

Electrocatalytic Enhancement of Methanol Oxidation at Pt–WO_x Nanophase Electrodes and In-Situ Observation of Hydrogen Spillover Using Electrochromism

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A Pt–WO_x nanophase electrode showed a considerably more enhanced electrocatalytic activity than Pt itself for methanol oxidation and exactly the reverse change in optical signal intensity with respect to electrochemical cell potential, compared with an electrochromic WO_x electrode. This provides evidence for hydrogen spillover from Pt to WO_x. Consequently, it was possible to directly observe the in-situ hydrogen transfer from platinum to tungsten oxide in a fuel cell electrode using electrochromism. The transfer of hydrogen ions, produced on the platinum during the electrooxidation of methanol, to the tungsten oxide ensures that the active reaction sites on the platinum remain clean, thus enhancing the electrooxidation current density.

Introduction

Because of the current interest in fuel cells that operate at relatively low temperatures (<80 °C), catalytic reactions such as the oxidation of fuels at the anode or the reduction of oxygen at the cathode have been a subject of considerable interest.^{1–5} The transfer of hydrogen to the support surface during the oxidation of fuels would require the platinum to contain a clean active site in order to achieve efficient dehydrogenation of the catalyst.⁶ This phenomenon is frequently referred to as the hydrogen spillover effect. In particular, Rolison et al. reported that hydrous ruthenium oxides (RuO_xH_y) play an important role in mediating proton transport during methanol electrooxidation.⁷ Due to the proton conducting contribution of RuO_xH_y, a mixed-phase nanosized electrocatalyst containing Pt metal and RuO_xH_y may be considered to be excellent in methanol electrooxidation. Similar to Pt–RuO_xH_y, we reported the enhanced catalytic activity in the Pt–WO_x consisting of Pt nanometallic phase and WO_x.⁸ This means that proton conducting oxides such as RuO_xH_y and WO_x may play a key role for the enhanced methanol electrooxidation.

Attempts have been made to observe hydrogen transporting phenomenon in heterogeneous (electro)catalytic reactions using FTIR,⁹ a scanning light pulse technique,¹⁰ and NMR.¹¹ However, to date, no clear conclusive evidence for such an effect from a catalyst during a chemical or an electrochemical reaction has been reported. Here we describe a Pt–WO_x nanophase electrode, prepared by a sputtering process that is similar in structure to a bulk nanoparticle catalyst electrode and the direct observation of hydrogen transfer from platinum to the substrate using electrochromism in the tungsten oxide.

Experimental Section

Pt–WO_x nanoparticles were synthesized at room temperature by conventional reduction with NaBH₄.^{3,4} Pt salt (H₂PtCl₆·xH₂O, Aldrich Chem. Co) was mixed with tungsten oxide power (WO₃, Aldrich Chem. Co) as a support in Millipore water (18 MΩ

cm) until complete dissolution was achieved. After several hours, the salts were reduced with NaBH₄ (Aldrich Chem. Co) under constant stirring. The resulting material was washed with deionized water and dried by freeze-drying.

Pt–WO_x and WO_x thin-film electrodes were grown using an RF magnetron co-sputtering system as described previously.⁸ Indium tin oxide (ITO, Samsung Corning Co, Ltd)-coated transparent glasses were used as the substrate. Cu grids were also used as substrates for analysis by transmission electron microscopy (TEM). Pt metal and WO₃ were used as the target materials. The base pressure was less than 5×10^{-6} Torr and the working pressure was 5×10^{-3} Torr for all films examined. The sputtering was performed under an atmosphere of inert Ar gas at 40 SCCM at room temperature (RT). The Pt–WO_x two-phase film was sputter-deposited for 2 min at RF powers of 20 W and 180 W on the Pt and WO₃ target, respectively, and was compared with a Pt one-phase film that had been sputter-deposited for 2 min at an RF power of 20 W. The WO_x film was also sputter-deposited for 2 min at RF power of 180 W.

X-ray diffraction (XRD) analyses of Pt-based catalysts were carried out using a Rigaku X-ray powder diffractometer equipped with a Cu K_α source. To estimate the size and composition of the platinum alloy particles, the (220) peak was fitted using the Lorentzian/Gaussian function. The size and composition were obtained using the Debye–Scherrer equation and Vegard's law (see Results and Discussion). The size of the metal particles was investigated by TEM on a JEOL instrument (JEM-2000FXII) at a 200 kV accelerating potential. Specimens were prepared by ultrasonically suspending the particles in deionized water. Drops of such suspensions were deposited on a standard Cu grid covered with a carbon film (200 mesh) and allowed to dry before being insertion into the microscope. The EDX analysis was performed at 200 kV using an EXL II, Oxford attached to the microscope.

