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Year 2006

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This articles was originally published as Zhang, DY, Ma. ZF, Wang, GX et al, Electro-Oxidation of Ethanol on Pt-WO₃/C Electrocatalyst, *Electrochemical and Solid-State Letters*, 9(9), 2006, A423-A426. Copyright The Electrochemical Society. Original journal available here.

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

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Pt_x-WO₃/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-WO₃/C electrocatalysts were characterized by X-ray diffraction and energy dispersive spectroscopy, the electrochemical characteristics and electro-oxidation of ethanol on the Pt_x-WO₃/C electrocatalysts were also studied by cyclic voltammetry, linear sweep, and chronoamperometry. The results show that the Pt_x-WO₃/C electrocatalysts have higher catalytic activity to ethanol electro-oxidation than the commercial Pt/C catalysts; perhaps caused by the "hydrogen spill-over effect." The reaction mechanisms of the ethanol electro-oxidation on the Pt_x-WO₃/C were inferred according to the electrochemical characteristics and the data in the reported literature.

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Manuscript submitted December 27, 2005; revised manuscript received May 5, 2006. Available electronically June 28, 2006.

During the last decades, direct methanol fuel cell (DMFC) has been widely investigated and considered as a possible power source for portable electronic apparatus application in the near future.¹ However, methanol has some particular disadvantages, e.g., it is relatively toxic, inflammable with a low boiling point (65°C), and it is also neither a primary fuel, nor a renewable fuel. Therefore, other short chain organic chemicals, such as ethanol, ethylene glycol, propanol,^{2,3} and dimethyl oxalate,⁴ were used to replace methanol. As one of the alternative fuels, ethanol is safe and has more energy density compared to methanol (8.01 vs 6.09 kWh/kg). Moreover, as a green fuel, ethanol can be easily produced in great quantity by fermentation of sugar-containing biomass. Therefore, ethanol is more attractive than methanol for direct alcohol fuel cells (DAFCs).^{5,6}

The adsorption and oxidation of ethanol on fuel cells anode have already been investigated.⁷ As is well-known, high activity and stability of Pt metal, especially under acidic environment, makes it a suitable electrocatalyst for electro-oxidation of many small chemical molecules. Nevertheless, pure platinum is not a very good anode catalyst for ethanol or methanol electro-oxidation at room or moderate temperature, because it is readily poisoned by the strongly adsorbed intermediates, among which CO_{ads} is always considered as one of the main poisoning species. Making Pt alloy with a second or a third metal is a convenient way to modify the electrocatalytic properties of platinum in order to overcome poisoning due to methanol or ethanol, especially the adsorbed CO. Several platinum-based anode catalysts, such as Pt-Ru,⁸ Pt-Sn,⁹ and Pt-Mo,^{10,11} have been developed for methanol and ethanol electro-oxidation. Electro-oxidation of ethanol on rhodium and iridium¹² has also been investigated and different reaction mechanisms have been proposed. As another potential catalyst, gold¹³ was found to show higher selectivity for ethanol electro-oxidation while its activity is lower than platinum. On the other hand, increasing the operating temperature for the polymer electrolyte membrane fuel cell (PEMFC) and DAFC systems can effectively increase the hydrogen and ethanol electro-oxidation reaction rate and decrease the overpotential. It was found² that at higher temperatures (170°C), Pt-Ru catalyst shows almost comparable activity for both methanol and ethanol electro-oxidation. But, as is well known, increasing the operation temperatures will require the development of new polymer electrolyte membranes for PEMFCs because the well-known Nafion membranes cannot operate at higher temperatures for a long time.

To improve the performance of DAFC based on the current polymer electrolyte membrane, it is of great importance to develop more active anode catalysts for ethanol electro-oxidation at low tempera-

tures. Pt/WO₃ and PtRu/WO₃ showed higher catalytic activity toward CO oxidation reaction than Pt attributing to hydrogen spill-over effect.^{14,15} Recently, tungsten or tungsten oxide has been considered as a promoter to Pt base catalyst for the improvement of alcohol electro-oxidation.^{16,17} W-modified Pt-Ru-W alloy catalysts for anodic oxidation of ethanol were developed by Uchida et al.,¹⁸ but fewer reports on tungsten oxide promoted Pt/C catalyst for the anodic oxidation of ethanol can be found. In this work, WO₃ was used as a promoter to modify the conventional Pt/C catalyst. Pt_x-WO₃/C catalysts were prepared by microwave colloid-reduction method, where *x*:1 refers to the different Pt:W atomic ratios. The tested ethanol electro-oxidation and its electrochemical performances on the prepared catalysts were compared to the commercial Pt/C electrocatalyst. The reaction mechanisms of the ethanol electro-oxidation on the Pt_x-WO₃/C electrocatalysts were inferred according to the electrochemical characteristics and the data in the reported literature.

