Electro-Oxidation of Ethanol on Pt-WO3/C Electrocatalyst

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Pt$_x$-WO$_3$/C electrocatalysts were prepared by microwave colloid-reduction method. Transmission electron microscopy examination showed uniform dispersion of platinum with particle sizes less than 5 nm. Structures of the Pt$_x$-WO$_3$/C electrocatalysts were characterized by X-ray diffraction and energy dispersive spectroscopy, the electrochemical characteristics and electro-oxidation of ethanol on the Pt$_x$-WO$_3$/C electrocatalysts were also studied by cyclic voltammetry, chronocoulometry, and chronoamperometry. The results show that the Pt$_x$-WO$_3$/C electrocatalysts have higher catalytic activity to ethanol electro-oxidation than the conventional Pt/C catalysts; perhaps caused by the “hydrogen spill-over effect.” The reaction mechanisms of the ethanol electro-oxidation on the Pt$_x$-WO$_3$/C were inferred according to the electrochemical characteristics and the data in the reported literature.

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Experimental

Pt$_x$-WO$_3$/C electrocatalysts were prepared using the colloid-reduction method. First, tungstenic acid precipitate was prepared by dissolving a certain amount of Na$_2$WO$_4$·2H$_2$O in high purity water and adding concentrated chloride hydrogen solution drop by drop without stirring until the solution became acidic (pH 1). This white, gelatinous precipitate was then dissolved by adding a concentrated chloride hydrogen solution drop by drop until the solution became acidic. Then, the solution was heated by microwave oven for 60 s. The mixture was washed with deionized water and dried to form the mixture of WO$_3$/C. Appropriate amounts of Vulcan XC 72 active carbon were added, and the solution was stirred vigorously for 24 h. Then, the solution was heated by microwave oven for 60 s. The mixture was washed with deionized water and dried to form the mixture of WO$_3$/C. Appropriate amounts of H$_2$PtCl$_6$ solution were used as precursor to precipitate Pt on WO$_3$/C by chemical reduction method. The structures of Pt$_x$-WO$_3$/C electrocatalysts were characterized by X-ray diffraction (XRD) on a Philips PW1730 diffractometer with Cu K$_{α}$ radiation ($λ = 1.54056$ Å). The x values of Pt/W atomic ratio were obtained by the energy dispersive spectrometer (EDS) analysis using a JEOL JSM-6460A scanning electron microscope. Transmission electron microscopy (TEM) was carried out using JEOL JEM 2010 system. The particle size was determined both by measuring the nanoparticles from TEM micrographs using Image Analysis Software and calculating from XRD patterns, respectively.

Electrochemical measurements were carried out using a CHI 660 electrochemical workstation (CH Instrument, Cordova, TN). Prepared Pt$_x$-WO$_3$/C catalysts and a commercial Pt/C catalyst (Vulcan XC-72 carbon supported 20%Pt; Johnson Matthey) were performed in a conventional three-electrode test cell consisting of glassy car...
bon (GC) with 3 mm diam as working electrode, Pt wire as the counter electrode, and saturated Hg/Hg2SO4 electrode as the reference electrode. In the results, all the potential values were transformed to the values vs reversible hydrogen electrode (RHE). The catalyst ink was prepared by dispersing 2 mg catalyst in 1 mL deionized water which was then ultrasonicated for 30 min at room temperature. 10 μL of the catalyst ink was pipetted on the top surface of the GC and dried. The cyclic voltammetry (CV) experiments were performed in 0.5 M H2SO4 solution containing 0.5 M C2H5OH at a scan rate of 50 mV s−1. All the solutions were prepared by using ultrapure water (Millipore,18 MΩ). The three-electrode test cell was purged with argon gas for nearly 30 min before starting the experiment. The measurement curves were recorded after scanning for 10 cycles at 0.05 V/s to obtain a stable response.

Results and Discussion

The x values denote Pt:W atomic ratio within Pt-x-WO3/C electrocatalysts is 2.6, 5.6, and 7.5, respectively, which was obtained by the EDS analysis. Figure 1 shows the TEM micrographs of Pt-x-WO3/C catalysts of different Pt:W atomic ratios. It can be seen that the particles are dispersed uniformly with mean particle size less than 5 nm.