Electrochemical and optical measurements were made using a three-electrode cell at 25 °C. A Pt wire and an Ag/AgCl (in saturated KCl) were used as the counter and reference electrodes, respectively. All potentials are reported vs NHE in this paper. Solutions of 0.05 M H₂SO₄ and 2.0 M CH₃OH in 0.05 M H₂SO₄ were stirred constantly and purged with nitrogen gas. All

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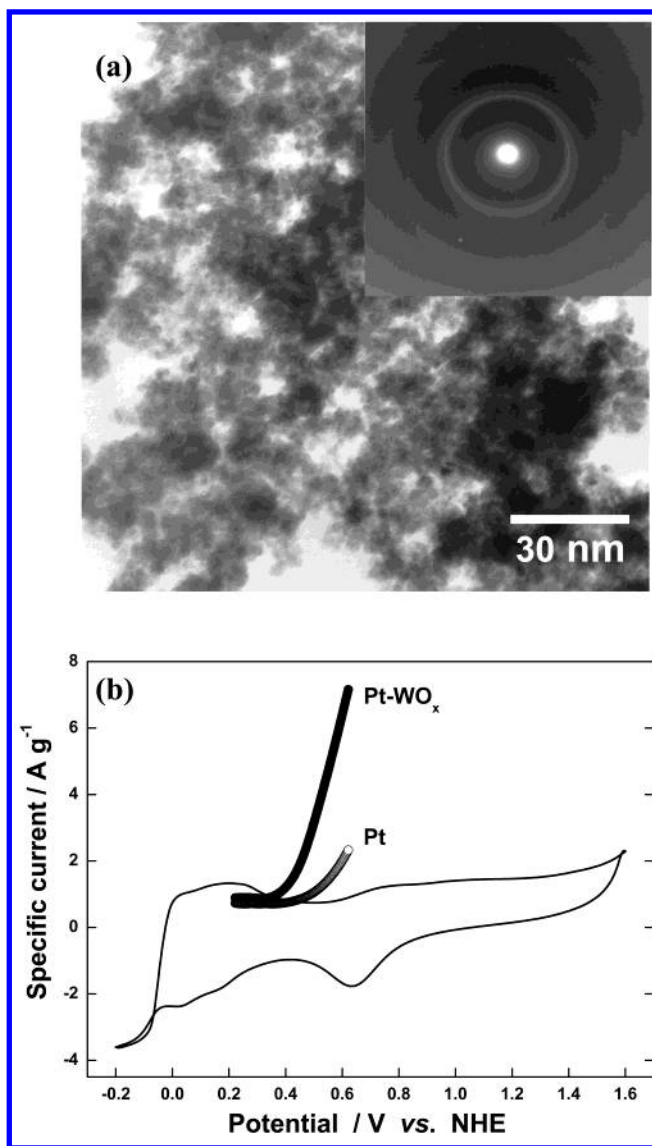


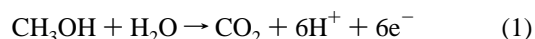
Figure 1. (a) Transmission electron microscopy analysis (insert: transmission electron diffraction pattern) of a Pt–WO_x nanoparticle powder catalyst and (b) voltammetric plots of Pt–WO_x and a Pt nanoparticle powder catalyst for methanol oxidation in 2.0 M CH₃OH + 0.05 M H₂SO₄ with the scan rate of 50 mV/s at room temperature. The baseline is a cyclic voltammogram of Pt–WO_x nanoparticle powder catalyst in 0.05 M H₂SO₄ at a scan rate of 50 mV/s.

chemicals used were of analytical grade. Electrochemical experiments were performed with an AUTOLAB instrument from Eco Chemie. To identify the properties of the Pt-based catalyst in H₂SO₄, cyclic voltammetry (CV) was performed.