Experimental

Pt_x-WO₃/C electrocatalysts were prepared using the colloid-reduction method. First, tungstic acid precipitate was prepared by dissolving a certain amount of Na₂WO₄·2H₂O in high purity water and adding concentrated chloride hydrogen solution drop by drop without stirring until the solution became acidic (pH 1).¹⁷ This white, gelatinous precipitate was then dissolved by adding a concentrated solution of oxalic acid and diluted to 60 cm³ to form a transparent colloid solution of WO₃·2H₂O. Then, an appropriate amount of Vulcan XC 72 active carbon was 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 WO₃/C. Appropriate amounts of H₂PtCl₆ solution were used as precursor to precipitate Pt on WO₃/C by chemical reduction method.¹⁹

The structures of Pt_x-WO₃/C electrocatalysts were characterized by X-ray diffraction (XRD) on a Philips PW1730 diffractometer with Cu Kα 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-WO₃/C catalysts and a commercial Pt/C catalyst (Vulcan XC-72 carbon supported 20%Pt, Johnson Matthey) was performed in a conventional three-electrode test cell consisting of glassy car-

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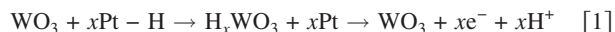
bon (GC) with 3 mm diam as working electrode, Pt wire as the counter electrode, and saturated Hg/Hg₂SO₄ electrode as the reference electrode. In the results, all the potential values were transformed to the values vs reversible hydrogen electrode (RHE). The catalyst ink was prepared by dispersing 2 mg catalyst in 1 mL deionized water which was then ultrasonicated for 30 min at room temperature. 10 μ L 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 M Ω). 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), shown 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 anodic oxidation of hydrogen, providing an alternative path for the reaction^{14,15}



However, there is no well-defined hydrogen adsorption-desorption region on the CV curves of PtRu/C and PtSn/C catalysts,^{22–24} based on the fact that the CO_{ads} on the Pt sites reacts with OH_{ads} at the adjacent RuO₂ and SnO₂, which does not form until the anodic potential is raised to ~ 0.3 V.^{25,26} Furthermore, since H _{x} WO₃ is formed at 0 V, it can adsorb OH_{ads}, thereby facilitating the oxidation of CO_{ads} and other reaction intermediates of the ethanol electro-oxidation.¹⁵

The performances of Pt _{x} -WO₃/C electrocatalysts in ethanol electro-oxidation are shown in Fig. 4. The current values were normalized per milligram of platinum. It can be clearly seen that in the investigated potential range, there are two oxidation peaks (marked as A and B) during the forward sweep process in both cases of Pt _{x} -WO₃/C and Pt/C and these two oxidation peaks of ethanol over Pt _{x} -WO₃/C are higher than those over Pt/C. This means from the current density point of view, Pt _{x} -WO₃/C presents higher catalytic activity to ethanol electro-oxidation in comparison with Pt/C. During the backward sweep process, an anodic peak (marked as C) is detected at ~ 0.56 V for Pt _{x} -WO₃/C and 0.52 V for Pt/C. Manohara and Goodenough²⁶ attributed this anodic peak in the reverse scan to

