization curves demonstrate better hydrogen electrooxidation activity and fuel cell performance for the Pt/WO$_3$ electrocatalyst synthesized in the study, compared to the Pt/XC-72 electrocatalyst. WO$_3$ electrocatalyst is capable of...

**Figure 10.** CV curves of a) 6.8 wt % Pt/WO$_3$ and b) 6.8 wt % Pt/XC-72 under oxidation at 1.6 V for 10 h in 0.5 M H$_2$SO$_4$ electrolyte, with a scan rate of 50 mV s$^{-1}$.

**Figure 11.** CV curves of 6.8 wt % Pt/WO$_3$ ($\ast$) and 6.8 wt % Pt/XC-72 ($\times$) under 0.6–1.2 V for 2000 cycles in 0.5 M H$_2$SO$_4$ electrolyte, with a scan rate of 50 mV s$^{-1}$.

**Figure 12.** Polarization and power density curves of the PEM fuel cells with different anodic electrocatalysts. Measurements were taken at 65°C with fully humidified reactants (flow rate was 20/100 mL min$^{-1}$ for H$_2$/O$_2$) and at 0.05 MPa. Pt loading was controlled at 0.07 mg cm$^{-2}$ on the anode side and 0.4 mg cm$^{-2}$ on the cathode side.

The results of the fuel cell tests also indicate that deposited Pt particles provide adequate electron pathways and improve the electrical conductivity of the WO$_3$ support. In addition, an ultra-thin catalyst layer could be obtained for the Pt/WO$_3$ catalyst with the same Pt loading because WO$_3$ has a much higher density than carbon, resulting in a significant reduction of mass transport limitation. Furthermore, WO$_3$ can react with hydrogen to give H$_x$WO$_{3-x}$ species, such as H$_{0.18}$WO$_3$, H$_{0.35}$WO$_3$, and substoichiometric oxides (WO$_{3-y}$)$_{+}$.

Thus, WO$_3$ is capable of...
conducting protons during hydrogen intercalation/de-intercalation into/out of the catalyst layer. The reactions are shown in Equations (3) and (4):

\[ \text{WO}_3 + x \text{H}^+ + x e^- = \text{H}_x \text{WO}_3 \quad (0 < x < 1) \]  
\[ \text{WO}_3 + 2y \text{H}^+ + 2y e^- = \text{H}_{2y}\text{WO}_3 - y \text{H}_2\text{O} \quad (0 < y < 1) \]

Therefore, when Pt nanoparticles are not contacted with Nafion ionomers, WO_3 is able to generate three-phase boundaries, leading to improved utilization of Pt. So the single cell using Pt/WO_3 showed better performance than Pt/C.

Conclusions

WO_3 nanoclusters have been synthesized by using a hard template replicating route and characterized by means of electron microscopy and electrochemical analysis. As catalyst support materials, the WO_3 nanoclusters are more electrochemical and thermally stable against oxidation than Vulcan XC-72. The catalyst durability is also studied for both Pt/WO_3 and Pt/XC-72 by the static potential method and a potential cycling experiment. Results show that Pt/WO_3 is significantly more stable than Pt/XC-72. The high stability and excellent electrocatalytic activity may be attributed to the high oxidation resistance of WO_3 and the strong Pt–WO_3 interactions. Results of the single-cell test show that the WO_3 nanoclusters can be considered as an alternative anode electrocatalyst support to improve the reliability and durability of PEMFCs. Further studies are required to apply this anode catalyst support in a working fuel cell to test the stability under a high potential (to simulate the fuel starvation condition).

Experimental Section

Synthesis of WO_3 and supported Pt catalyst

Mesoporous SBA-15 was prepared from a tri-block copolymer pluronic P123 (EO20PO70EO20, Aldrich) and tetraethyl orthosilicate (TEOS, Aldrich) as the silica source, according to Zhao et al. Typically, tri-block copolymer (4 g) was added to distilled H_2O (93 g) and concentrated HCl (25 g, 37 wt.%). The solution was stirred for 1 h at 313 K, and then TEOS (8.8 g) was added drop-wise, and the mixture was stirred for 24 h. The final product was heated for 24 h at 393 K under static conditions for hydrothermal treatment followed by filtration, washing with distilled water and ethanol, drying at 353 K, and calcination at 823 K. The WO_3 nanoclusters were prepared using as-prepared SBA-15 as a hard template and silicotungstic acid as the tungsten source. SBA-15 (1 g) was stirred in ethanol (30 g) containing silicotungstic acid (1.0 × 10^{-3} mol) at room temperature for 24 h. After ethanol evaporation, the sample was calcined at 873 K for 4 h to give a decomposed product of WO_3 inside SBA-15 channels. The removal of the SBA-15 template was performed by dissolving silica in an aqueous HF solution (1.3 M) and centrifuging, washing with copious amounts of distilled water, and then drying at 40 °C under vacuum. The immobilization of Pt nanoparticles on WO_3 nanoclusters was carried out with pre-formed Pt colloidal particles. H_xPtCl_yxH_2O containing 6.3 mg Pt was added to ethylene glycol (30 mL) in a 100 mL beaker, stirred for 30 min and intermittently heated (pulse every 10 s for six times) in a microwave oven (2450 MHz, 800 W) to ensure the complete reduction of Pt^{4+} to metallic Pt. The obtained Pt colloidal solution was added to the WO_3 nanoclusters (50 mg) dispersed in ethanol (10 mL) by sonication, followed by the addition of nitric acid (2 M, 5 mL) to enhance the attachment of Pt particles to the WO_3 nanoclusters. The pH value of the final solution was approximately 2. The solution was stirred for 24 h. The precipitate was washed with water and dried at 40 °C under vacuum. The inductively coupled plasma (ICP) result showed that the loading of the Pt/WO_3 catalysts was approximately 6.8 wt.%. Then conventional carbon-supported Pt catalyst with the same loading of 6.8 wt.% was also prepared to compare the durability of the supports.

