



Electrochemical activity testing of Pt/metal oxide/glassy carbon electrodes for ethylene glycol oxidation

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ABSTRACT

Stable metal oxides non-soluble in acidic medium has been prepared and characterized. The influence of metal oxide (MO_x) type on the activity of Pt towards ethylene glycol oxidation in acidic medium has been examined. All modified Pt/ MO_x /glassy carbon (GC) electrodes exhibited a better activity compared to polycrystalline Pt. While Pt/ SnO_2 /GC electrode produced the highest oxidation current, Pt/ CeO_2 /GC exhibited the best tolerance against poisoning process. © 2009 Trade Science Inc. - INDIA

INTRODUCTION

Improvement in alcohol oxidation is still an important task in fuel cell technology. Pt is at present the best – known catalyst for the adsorption and dissociation of small organic molecules. However, it is generally accepted that Pt alone is not sufficient to oxidize alcohol at a reasonable rate, mainly because of surface poisoning. Also, Pt exhibits a limited ability for breaking C-C bond. Besides adsorbed CO, several two-C intermediates have been reported at polycrystalline Pt^[1-4]. For possible application in a fuel cell, ethylene glycol should be oxidized completely. This requires C-C cleavage, which is still a hard challenge^[5,6]. To achieve this, it is necessary to modify the composition and the structure of the anode catalyst^[7-11]. In addition to that complete oxidation as well as oxidation of poisoning intermediate requires an additional oxygen atom. It was reported that some metal oxides can act as oxygen storage component^[12,13]. Among them CeO_2 was found to have the ability to release oxygen reversibly^[14].

Ethylene glycol (EG) is much less volatile and less

toxic than methanol. It is electrochemically oxidizable^[15-17] and its complete oxidation in acidic medium produces 10 e⁻ per EG molecule compared to 6e⁻ for methanol. Recently, the synergistic effect of CeO_2 modified Pt/C towards EG oxidation in alkaline medium has been established^[18]. Due to the interest on direct alcohol fuel cells using an acidic polymer electrolyte membrane, increasing effort is being dedicated to study EG in acidic media^[19,20]. The usage of MO_x catalysts in acidic fuel cell technology is limited due to their solubility in acidic media

In the present study, three different MO_x non-soluble in acidic media have been prepared and used to modify the Pt/GC electrode. The stability and activity of Pt/ MO_x /GC electrodes towards EG oxidation in acidic media have been examined using cyclic voltammetric and chronoamperometric techniques.

EXPERIMENTAL

Chemicals and solutions

Analytical grade chemicals H_2SO_4 (BDH), ethyl-

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ene glycol (Pprlabo), H_2PtCl_6 (Merck), SnO_2 (Merck), $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\cdot 5\text{H}_2\text{O}$ (BDH), $\text{Ce}(\text{NO}_3)_3\cdot x\text{H}_2\text{O}$ (Merck) have been used for catalyst preparation and electrochemical measurements.

All solutions were prepared from water obtained with a Megapure system (MP-A6 Corning).

Metal oxide preparation

WO_3 and CeO_2 were prepared by direct thermal decomposition of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3\cdot x\text{H}_2\text{O}$, respectively. SnO_2 was prepared as described elsewhere^[21-23]. NH_4OH (25 wt. %) solution was added drop wise to aqueous solution of $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ under vigorous stirring; the final pH of solution was adjusted to 8. The obtained $\text{Sn}(\text{OH})_4\cdot x\text{H}_2\text{O}$ as a white precipitate was filtered, washed thoroughly with 2% $\text{CH}_3\text{COONH}_4$ to eliminate the excess chloride, dried at 120 °C for 24 h and finally calcinated for 4 h.

Electrochemical measurements

All electrochemical experiments have carried out using Voltalab model PGZ 100 and a conventional three-electrode cell. Platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Glassy carbon disc (Sigradur^{R-G}, Sigri Electrographite GMBH, Germany) of geometric surface area 0.39 cm² were used as the working electrode to support the Pt/ MO_x particles. Before the modification, the GC electrodes were polished on a microcloth (Bühler) using aluminum oxide of different diameters (13, 3, 1, 0.3 and 0.05 μm)^[24,25].

