



Short communication

Methanol electrooxidation promoted by UV–vis light irradiation

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ABSTRACT

The present study reports on the promotion of methanol oxidation on Pt using UV–vis light irradiation. The anodic current rapidly responds to UV–vis light irradiation, and the rise and fall of the anodic current coincide with intermittent light irradiation during MeOH electrooxidation at various potentials. This photochemical effect depends on the applied potential and the wavelength of the applied UV–vis light. Irradiation with a short wavelength produces a more pronounced photochemical effect. The enhancement of CO electrooxidation with the aid of the oxygen-containing species formed on the Pt catalyst under UV-light irradiation plays an important role in the promotion of methanol oxidation.

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1. Introduction

A fuel cell is an electrochemical cell that converts the chemical energy of a fuel into electrical energy with high efficiency. Among the various types of fuel cells, proton exchange membrane fuel cells (PEMFCs) have the potential to supply power for portable and stationary applications. Direct methanol fuel cells (DMFCs) are PEMFCs that use MeOH as fuel; their performance highly depends on the methanol oxidation reaction (MOR) on anode catalysts. Numerous efforts, including the development of new catalysts [1] as well as detailed mechanism studies [2], have been made to improve the slow anode kinetics and CO tolerance of catalysts in DMFCs.

MOR catalyzed by Pt undergoes two critical reaction steps [3]. In the first step, hydrogen electrooxidation occurs after MeOH is adsorbed on Pt through the breaking of each of the C–H bonds, as shown below:



Subsequently, CO_{ad} is oxidized by oxygen-containing species (generally known as OH_{ad}) to form CO_2 :



Reaction (2) is generally considered the rate-determining step of the MOR [4]. Pt is a good catalyst for methanol adsorption below 0.64 V (vs. a saturated calomel electrode, SCE) [3]. However,

terminally bonded and bridge-bonded CO on Pt slow down the MOR by blocking MeOH adsorption on Pt sites [5]. O-containing species such as OH_{ad} [6] and PtO [7] are formed on Pt surfaces during Pt electrooxidation in acidic solutions. O-containing species next to adsorbed CO are helpful for CO removal on Pt [3,5]. Blending Ru in a Pt catalyst is a typical technique used to improve the CO tolerance because Ru can dissociate water to generate OH.

Recently, light illumination was reported to enhance the electrochemical oxidation of methanol on a TiO_2 nanotube-supported Pt [8] or Pt–Ru– TiO_2 photoelectrocatalyst [9]. $\text{TiO}_2(\text{h}^+)$ created via UV-light irradiation can oxidize methanol molecules to improve the MOR kinetics. On the other hand, UV-light irradiation can induce CO desorption from Pt because the chemical bond between Pt and CO is changed by the excitation of a Pt electron to the $2\pi_a$ state via the Pt conduction band, leading to the photodesorption of CO [10]. Therefore, light irradiation may directly promote the MOR kinetics via photodesorption of CO to prevent Pt deactivation during MeOH electrooxidation.

In the present paper, a new method of improving MOR kinetics by increasing the CO tolerance of the Pt catalyst is suggested. A possible mechanism is proposed based on electrochemical analysis and energy dispersive X-ray analysis (EDX).

2. Experimental details

A glassy carbon (GC) electrode modified by carbon-supported Pt (Pt–C, 40 wt% Pt) from E-TEK (USA) was used as the working electrode. The electrode was prepared as follows: 8 mg of the Pt–C catalyst powder was ultrasonically mixed with 0.1 mL of 5 wt%

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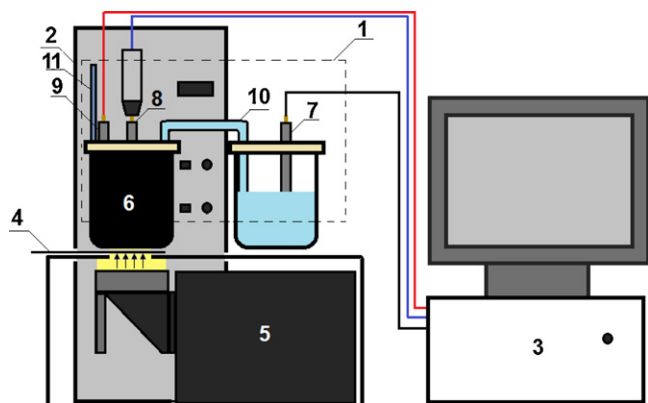


Fig. 1. Schematic diagram of the experimental set-up: (1) three-electrode cell, (2) rotating disc electrode, (3) electrochemical workstation, (4) shutter, (5) illuminant, (6) quartz beaker with an occluder, (7) saturated calomel electrode, (8) working electrode, (9) counter electrode (Pt wire), (10) salt bridge, and (11) temperature monitor.