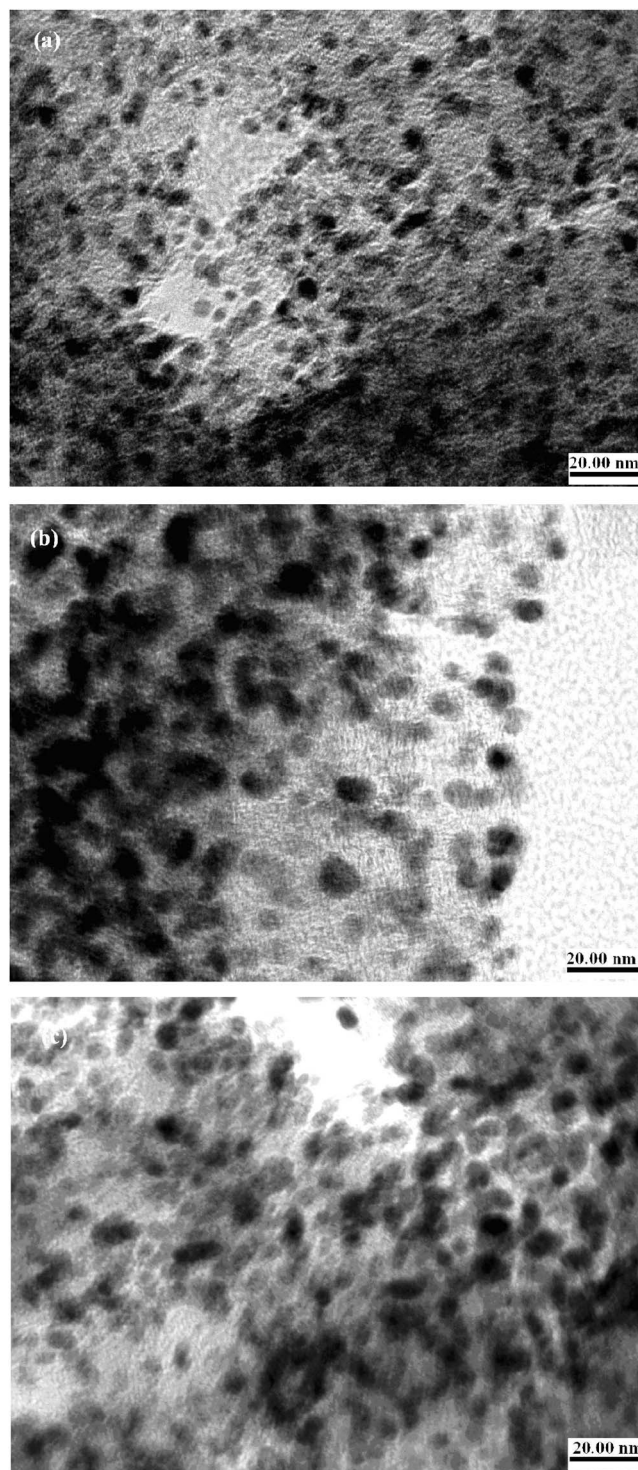


Figure 1. TEMs of Pt _{x} -WO₃/C electrocatalysts: (a) Pt_{2.6}-WO₃/C, (b) Pt_{5.6}-WO₃/C, and (c) Pt_{7.5}-WO₃/C.

the removal of the incompletely oxidized carbonaceous species formed in the forward scan in an electrolyte. Song and Tsiakaras⁷ 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,^{27,28} 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

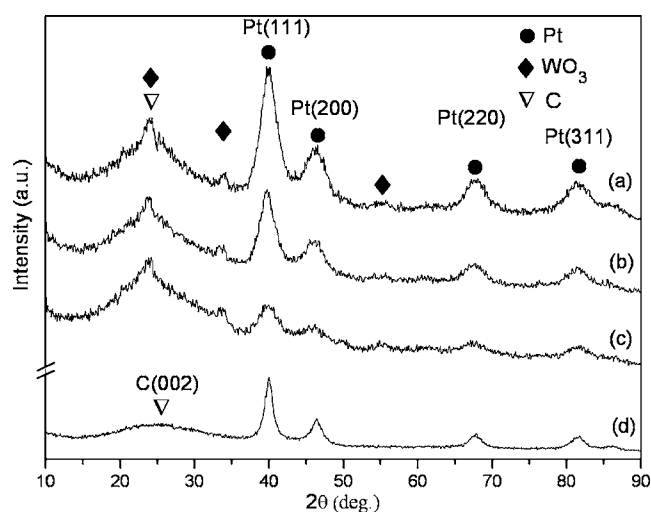


Figure 2. XRD patterns of Pt_x - WO_3 /C electrocatalysts with different Pt:W atomic ratios: (a) $Pt_{2.6}$ - WO_3 /C, (b) $Pt_{5.6}$ - WO_3 /C, (c) $Pt_{7.5}$ - WO_3 /C, and (d) 20 wt% Pt/C.

as D) in the backward scan observed both on $Pt_{2.6}$ - WO_3 /C and $Pt_{5.6}$ - WO_3 /C electrocatalysts, which cannot be detected on Pt/C, further confirmed it. The slight decrease in performance on $Pt_{2.6}$ - WO_3 /C may be due to the agglomeration of WO_3 which reduces the specific interfacial area during Pt and WO_3 .