The XRD patterns of the Pt-x-WO3/C electrocatalysts were shown in Fig. 2. The diffraction peaks at 40°, 46°, 68°, and 81° are in response to the Pt(111), (200), (220), and (311) planes, respectively, which represent the typical character of a polycrystalline Pt face centered cubic (fcc) phase. The (220) reflections of Pt were used to calculate the average particle size according to the Scherrer formula.20 The particle size obtained from XRD patterns and TEM results are compared in Table I. Apart from the four diffraction peaks of platinum, there appears diffraction peaks at around 24°, 34°, and 55°. The peak at 24° is due to the co-effect of the 002 plane (26°) of the hexagonal structure of Vulcan XC-72 carbon and WO3 which has three obvious peaks at about 23°, 34°, and 55°. Furthermore, the Pt:W atomic ratios of the prepared electrocatalysts given by the EDS results are also listed in Table I.

CVs of Pt-x-WO3/C and Pt/C electrocatalysts in 0.5 M H2SO4 solutions are shown in Fig. 3. In this case, all curves have an obvious hydrogen adsorption-desorption region (0–0.25 V), show an increase in the currents with increasing the WO3 content, except a slight decrease when Pt:W atomic ratio reach 2.6:1. This may be attributed to the “hydrogen spill-over effect” that was proposed by Glemser and Naumann.21 WO3 could act as intermediates in the reaction and Goodenough26 attributed this anodic peak in the reverse scan to the removal of the incompletely oxidized carbonaceous species formed in the forward scan in an electrolyte. Song and Tsiakaras27,28 attributed the oxidation peak during the backward sweep process to the further oxidation of the adsorbed intermediate species of ethanol. From Fig. 4, it can also be seen that, in Pt-x-WO3/C, these backward oxidation peaks are higher than those in Pt/C. Associating with our previous work,27 it could be attributed to the more promoting role of WO3 in the oxidative removal of the adsorbed intermediate species of ethanol oxidation. Furthermore, an extra small peak (marked
as D) in the backward scan observed both on Pt2.6-WO3/C and Pt5.6-WO3/C electrocatalysts, which cannot be detected on Pt/C, further confirmed it. The slight decrease in performance on Pt2.6-WO3/C may be due to the agglomeration of WO3 which reduces the specific interfacial area during Pt and WO3.

The linear sweep voltammograms for ethanol oxidation on Pt-WO3/C and Pt/C electrocatalysts are shown in Fig. 5. The electro-oxidation of ethanol started at about 0.43 V for both Pt5.6-WO3/C and Pt7.5-WO3/C electrocatalysts, 0.15 V lower than Pt/C which started at 0.58 V. The onset potential of Pt2.6-WO3/C electrocatalyst was 0.3 V, 0.28 V lower than that of Pt/C. It is clear that the addition of WO3 leads to the negative shift of the onset potential of the oxidation peak, which means a decrease in the overpotential as well as an increase in oxidation reacting rate.

Chronoamperometry data in 0.5 M H2SO4 with 0.5 M ethanol at 0.5 V (vs RHE) for Ptx-WO3/C electrocatalysts and commercial Pt/C are shown in Fig. 6. The initial high current corresponds mainly to double-layer charging. The current decays with time in a parabolic manner and reaches an apparent steady state within 500 s. It can be seen that the current density of ethanol electro-oxidation on the Ptx-WO3/C catalyst is higher than on the Pt/C catalyst at 0.5 V vs RHE. According to the reported reaction mechanism of ethanol oxidation on Pt in acid medium27-30 and the works that have been done by Tseung and Chen,14,15 the reaction mechanism of ethanol oxidation on Ptx-WO3/C electrocatalyst can be inferred, associated with this work, as follows

\[
\text{Pt} + \text{CH}_3 - \text{CHO} \rightarrow \text{Pt} - (\text{CO} - \text{CH}_3)_{\text{ads}} + \text{H}^+ + \text{e}^- \quad [3]
\]

\[
\text{Pt} + \text{Pt} - (\text{CO} - \text{CH}_3)_{\text{ads}} \rightarrow \text{Pt} - (\text{CO})_{\text{ads}} + \text{Pt} - (\text{CH}_3)_{\text{ads}} \quad [4]
\]

\[
\text{Pt} - \text{WO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{WO}_3 + \text{Pt} - \text{OH}_{\text{ads}} \quad [5]
\]