Nafion solution (DuPont, USA) and 1.5 mL anhydrous ethanol for 20 min to form a homogenous catalyst ink. The catalyst ink (20 μL) was then pipetted onto the surface of a pretreated GC disk electrode 3 mm in diameter and then dried at room temperature. Finally, 0.57 mg cm^{-2} of Pt was loaded onto the glassy carbon electrode.

Fig. 1 shows the experimental setup. To avoid disturbing the electrochemical measurements, intermittent light irradiation was performed by opening and closing a shutter set between the test cell and the illuminant (PLS-SXE300, Trustech Corp.), which emitted light with wavelengths ranging from 300 to 660 nm (Fig. 2). Unless otherwise specified, the wavelength of the applied light was between 300 and 660 nm. The irradiation intensity was 212 mW cm^{-2} . Each monochromatic light wavelength was obtained by filtering light from the illuminant. The anodic current of potentiostatic MeOH oxidation under monochromatic light irradiation was recorded at 0.55 V.

Cyclic voltammetry (CV) measurements were performed in a three-electrode system. The rotating disc electrode (RDE) CVs were recorded between -0.2 and 1.0 V (vs. SCE) using BASi RDE2 (BAS Co., USA). A piece of Pt wire and an SCE were used as the counter and reference electrodes, respectively. All potentials refer to the SCE. The Tafel plots of the Pt-C/GC electrode in 0.50 M H_2SO_4 solution containing 0.50 M MeOH were obtained through capacitance correction because a porous Pt-C/GC electrode also behaves like

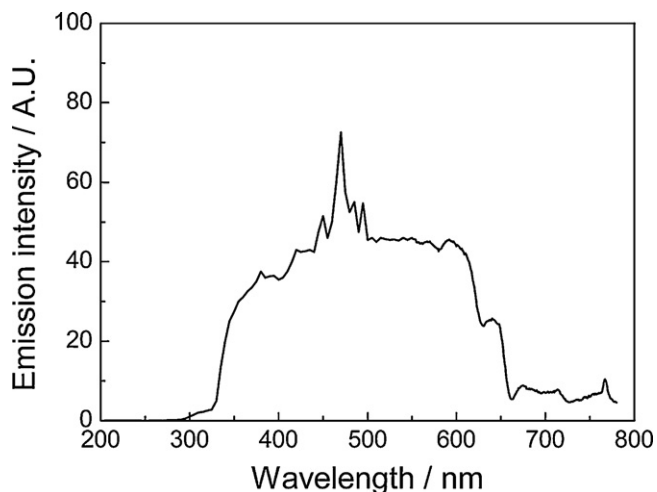


Fig. 2. Emission spectrum of the illuminant (PLS-SXE300).

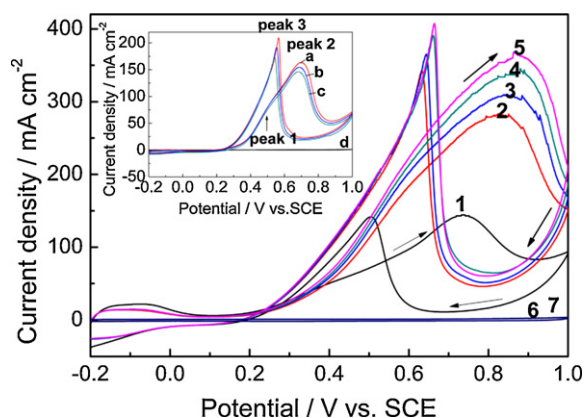


Fig. 3. CVs of the Pt-C/GC electrode under light irradiation at (1) 0, (2) 35, (3) 74, (4) 158, and (5) 212 mW cm^{-2} . CVs of the C/GC electrode under light irradiation at (6) 212 and (7) 0 mW cm^{-2} . Inset: RDE CVs of the Pt-C/GC electrode at a rotation rate of (a) 0, (b) 400, and (c) 2000 rpm. (d) The C/GC electrode at 0 rpm. $[\text{H}_2\text{SO}_4] = 0.50$ M, $[\text{MeOH}] = 0.50$ M. Scan rate: 50 mV s^{-1} at 25 $^\circ\text{C}$.

a capacitor. The anodic current values of the Pt-C/GC electrode at 0.15 V were used as the correction currents in the Tafel plots.