The linear sweep voltammograms for ethanol oxidation on Pt- WO_3 /C and Pt/C electrocatalysts are shown in Fig. 5. The electro-oxidation of ethanol started at about 0.43 V for both $Pt_{5.6}$ - WO_3 /C and $Pt_{7.5}$ - WO_3 /C electrocatalysts, 0.15 V lower than Pt/C which started at \sim 0.58 V. The onset potential of $Pt_{2.6}$ - WO_3 /C electrocatalyst was 0.3 V, 0.28 V lower than that of Pt/C. It is clear that the addition of WO_3 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 H_2SO_4 with 0.5 M ethanol at 0.5 V (vs RHE) for Pt_x - WO_3 /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 Pt_x - WO_3 /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 Pt_x - WO_3 /C electrocatalyst can be inferred, associated with this work, as follows

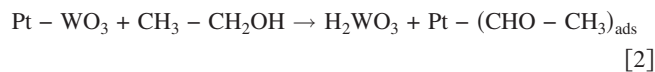


Table I. The composition and particle size of the Pt_x - WO_3 /C catalysts.

Electrocatalysts	Pt component, wt %	W component, wt %	Pt:W atomic ratio, EDX	Average particle size by XRD (nm)	Average particle size by TEM (nm)
$Pt_{2.6}$ - WO_3 /C	19.23	6.91	2.6:1	3.2	3.7 ± 2.0
$Pt_{5.6}$ - WO_3 /C	12.55	2.14	5.6:1	3.6	4.2 ± 1.8
$Pt_{7.5}$ - WO_3 /C	15.29	1.12	7.5:1	3.0	3.4 ± 1.4

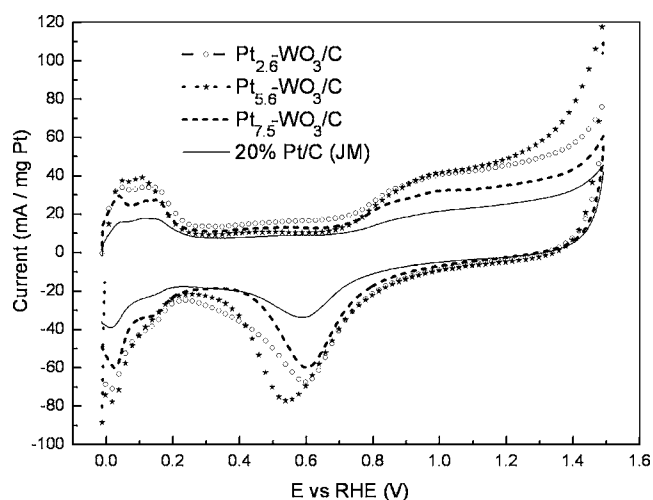
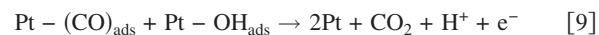
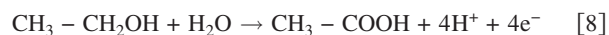
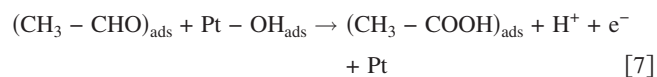
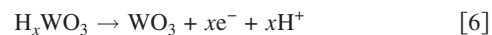
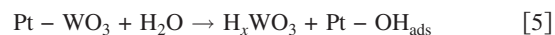
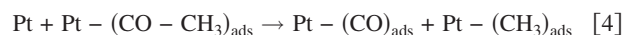


Figure 3. CVs of Pt_x - WO_3 /C electrocatalysts in 0.5 M H_2SO_4 with a sweep rate of 50 mV/s.