Pt/ MO electrode was prepared as described previously by Campos et al.^[26]: A definite amount of metal oxide was added to a 25ml solution of 0.3mM of H_2PtCl_6 in 0.1M H_2SO_4 . Electrodeposition was done with continuous stirring of a solution containing metal oxide as a suspension by applying a constant potential of -200mV/(SCE) to the glassy carbon electrode for 10 min. The Pt/ MO_x /GC electrodes were characterized by surface and electrochemical techniques.

Testing the Pt/ MO_x /GC electrodes for ethylene glycol oxidation was done in 0.5M EG + 0.1M H_2SO_4 by chronoamperometric and voltammetric techniques.

Characterization

Elemental composition of the film was determined

using energy dispersive X-ray (EDAX), horida-ex-200, Japan. The Surface morphological studies were carried out with Scanning electron microscopy SM 5410, JEOL, Japan.

RESULTS AND DISCUSSION

The intrinsic solubility of metal oxide was determined by soaking 0.5 g of prepared metal oxide in 100 ml of H_2SO_4 for 2 days, sonicated for 5 min using P Selecta ultrasonic bath, filtered using nano-por devices, drayed at 120 °C until constant weight was obtained. The percent of recovery was $99.6 \pm 0.2\%$.

Preparation of the composite electrode

Figure 1 is the current-time plot for the deposition from a "bath solutions" containing 0.24 g in metal oxide and 0.3 mM H_2PtCl_6 in 0.1M H_2SO_4 . Since the suspension was under continuous stirring during the deposition step, the deposition was limited by mass transport by convection and not by diffusion control. During the first seconds of the electrodeposition, a significant amount of the current was due to the charging of the double layer and at longer times the current maintained constant with time.

Surface characterization of the electrodes

The electrodeposits were characterized by scanning electron microscopy (SEM) and X-ray (EDAX).

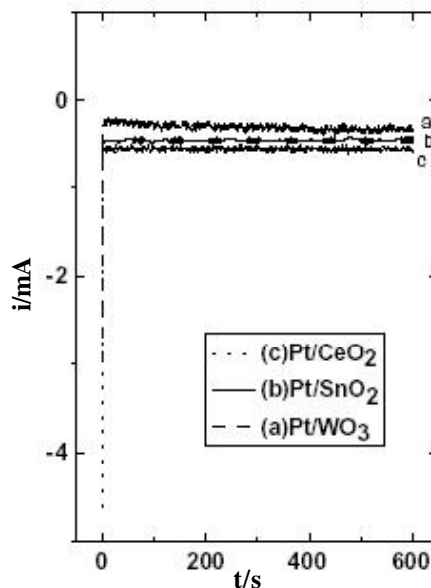


Figure 1 : Chronoamperometry of the electrodeposition of Pt/ MO_x on GC electrode using 0.24g MO_x and 3.89mg H_2PtCl_6 in 0.1M H_2SO_4 . Edep. = -200 mV/SCE.

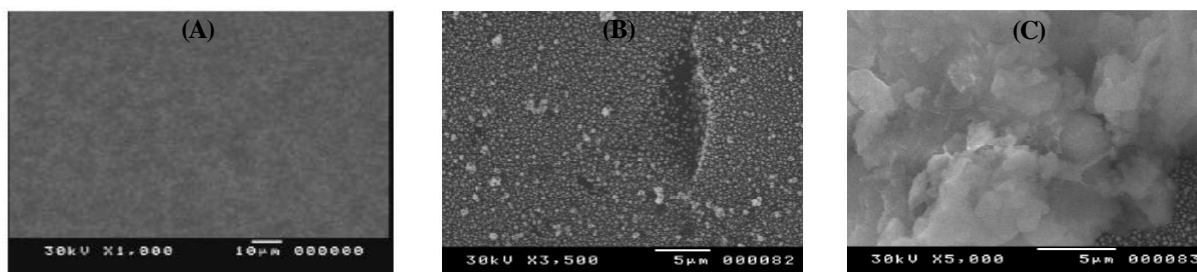


Figure 2 : Scanning electron microscopy images of (A) Clean glassy carbon electrode, (B) Glassy carbon electrode after its modification with Pt/WO₃ (3500X) and (C) At a magnification of 5,000X.

