ELECTROCHEMICAL ACTIVITY TESTING OF PT/METAL OXIDE/GLASSY CARBON ELECTRODES FOR ETHYLENE GLYCOL OXIDATION

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ABSTRACT

Some 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.

1. INTRODUCTION

Improvement in alcohol oxidation is still an important task in fuel cell technology. Pt is the best – known catalyst for the adsorption and dissociation of small organic molecules. However, it is generally accepted that pure 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 C-C intermediates have been reported at polycrystalline Pt [**Schmidt et al., (1996); Iwasita & Pastor (1994); Xia et al., (1997) and Delime et al., (1999)**]. For possible application in a fuel cell, ethylene glycol should be oxidized completely. This require C-C cleavage, which is still a hard challenge [**Hitmi et al., (1994) and Chang et al., (1990)**]. To achieve this, it is necessary to modify the composition and the structure of the anode catalyst [**Hable & Leug (1993); Gotz & Wendt (1998); Fujiwara et al., (1999); Oliverira et al., (2002) and Leger (2001)**]. 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 [**Nunan et al., (1992) and Yao & Yao (1984)**]. Among them CeO_2 was found to have the ability to release oxygen reversibly [**Perkins et al., (2001)**].

Ethylene glycol (EG) is much less volatile and less toxic than methanol. It is electrochemically oxidizable [**Enea & Ango (1989); Belgsir et al., (1991) and Matsuoka et al., (2002)**] and its complete oxidation in acidic medium produce 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 [**Xu et al., (2005)**]. 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 [**Lamy et al., (2003) and De Lima et al., (2003)**]. The usage of MO_x catalysts in acidic fuel cell technology is limited due to their solubility in acidic media. The aim of the present study is to prepare three different MO_x non-soluble in acidic media have been prepared and then use to modify the Pt/GC electrode to investigate the stability and activity of Pt/MO_x/GC electrodes towards EG oxidation in acidic media have been examined using cyclic voltammetric and chronamperometric techniques.

2. EXPERIMENTAL

2.1 Chemicals and solutions

Analytical grade chemicals H_2SO_4 (BDH), ethylene glycol (Prolabo), H_2PtCl_6 (Merck), SnO_2 (Merck), $(NH_4)_{10}W_{12}O_{41}.5H_2O$ (BDH), $Ce(NO_3)_3.xH_2O$ (Merck) have been used for catalyst preparation and electrochemical measurements.

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

2.2. Metal oxide preparation

WO_3 and CeO_2 were prepared by direct thermal decomposition of $(NH_4)_{10}W_{12}O_{41}.5H_2O$, $Ce(NO_3)_3.xH_2O$, respectively. SnO_2 was prepared as described elsewhere [**Matsuhashu et al., (2001); Matsuhashu et al., (2001) and Ahmed et al., (2008)**]. NH_4OH (25 wt. %) solution was added drop wise to aqueous solution of $SnCl_4$ under vigorous stirring; the final pH of solution was adjusted to 8. The obtained $Sn(OH)_4$ XH_2O as a white precipitate was filtered, washed thoroughly with 2% CH_3COONH_4

to eliminate the excess chloride, dried at 120°C for 24 h and finally calcinated for 4 h.

2.3. 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 cm^2 was 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) [**Elshafei (1989) and Elshafei (1999)**].

Pt/MO electrode was prepared as described previously by [**Campos et al., (2005)**]. A definite amount of metal oxide was added to a 25ml solution of 0.3mM of H$_2$PtCl$_6$ in 0.1M H$_2$SO$_4$. 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$_2$SO$_4$ by chronoamperometric and voltammetric techniques.

2.4. 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.

3. 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$_2$SO$_4$ for 2 days, sonicated for 5 min using P Selecta ultrasonic bath, filtered using nano-pore devices, drayed at 120°C until constant weight was obtained. The percent of recovery was 99.6 ± 0.2%.

3.1. Preparation of the composite electrode

Fig.1 shows 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. Science 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 a constant value with time.
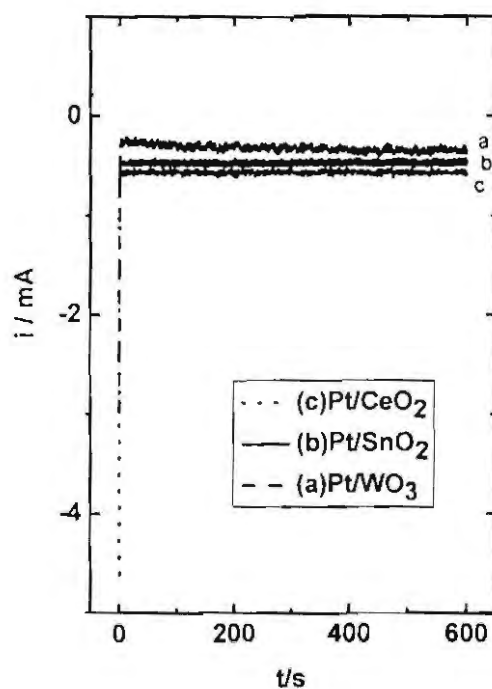

Fig.(1): Chronoamperometry of the electrodeposition of Pt/MO_x on GC electrode using 0.24g MO_x and 3.89mg H_2PtCl_6 in 0.1M H2SO4. Edep.= -200 mV/SCE.