Results and Discussion

Figure 1a shows a nanoparticle powder catalyst consisting of Pt and tungsten oxide (Pt–WO_x) prepared by the nanoparticle synthetic method described above, confirming the presence of 4–5 nm nanosized Pt with tungsten oxide as evidence by the ring pattern of transmission electron diffraction (TED) in the insert of the Figure 1a. The specific current, methanol electrooxidation current per loading gram of catalyst, of the Pt–WO_x and Pt nanocatalyst in 2.0 M CH₃OH + 0.05 M H₂SO₄ with an applied potential is compared as shown in Figure 1b. Quantitative characterization for catalytic activity of nanometer-scale Pt catalyst has been suggested using adsorption

and desorption of hydrogen or CO stripping on platinum surface.¹² However, in this study, since the hydrogen adsorption and desorption peaks for Pt and WO_x were overlapped in the almost same potential region, the catalytic activity of the electrode was compared by measuring the total mass of the Pt and Pt–WO_x on the carbon electrode. That is, current density in Figure 1b refers to A/g(Pt) for the Pt nanoparticle and A/g(Pt–WO_x) for the Pt–WO_x particle, respectively. Since Pt in Pt–WO_x is 60 wt %, Pt–WO_x would show much higher catalytic activity if A/g(Pt) scales were used in both nanoparticle catalysts. Further, roughly considering adsorption and desorption of hydrogen on the Pt surface of the Pt nanoparticle catalysts and 60 wt % of Pt in Pt–WO_x, methanol electrooxidation current density per area (mA/cm²) of Pt and Pt–WO_x with respect to potential could be possible and superior activity was also shown in the Pt–WO_x catalysts (not shown here). Theoretically, the oxidation of methanol proceeds at 0.04 V vs NHE according to eq 1:



Therefore, the lower onset potential and/or higher current indicates clear evidence of the superior electrocatalytic activity for methanol electrooxidation, as shown in the Pt–WO_x electrode in Figure 1b.

It is generally known that the catalytic activity of Pt–WO_x exceeds that of Pt without tungsten oxide because of the spillover effect to tungsten oxide in the case of Pt–WO_x.^{5,6} However, an in-situ observation of this spillover effect is rare in the case of Pt–WO_x powder catalysts. Accordingly, a nanophase thin film electrode consisting of Pt and WO_x was fabricated on indium tin oxide (ITO) as the transparent electrode by means of a sputtering method previously described⁸ in order to observe such an effect using the optical properties of tungsten oxide, that is, electrochromism. The principle instrumentation for the in-situ direct observation of hydrogen transfer phenomena using electrochromism was an electrochemical cell for methanol electrooxidation and an optical unit consisting of a He–Ne laser (633 nm) as the light source, along with a power meter for the detection of optical signal modulation.¹³ During the electrochemical reaction with respect to the potential, the laser (633 nm) was transmitted through the thin film electrode and the modulation of the signal intensity was continually detected at intervals of 0.5 s.

As shown in Figure 2a, the Pt–WO_x thin film electrode consists of a nanosized Pt crystalline phase (~4 nm, dark point in the TEM image) and an amorphous tungsten oxidative phase (relatively bright region) indicating the presence of a Pt nanosized phase from the ring pattern in the TED (inset of the Figure 2a). The configuration of the Pt–WO_x thin film electrode is the same as that of a conventional nanoparticle catalyst, as seen in Figure 1a. In terms of electrochemical properties and catalytic activity for methanol oxidation, the Pt–WO_x nanophase thin film electrode is superior to a Pt thin film electrode without tungsten oxide as shown in Figure 2b, which is in good agreement with those of bulk nanoparticle catalysts, shown in the Figure 1b.

In addition, a Pt–WO_x electrode approximately 100 nm in thickness, which is formed on the transparent ITO substrate transmits the light source (He–Ne Laser) and thus can be used to detect the variation in the intensity of the transmitted laser in the detector. In general, electrochromism is defined as reversible change in optical properties under an applied potential.^{13–15} Optical modulation is achieved when an electrochromic material such as tungsten oxide is electrochemically