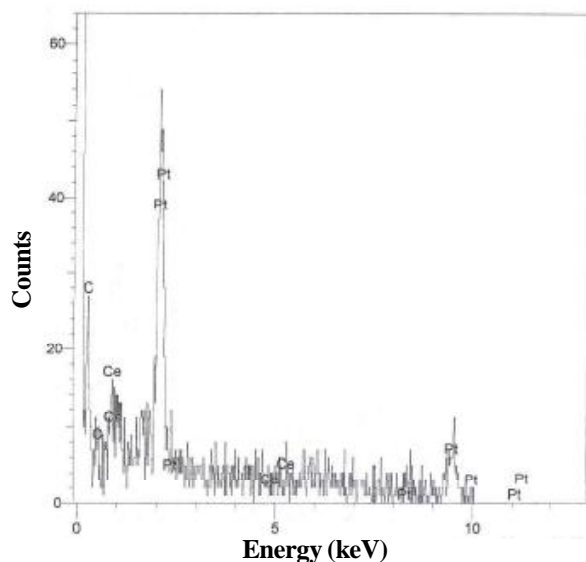


Figure 3 : EDAX image of Pt/CeO₂/GC composite electrode.

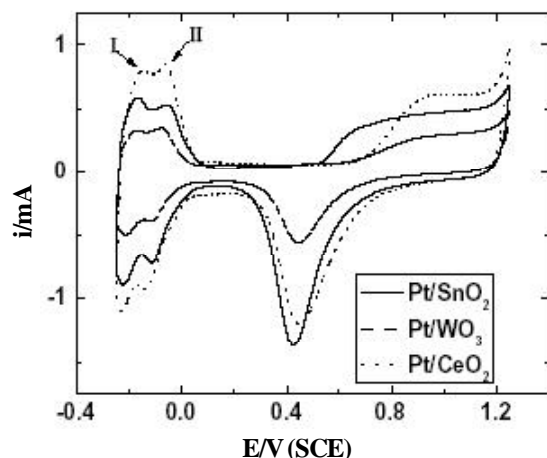


Figure 4 : Cyclic voltammograms for Pt/MO_x/GC electrodes in 0.1M H₂SO₄. (—) Pt/SnO₂/GC, (-----) Pt/WO₃/GC and (.....) Pt/CeO₂/GC. Scan rate: 50 mV s⁻¹.

Figure 2 presents the SEM images of the glassy carbon electrode before and after the electrodeposition of Pt/WO₃ composite electrode as an example. The SEM image of clean glassy carbon electrode is shown in figure 2A. The micrograph shows an homogeneous surface free of particles. After deposition of tungsten and

TABLE 1 : Pt/M ratios obtained by EDAX of modified glassy carbon electrode.

Deposition bath	0.24g CeO ₂ + 0.3Mm H ₂ PtCl ₆ in 25 ml H ₂ SO ₄	0.24g SnO ₂ + 0.3mM H ₂ PtCl ₆ in 25 ml H ₂ SO ₄	0.24g WO ₃ + 0.3mM H ₂ PtCl ₆ in 25 ml H ₂ SO ₄
Pt/M ratio (EDAX)	[Pt]/[Ce] = 22.8	[Pt]/[Sn] = 18.6	[Pt]/[W] = 8

The deposition time was 600 s in all cases and E_{dep} = -200 mV/SCE.

platinum the surface of the electrode change to that shown in figure 2B where the obvious presence of some materials shows that glassy carbon electrode was modified. At larger magnification (5,000X) the presence of some dendrite growth indicates that the deposit has a high surface area (figure 2c).