The Pt-213 electrode (sample 0#) was treated with chromic acid (5 M) for two hours prior to ultrasonic washing with acetone and air-drying at 25 $^\circ\text{C}$. Sample 1# was electrooxidized at 1.0 V for 5 min in 0.50 M H_2SO_4 solution. Sample 2# was electrooxidized at 1.0 V for 5 min in 0.50 M H_2SO_4 solution under light irradiation. After washing with acetone, the treated samples were dried at 25 $^\circ\text{C}$ prior to EDX analysis.

3. Results and discussion

Fig. 3 shows the CVs of the Pt-C electrode in a MeOH solution under UV-vis light irradiation at various intensities. The anodic current significantly increased when the electrode was irradiated. However, further increase in the irradiation intensity failed to produce a large increase in the anodic current.

Neither methanol nor water absorbs light with wavelengths between 300 and 660 nm, indicating that light irradiation did not improve the reactivity of methanol or water during MOR. The carbon support in the Pt-C catalyst did not affect the photochemical reaction, as indicated by the absence of a distinct current when the carbon-modified GC electrode was used with or without light irradiation (Fig. 3). A slight temperature increase near the Pt-C/GC electrode was observed during UV-vis light irradiation at 212 mW cm^{-2} illuminance for 4 min. However, the temperature rise caused by UV-vis light irradiation and its effect on the MOR kinetics were not critical (Fig. 4), indicating that the MOR kinetics was improved by the irradiation via a photochemical reaction. The inset of Fig. 3 shows the CVs obtained from an RDE. The peak current of the MOR did not change significantly when the rotation rate increased, indicating that mass transfer was not critical to MOR.

A reported MOR mechanism [11] suggested that methanol adsorption did not occur below -0.19 V because of the full Pt-H coverage where hydrogen was generated in the cathodic CV measurement process. The active Pt sites for methanol adsorption became available after electrooxidation of the adsorbed hydrogen on Pt. Based on this MOR mechanism, the anodic current increased because of hydrogen electrooxidation due to the breaking of each C-H bond in MeOH according to Reaction (1), when the potential was swept to a more positive value (above 0.2 V) without light irradiation (inset of Fig. 3). Subsequently, the terminally bonded and bridge-bonded CO were formed [5]. When the anodic sweeping potential reached 0.64 V, the metallic Pt was slowly electrooxidized to form O-containing species (Pt-O_{sp}) [3]. However, the formation

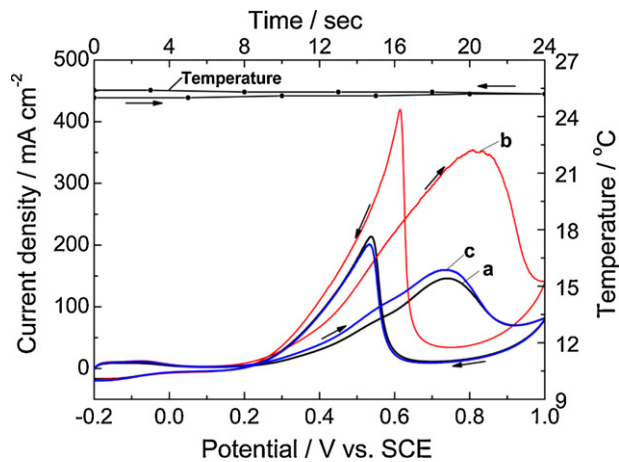


Fig. 4. Comparison of the CV under UV-vis light irradiation at 25 °C (b) with that at 25 °C (a) or 27 °C (c) without light irradiation. Pt-C/GC electrode, scan rate: 50 mV s⁻¹. The temperature was monitored during CV measurements under UV-vis light irradiation.

of CO_{ad} was much faster than that of Pt-O_{sp} so that only a small amount of the CO adsorbed on Pt was electrooxidized above 0.64 V with the aid of Pt-O_{sp}. As a result, the anodic current of MeOH decreased when the MOR occurred above 0.64 V.