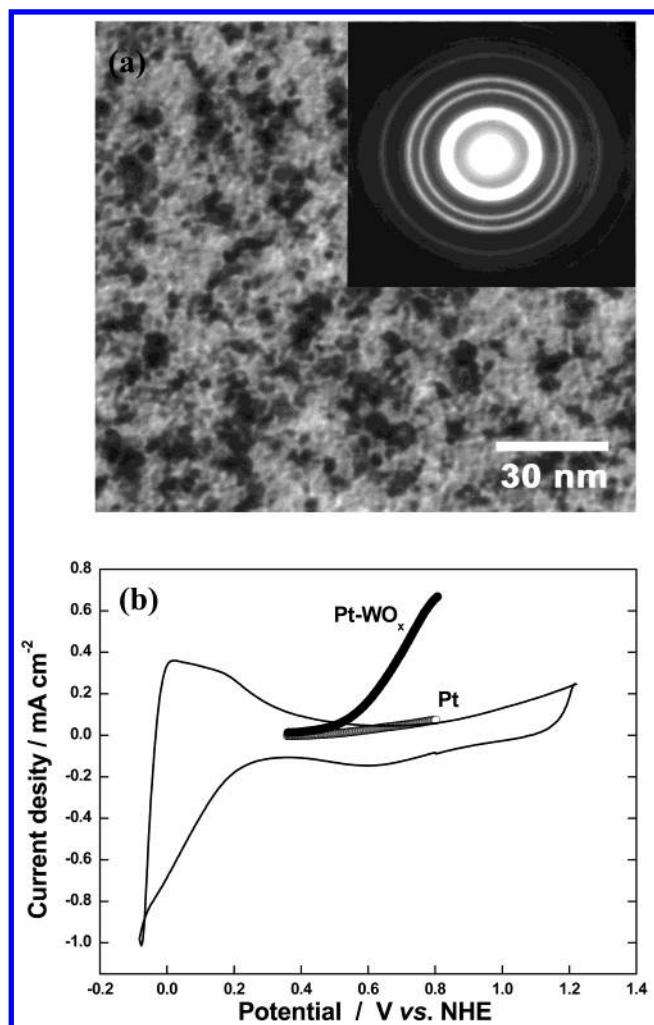
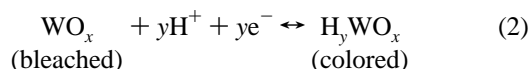


Figure 2. (a) Transmission electron microscopy analysis (insert: transmission electron diffraction pattern) of a Pt-WO_x nanophase thin film electrode and (b) voltammetric plots of Pt-WO_x and Pt thin film electrodes for methanol oxidation in 2.0 M CH₃OH + 0.05 M H₂SO₄ with the scan rate of 50 mV/s at room temperature. The base is a cyclic voltammogram of Pt-WO_x nanophase thin film electrode in 0.05 M H₂SO₄ at a scan rate of 50 mV/s.

oxidized and reduced according to eq 2:



The tungsten oxide is colored when an ion (i.e., hydrogen ion) is intercalated into the oxide, a process called cathodic coloration. If the hydrogen ions produced on the Pt at the Pt-WO_x thin film electrode during an electrochemical process such as the oxidation of methanol were transferred on the WO_x, these hydrogen ions would be intercalated into the tungsten oxide and the resulting intensity of the optical signal would be reduced.

Figure 3 shows the variation in transmittance of nanophase thin film electrodes (WO_x, Pt, and Pt-WO_x) with respect to an applied potential. The optical signal intensity of the WO_x electrode was reduced (colored) at -0.5 V vs NHE and increased (bleached) at +0.5 V vs NHE in parallel with the potential of the electrochemical cell while the Pt electrode (no electrochromic material) showed no change in intensity with respect to potential. However, it is surprising that the optical signal modulation of the Pt-WO_x nanophase thin film electrode is exactly the reverse of the WO_x electrode. This indicates that

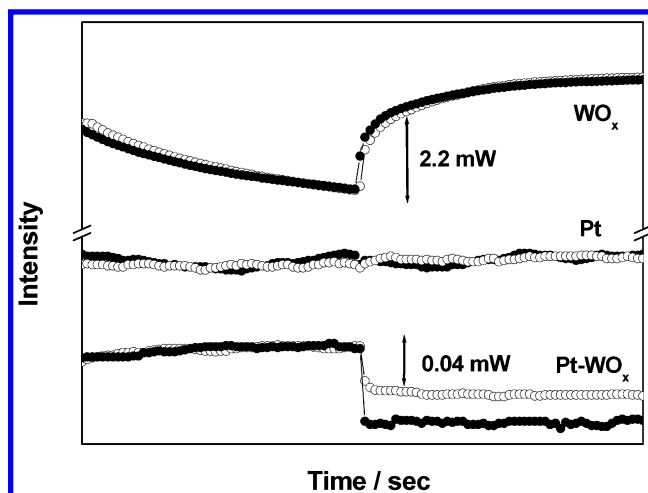


Figure 3. Optical intensity modulation of WO_x, Pt, and Pt-WO_x nanophase thin film electrodes as a function of electrochemical cell potential (-0.5 V to +0.5 V at intervals of 0.5 s). The open and solid circles represent optical signal modulation in 0.05 M H₂SO₄ and 2.0 M CH₃OH + 0.05 M H₂SO₄, respectively.