Material characterization

The XRD patterns were obtained by using a Philips X’pert Pro X-ray diffractometer equipped with a CuK_α source at 40 kV and 30 mA. Nitrogen adsorption experiments were performed at 77 K by using a Micromeritics ASAP 2010 system. Surface areas of the samples were calculated using the Brunauer–Emmett–Teller (BET) equation, whereas pore size distributions were estimated by the Barrett–Joyner–Halenda (BJH) method from adsorption branches of isotherms. X-ray photoelectron spectroscopy (XPS) spectra were measured with a VG ESCALAB MK2 spectrometer using an AlK_α source operated at 12.5 kV and 250 W, with the pass energy set at 20 eV. Binding energies were referenced to the C1s peak from adventitious hydrocarbon contamination set at 284.6 eV. The distribution of elemental concentrations was performed using the mapping analysis of a scanning electron microscope (JEOL 6360LV, Japan) equipped with energy dispersive analysis of X-ray spectrometer (EDAX). TEM images were obtained with the JEOL JEM-2000EX microscope at an accelerating voltage of 120 kV and the high-resolution TEM (HRTEM) characterization was carried out by using an FEI Tecnai G2 F30 microscope. A thermal analyzer (NETZSCCH STA 449F3) was used to determine the thermal stability of the supports (Vulcan XC-72, WO_3). The temperature was ramped from room temperature to 1000 °C at 10 °C min^{-1}, and the air flowing was set at 40 mL min^{-1}. The metal loading of Pt deposited on the WO_3 support was determined by means of ICP atomic emission spectrometry (ICP–AES).

Electrochemical characterization

Electrochemical measurements were conducted on a CHI730 work-station (CH Instrument, USA) with a three-electrode cell using a Pt sheet and saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. Catalyst ink composed of samples (5 mg), Nafion solution (50 μL, 5 wt.%), Alfa Aesar), and ethanol (4 mL) was dispersed ultrasonically, and 10 μL was transferred onto the glassy carbon substrate (d = 4 mm). The cyclic voltammetry (CV) measurements were performed in H_2SO_4 solution (0.5 M), which was purged with high purity nitrogen gas before measurements. The potential sweep range was from 0 to 1.2 V, and the scan rate was 50 mV s^-1. For the surface oxidation experiments of Vulcan XC-72 and WO_3, a constant potential of 1.6 V was applied for 10 h to test the stability of the support. For Pt-catalyzed Vulcan XC-72 and WO_3, a potential cycling test from 0.6 to 1.2 V for 2000 cycles was conducted to examine the electrochemical stability. All the potentials in this paper are versus normal hydrogen electrode (NHE).
Tungsten Trioxide Nanoclusters for Polymer Electrolyte Membrane Fuel Cells

Polymer electrolyte membrane fuel cell operation

A home-made catalyzed-gas diffusion layer was used as the cathode for the fuel cell experiments. The cathode catalyst loading was 0.4 mgPt cm$^{-2}$. The anode catalyst ink was prepared by ultrasonically blending the Pt/WO$_3$ catalyst with a Nafion solution (5 wt%, Alfa Aesar) and ethanol for 2 h. The catalyst ink was then sprayed onto a prefabricated gas diffusion layer (Torry carbon paper, 7 wt% polytetrafluoroethylene) with a loading of 0.07 mgPt cm$^{-2}$ for Pt/WO$_3$. Similarly, a Pt/XC-72 anode with the same loading was also prepared. The anode and cathode electrodes were hot-pressed onto both sides of a Nafion 112 membrane (DuPont) at 140 $^\circ$C. The anode catalyst ink was prepared by ultrasonically blending the Pt/WO$_3$ catalyst with a Nafion solution (5 wt%, Alfa Aesar) and ethanol for 2 h. The catalyst ink was then sprayed onto a prefabricated gas diffusion layer (Torry carbon paper, 7 wt% polytetrafluoroethylene) with a loading of 0.07 mgPt cm$^{-2}$ for Pt/WO$_3$. Similarly, a Pt/XC-72 anode with the same loading was also prepared. The anode and cathode electrodes were hot-pressed onto both sides of a Nafion 112 membrane (DuPont) at 140 $^\circ$C under 0.1 MPa for 1 min to prepare a membrane electrode assembly. The single-cell tests were conducted in a 5 cm$^2$ polymer electrolyte membrane fuel cell (PEMFC) at 65 $^\circ$C with the fuel (hydrogen) and the oxidant (oxygen) humidified by bubbling through distilled water both at 65 $^\circ$C. The operating gas pressures were kept at 0.05 MPa for both electrodes.

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