Fig. 5A and B shows the wavelength of the applied monochromatic light and the response of monochromatic light irradiation to the MOR current during potentiostatic MeOH oxidation, respectively. The photochemical effect depends on the wavelength of the applied light. Light with a short wavelength exhibits a more pronounced photochemical effect. Fig. 6 illustrates the chronoamperometric curves during the potentiostatic oxidation of MeOH at various potentials with intermittent light irradiation. The anodic current rapidly responded to light irradiation, and the rise and fall of the anodic current coincided with light irradiation. These results reveal that light irradiation has a positive photochemical effect on MOR.

The effectiveness of UV-vis light irradiation is proportional to the anodic current of MeOH without light irradiation (Fig. 6). The desorption of CO from the active Pt sites induced by UV-light [10] may be partly responsible for the photopromotion of MOR. However, the chronoamperometric curves exhibit the same light irradiation effect at the same potential despite the steady increase in the adsorbed CO during the potentiostatic MeOH oxidation. These results imply that the light irradiation effect on the MOR is related to the anodic potential.

Without UV-vis light irradiation, O-containing species can be established on Pt during Pt electrooxidation at potentials higher

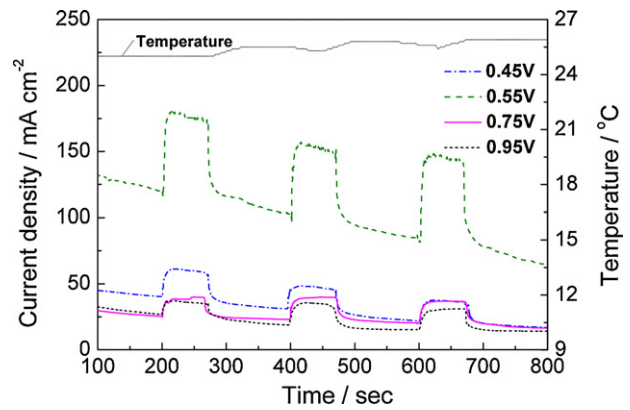


Fig. 6. Response of the anodic current to UV-vis light irradiation during the potentiostatic oxidation of MeOH at various potentials.

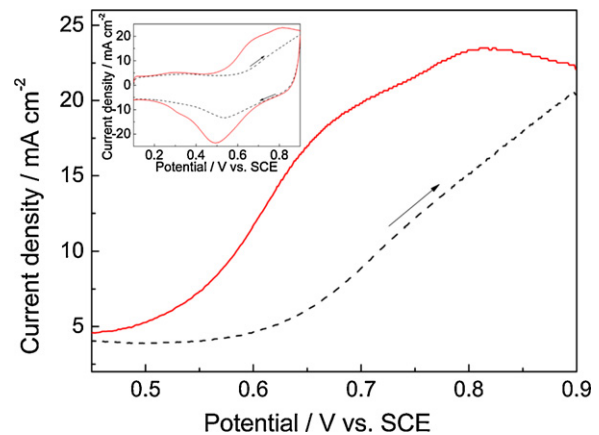


Fig. 7. CVs of the Pt-C/GC electrode in 0.50 M H₂SO₄ solution with (solid lines) and without UV-vis light irradiation (dashed lines). Inset: full graph. Scan rate: 50 mV s⁻¹ at 25 °C.

than 0.64 V (Figs. 7 and 8). UV-vis light irradiation triggers Pt-O_{sp} formation at lower potentials (e.g., 0.51 V). In other words, the Pt-O_{sp} triggered by UV-vis light irradiation is unstable at potentials lower than 0.64 V. With UV-vis light irradiation in this potential range, Pt-O_{sp} attacks the adsorbed CO to generate active Pt sites for MeOH adsorption, leading to a rapid increase in the anodic current. With the light shutter off, Pt-O_{sp} can no longer exist at