The ethanol electro-oxidation mechanism on Pt_x - WO_3 /C involves parallel and consecutive oxidation reactions. The presence of WO_3 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

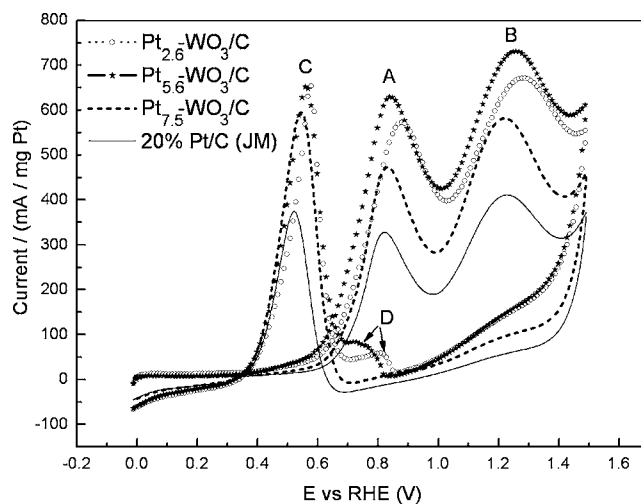


Figure 4. CVs of Pt_x - WO_3 /C electrocatalysts in 0.5 M H_2SO_4 with 0.5 M ethanol. Sweep rate was 50 mV/s.

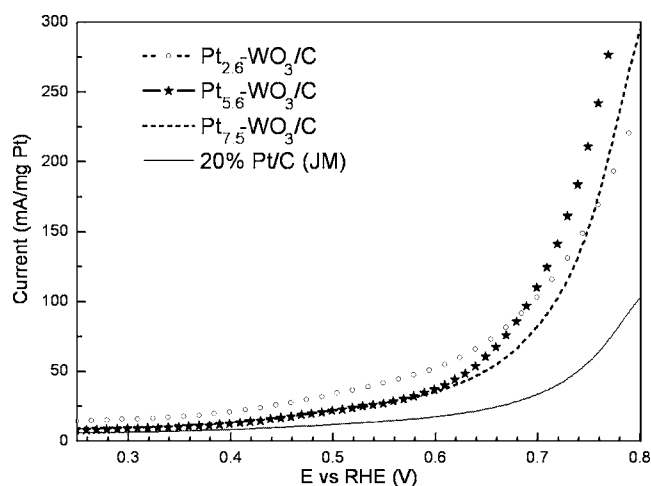


Figure 5. Linear sweep voltammograms of Pt_x-WO_3/C electrocatalysts in 0.5 M H_2SO_4 with 0.5 M ethanol. Sweep rate was 50 mV/s.

the electrocatalysts for the oxidation of CO_{ads} by releasing more Pt active sites for OH_{ads} species (Reactions 5 and 6), which react with CO_{ads} to form CO_2 .

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

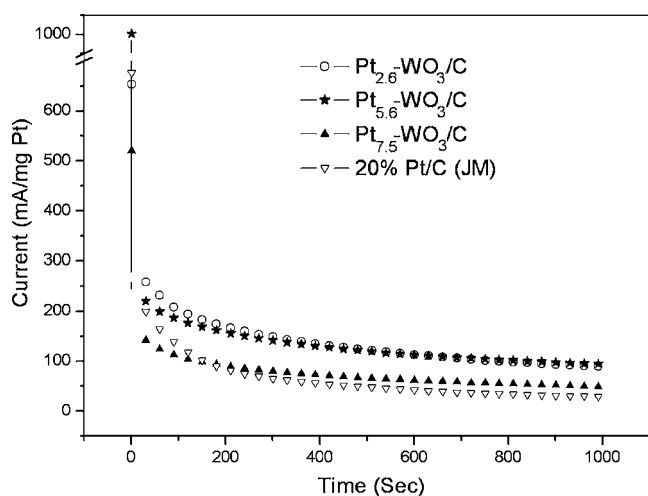


Figure 6. Chronoamperometric curves of Pt_x-WO_3/C electrocatalysts in 0.5 M H_2SO_4 with 0.5 M ethanol at 500 mV vs RHE.

presence of ethanol. It results from the WO_3 effect through Reactions 5-7 which can occur at a much lower potential¹⁸ 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.

Acknowledgements

The authors are grateful for the financial support of this work by the National Science Foundation of China under the approval no. 50236010, 20476055, and Shanghai SHUGUANG program (03SG12), respectively.

Shanghai Jiao Tong University assisted in meeting the publication costs of this article.

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