the hydrogen transfer phenomenon on the WO_x is affected and modified by the Pt nanophase near the oxide matrix, which serves as an electrochromic material. The optical signal intensity of the Pt-WO_x nanophase thin film electrode is reduced when the potential is applied from the negative to the positive. Hydrogen on the Pt catalyst would be transferred to the WO_x in the Pt-WO_x nanophase thin film electrode at a positive potential (+0.5 V) and then become colored, resulting in a reduction in the optical signal intensity as shown in eq 3:



However, the bleached state was observed in only the WO_x electrode without Pt at the same positive potential, thus showing typical electrochromism. Moreover, the difference in intensity of the Pt-WO_x nanophase thin film electrode is increased in 2.0 M CH₃OH + 0.05 M H₂SO₄ compared to 0.05 M H₂SO₄ and no methanol. It appears that since the additional hydrogen ions produced as the result of methanol oxidation would be involved in intercalation in the WO_x, a higher colored state would be generated thus causing a reduction in optical intensity.

Conclusions

In-situ hydrogen spillover from a catalyst to the substrate during electrocatalytic reaction was observed using electrochromism. A Pt-WO_x nanophase electrode deposited by a sputtering method showed a much more enhanced electrocatalytic activity than Pt itself for methanol oxidation, which was shown to be similar to that of a bulk nanoparticle catalyst electrode. The Pt-WO_x nanophase thin film electrode then showed exactly the reverse change in optical signal intensity with respect to electrochemical cell potential, compared to a WO_x electrode, a typical electrochromic material, suggesting the occurrence of hydrogen spillover from Pt to WO_x. As a result, the transfer of hydrogen ions, produced on the platinum during the electrooxidation of methanol, to the tungsten oxide ensures clean active reaction sites on the platinum thus enhancing the electrooxidation current density. We believe the electrocatalytic enhancement and in-situ measurement of spillover effect in methanol oxidation at Pt-WO_x provide a key insight into electrooxidation mechanisms and the design of (electro)catalytic materials considering the role of the substrate in fuel cells and heterogeneous catalysis. This result can be also

applied directly to the electrodes in micro-fuel cells, and corresponding experiments are currently underway.

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References and Notes

- (1) Hamnett, A. *Catal. Today* **1997**, *38*, 445.
- (2) Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangan, S.; Smotkin, E. S.; Mallouk, T. E. *Science* **1998**, *280*, 1735.
- (3) Park, K.-W.; Choi, J.-H.; Kwon, B.-K.; Lee, S.-A.; Sung, Y.-E.; Ha, H.-Y.; Hong, S.-A.; Kim, H.; Wieckowski, A. *J. Phys. Chem. B* **2002**, *106*, 1869.
- (4) Lee, S.-A.; Park, K.-W.; Choi, J.-H.; Kwon, B.-K.; Sung, Y.-E. *J. Electrochem. Soc.* **2002**, *149*, 1299.
- (5) Tseung, A. C. C.; Chen, K. Y. *Catal. Today* **1997**, *38*, 439.
- (6) Hobbs, B. S.; Tseung, A. C. C. *Nature* **1969**, *222*, 556.
- (7) Long, J. W.; Stroud, R. M.; Swider-Lyons, K. E.; Rolison, D. R. *J. Phys. Chem. B* **2000**, *104*, 9772. (b) Rolison, D. R.; Hangan, P. L.; Swider, K. E.; Long, J. W. *Langmuir* **1999**, *15*, 774.
- (8) Park, K.-W.; Ahn, K.-S.; Choi, J.-H.; Nah, Y.-C.; Kim, Y.-M.; Sung, Y.-E. *Appl. Phys. Lett.* **2002**, *81*, 907.
- (9) Cevallos Candau, J. F.; Conner, W. C. *J. Catal.* **1987**, *106*, 378.
- (10) Holmberg, M.; Lundstrom, I. *Appl. Surf. Sci.* **1996**, *93*, 67.
- (11) King, T. S.; Wu, X. *J. Am. Chem. Soc.* **1986**, *108*, 6056.
- (12) Schmidt, T. J.; Gasteiger, H. A.; Stäb, G. D.; Urban, P. M.; Kolb, D. M.; Behm, R. J. *J. Electrochem. Soc.* **1998**, *145*, 2354.
- (13) Ahn, K.-S.; Nah, Y.-C.; Yum, J. H.; Sung, Y.-E. *Jpn. J. Appl. Phys.* **2002**, *41*, 212.
- (14) Ahn, K.-S.; Nah, Y.-C.; Sung, Y.-E. *J. Appl. Phys.* **2002**, *92*, 1268.
- (15) Granqvist, C. G. *Handbook of Inorganic Electrochromic Materials*; Elsevier Science, B. V.: Amsterdam, 1995.