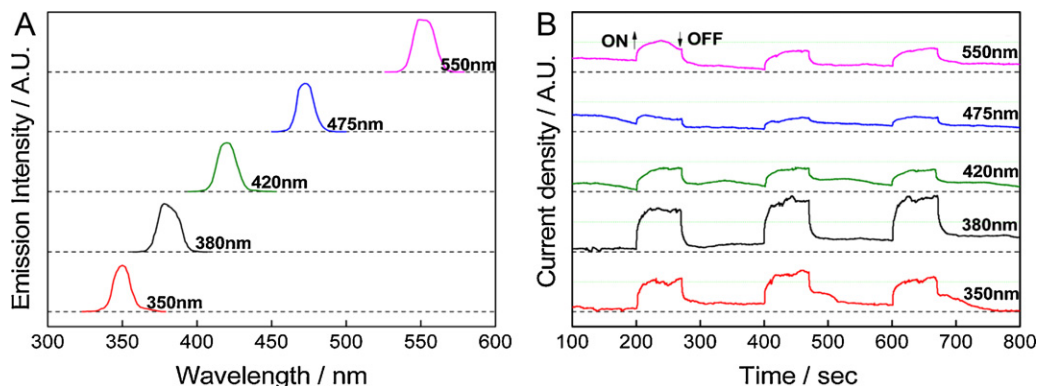


Fig. 5. (A) Wavelength of monochromatic light. (B) Response of the anodic current to light irradiation with various wavelengths during the potentiostatic oxidation of MeOH at 0.55 V in 0.50 M H₂SO₄ solution containing 0.50 M MeOH at 25 °C.

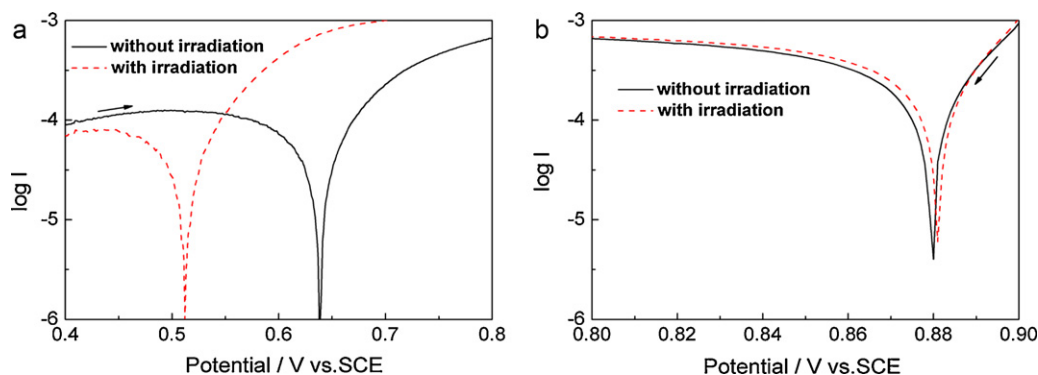


Fig. 8. Tafel plots of the Pt-C/GC electrode in 0.50 M H₂SO₄ solution at 25 °C with or without UV–vis light irradiation in (a) the anodic process and (b) the cathodic process.

Table 1

Oxygen content on the surface of the Pt-213 electrode after anodic oxidation at 1.0 V for 5 min with (2#) or without (1#) light irradiation in 0.50 M H₂SO₄ (identified by EDX).

Number	Treatment	Oxygen content (at.%)
0#	Original	18.71
1#	Anodic oxidation	30.98
2#	Anodic oxidation under irradiation	41.81

potentials lower than 0.64 V, and the adsorbed CO can no longer be electrooxidized with the aid of Pt–O_{sp}. As a result, the MOR kinetics rapidly declined (Fig. 6). At potentials higher than 0.64 V, the oxygen-containing species were stable and caused a decrease in the amount of adsorbed CO. Therefore, light irradiation demonstrated a less pronounced photoreaction effect at potentials higher than 0.75 V. However, light irradiation continued promoting MOR even at 1.0 V. The results of the EDX analysis (Table 1) reveal a distinctly higher oxygen content on the Pt electrode after anodic oxidation under light irradiation compared with those on the original electrode and the electrode after anodic oxidation. These results confirm that light irradiation promotes the formation of oxygen-containing species, which is consistent with the CV results in Fig. 7.

In the backward potential sweep (Fig. 3), the anodic current of MeOH on the Pt-C/GC electrode under light irradiation was observed at higher potentials. The increase in the anodic current was more rapid compared with the increase without light irradiation. This significant increase in the anodic current at lower potentials can be attributed to the electrooxidation of the CO adsorbed on Pt with the aid of the Pt–O_{sp} generated by light irradiation. The anodic current decreased after reaching a peak value because CO slowly reoccupied the active Pt sites. The electroreduction of Pt–O_{sp} is notably independent of light irradiation (Fig. 8b). Therefore, light irradiation plays an important role during MOR only in the formation of oxygen-containing species.

4. Conclusions

The anodic current of MeOH rapidly responded to UV–vis light irradiation, which enhanced the formation of O-containing species on Pt at lower potentials, and consequently promoted the electrooxidation reaction of adsorbed CO. Therefore, UV–vis light irradiation promoted the MOR on Pt.

Acknowledgments

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