\[
\text{H}_2\text{WO}_3 \rightarrow \text{WO}_3 + x\text{e}^- + x\text{H}^+ \quad [6]
\]

\[
(\text{CH}_3 - \text{CHO})_{\text{ads}} + \text{Pt} - \text{OH}_{\text{ads}} \rightarrow (\text{CH}_3 - \text{COOH})_{\text{ads}} + \text{H}^+ + \text{e}^- + \text{Pt} \quad [7]
\]

\[
\text{CH}_3 - \text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3 - \text{COOH} + 4\text{H}^+ + 4\text{e}^- \quad [8]
\]

\[
\text{Pt} - (\text{CO})_{\text{ads}} + \text{Pt} - \text{OH}_{\text{ads}} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + \text{e}^- \quad [9]
\]

The ethanol electro-oxidation mechanism on Ptx-WO3/C involves parallel and consecutive oxidation reactions. The presence of WO3 speeds up the reactive rate, because the first stage of Reaction 2 involves dehydrogenation reaction where the “hydrogen spill-over effect” on the Pt surface is operative. It also enhanced the activity of

### Table I. The composition and particle size of the Ptx-WO3/C catalysts.

<table>
<thead>
<tr>
<th>Electro catalysts</th>
<th>Pt component, wt %</th>
<th>W component, wt %</th>
<th>Pt:W atomic ratio</th>
<th>Average particle size by XRD (nm)</th>
<th>Average particle size by TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt2.6-WO3/C</td>
<td>19.23</td>
<td>6.91</td>
<td>2.6:1</td>
<td>3.2</td>
<td>3.7 ± 2.0</td>
</tr>
<tr>
<td>Pt5.6-WO3/C</td>
<td>12.55</td>
<td>2.14</td>
<td>5.6:1</td>
<td>3.6</td>
<td>4.2 ± 1.8</td>
</tr>
<tr>
<td>Pt7.5-WO3/C</td>
<td>15.29</td>
<td>1.12</td>
<td>7.5:1</td>
<td>3.0</td>
<td>3.4 ± 1.4</td>
</tr>
</tbody>
</table>

![Figure 2. XRD patterns of Pt1-xWO3/C electrocatalysts with different Pt:x atomic ratios: (a) Pt2.6-WO3/C, (b) Pt5.6-WO3/C, (c) Pt7.5-WO3/C, and (d) 20 wt% Pt/C.](image)

![Figure 3. CVs of Pt1-xWO3/C electrocatalysts in 0.5 M H2SO4 with a sweep rate of 50 mV/s.](image)

![Figure 4. CVs of Pt1-xWO3/C electrocatalysts in 0.5 M H2SO4 with 0.5 M ethanol. Sweep rate was 50 mV/s.](image)
WO$_3$/C shows superior electrocatalytic activity to ethanol oxidation active sites for OH ads species (Reactions 5 and 6), which react with CO$_{ads}$ to form CO$_2$.

Figure 5. Linear sweep voltammograms of Pt$_x$WO$_3$/C electrocatalysts in 0.5 M H$_2$SO$_4$ with 0.5 M ethanol. Sweep rate was 50 mV/s.

Conclusions

Pt$_x$-WO$_3$/C electrocatalysts were prepared by loading Pt on WO$_3$ modified carbon, which is synthesized by microwave colloid-reduction method. From both XRD and TEM results, the Pt particles were uniformly dispersed with mean particle sizes less than 5 nm. Based on the above electrochemical experimental results, Pt$_x$-WO$_3$/C shows superior electrocatalytic activity to ethanol oxidation to Pt/C. The results also showed that the activity of the Pt$_x$-WO$_3$/C electrocatalysts with different Pt:W atomic ratios increased with the increase of the WO$_3$ content both in absence and presence of ethanol. It results from the WO$_3$ effect through Reactions 5-7 which can occur at a much lower potential$^{16}$ than Sn and Ru which effect by adsorbing hydrogen spill-over effect of WO$_3$ effectively improved the performance of ethanol oxidation on Pt anodic catalyst, by increasing the current density and decreasing the onset potential. The performance of Pt$_x$-WO$_3$/C electrocatalyst in direct ethanol fuel cell and unique effect mechanism are worthy of further study. It is also worth investigating the use of WO$_3$ to promote the very extensively studied PtRu/C and PtSn/C catalysts for direct ethanol fuel cells.

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References