Some spectrometric measurements using the energy dispersive x-ray spectroscopy (EDAX) technique were done in order to analyze the chemical composition of the modified electrode. The EDAX spectrum of Pt/CeO₂/GC electrodes composite electrode (figure 3) shows different peaks due to the presence of cerium and platinum in addition to that for carbon and oxygen. This is of course further evidence of the presence of these materials on the modified electrode. TABLE 1 shows the Pt/M ratio obtained by EDAX of modified glassy carbon electrode. As can be seen for this table, composite electrode with different composition can be prepared by just changing the “bath solution” composition.

Cyclic voltammetry experiments

Figure 4 shows the cyclic voltammograms of various modified Pt/MO_x/GC in 0.1M H₂SO₄. Peaks observed below 0.1V are due to hydrogen adsorption/desorption process. During the forward potential scan, the increase in current increase at potential > 0.5V are due to the oxidation of Pt surface which reduce in the reverse scan forming a reeducation peak between 0.5

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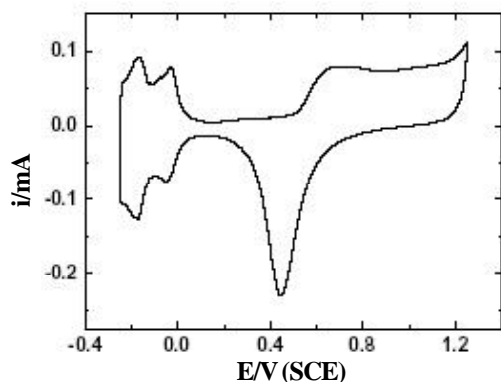


Figure 5: Cyclic voltammograms for polycrystalline Pt electrode in $0.1\text{M H}_2\text{SO}_4$. Scan rate: 50 mV s^{-1} .

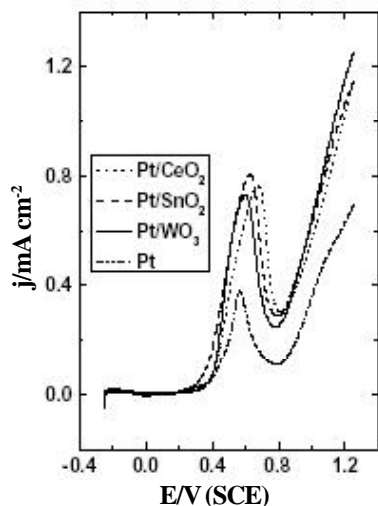


Figure 6: Current-potential curves for EG electro-oxidation on (—) Pt/SnO₂/GC, (-----) Pt/WO₃/GC, (.....) Pt/CeO₂/GC and Pt (- · - ·) in $0.1\text{M H}_2\text{SO}_4 + 0.5\text{M EG}$. Scan rate: 50 mV s^{-1} .

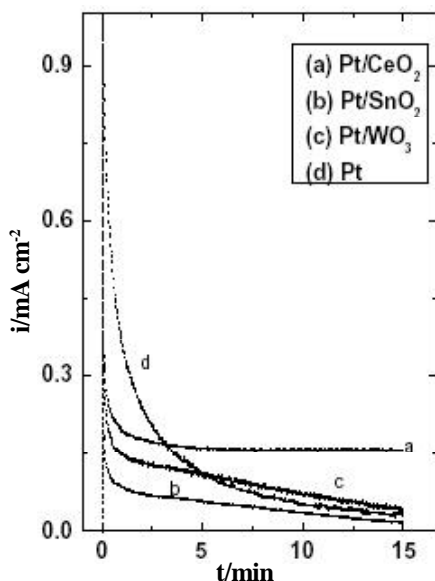


Figure 7: Chronoamperometric curves recorded at 0.5V vs. SCE for (—) Pt/SnO₂/GC, (-----) Pt/WO₃/GC, (.....) Pt/CeO₂/GC and Pt (- · - ·) in $0.1\text{M H}_2\text{SO}_4 + 0.5\text{M EG}$.

and 0.4 V depending on the type of composite electrode. As can be seen from this figure, the general shape of the voltammograms of the three composite electrodes are close to that of normal polycrystalline Pt recorder under the same condition (figure 5). However, careful examination to these voltammograms indicates that there a difference in the peak heights of peaks I and II. This is connected to the crystallographic orientation of the Pt crystal surface. Peak I was ascribed to Pt(110) site while peak (II) to Pt(100) site^[27]. So, increasing the height of peak (II) as in case of Pt/CeO₂/GC and Pt/WO₃/GC indicates that the Pt surface is more rich in Pt(100) site more than in Pt/SnO₂/GC electrode. As a result of the increase in the Pt(100) site on the surface of the 1st two electrodes, the onset potential for Pt oxide formation process was shifted to more positive potential than the last one which is rich with Pt(110) site. This is in accordance with the data recorded for Pt single crystals.

The catalytic activity of the composite electrodes for the electrooxidation of ethylene glycol in acidic solution has been examined. Figure 6 presents the cyclic voltammograms for EG oxidation at the three different composite electrodes. For comparison, voltammogram of polycrystalline Pt, recorded under the same experimental condition, is included. For the sake of clarity, only the positive-going sweeps were plotted. It is clearly seen that, the onset oxidation of ethylene glycol at the three modified electrode shifted to less positive value with the highest shift (100 mV) for Pt/SnO₂/GC electrode. In addition to that, the oxidation current obtained at the three modified electrodes around the peak potential is very close to each other but it is approximately twice that obtained using polycrystalline Pt electrode. This enhancement in catalytic activity can be attributed to the oxidation of the poisoning species at less positive potentials. The promotion of poisoning species oxidation has been attributed to the bifunctional mechanism^[28-31] together with the modification of the electronic properties of Pt via what is so called ligand effect^[32-34]. However, the role of particle size effect as well as crystallographic ordination of deposited Pt cannot be excluded.

Testing the tolerance ability of the modified electrode towards poisoning process during ethylene glycol oxidation is very important from the practical point of view. For this reason, the current density for ethyl-

ene glycol oxidation has been recorded as a function of time at 0.5V/SCE over more than 15 min. The resultant curves are shown in figure 7. As can be seen from this figure, Pt electrode exhibits the highest current density at the beginning of ethylene glycol oxidation, however its activity drops so fast due to its surface poisoning by intermediate products. On the other hand, the three modified Pt/MO_x/GC electrodes exhibit a better tolerance against poisoning species accumulation. The highest tolerance ability was obtained at Pt/CeO₂/GC modified electrode. The enhancement factor (ratio of oxidation currents for Pt with and without modification) obtained for CV at 0.5V together with the current densities obtained from i-t curves after 15 min are given in TABLE 2. As can be seen from this table, the enhancement factor was found to decrease in the order: Pt/SnO₂/GC ~ Pt/WO₃/GC > Pt/CeO₂/GC > Pt. On the other hand, the tolerance against poisoning accumulation was found to decrease in the order: Pt/CeO₂/GC > Pt/WO₃/GC > Pt > Pt/SnO₂/GC.

TABLE 2 : Current density and catalytic factor of EG oxidation at Pt and Pt/MO_x/GC electrodes at 0.5V/SCE.

Electrode	Catalytic factor ^a	j (μA cm ⁻²) ^b
Pt/SnO ₂ /GC	2.6	160
Pt/WO ₃ /GC	2.4	40.2
Pt/CeO ₂ /GC	1.8	16.2
Pt	1	33

^aRatio of oxidation currents of (Pt/MO_x/GC) / (Pt) obtained from CV at 0.5V, ^bCurrent density of (Pt/MO_x/GC) / (Pt) obtained from i-t at 0.5V after 15 min electrolysis.

CONCLUSIONS

Pt/MO_x/GC composite electrodes have been prepared simply by dispersing the MO_x suspension in the platinum deposition bath. Modified electrodes were found to enhance the EG oxidation current together with shifting the onset of its oxidation to less positive value. Pt/CeO₂/GC electrode exhibited the best tolerance behavior against poisoning process.

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