3.2. Surface characterization of the electrodes

The electrodeposits were characterized by scanning electron microscopy (SEM) and X-ray (EDAX). Fig.2 presents the SEM images of the glassy carbon electrode before and after the electrodeposition of Pt/WO_3 composite electrode as an example. The SEM image of clean glassy carbon electrode is shown in fig.2A. The micrograph shows an homogeneous surface free of particles. After deposition of tungsten and platinum the surface of the electrode changes to that shown in fig .2B where the obvious presence of some materials indicates 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 (fig. 2c).
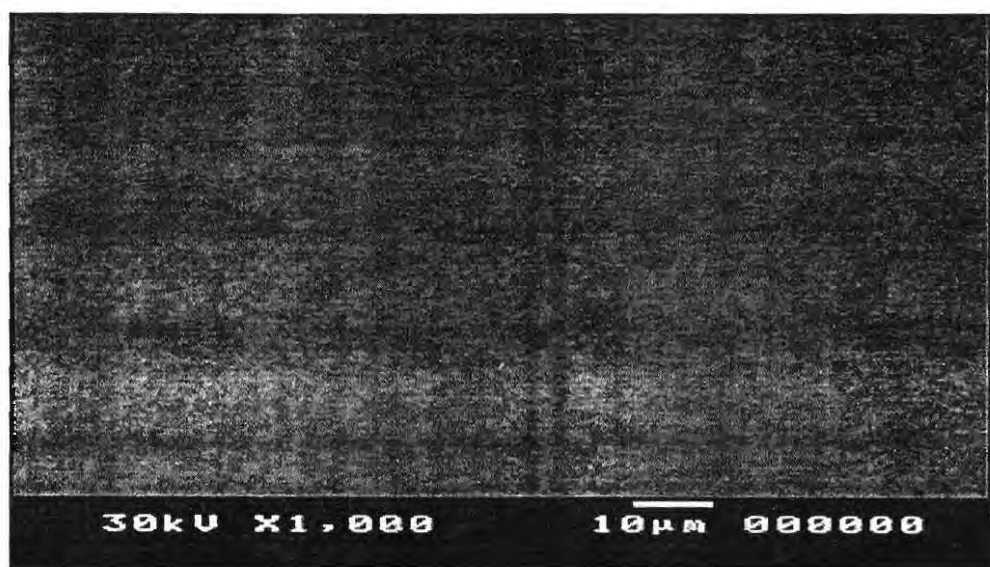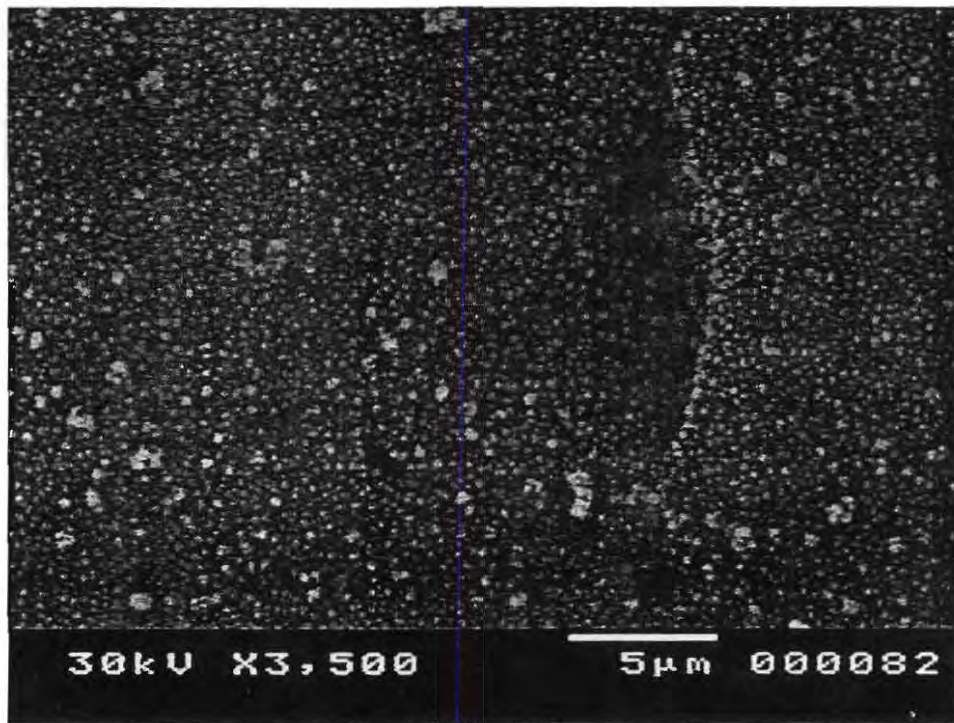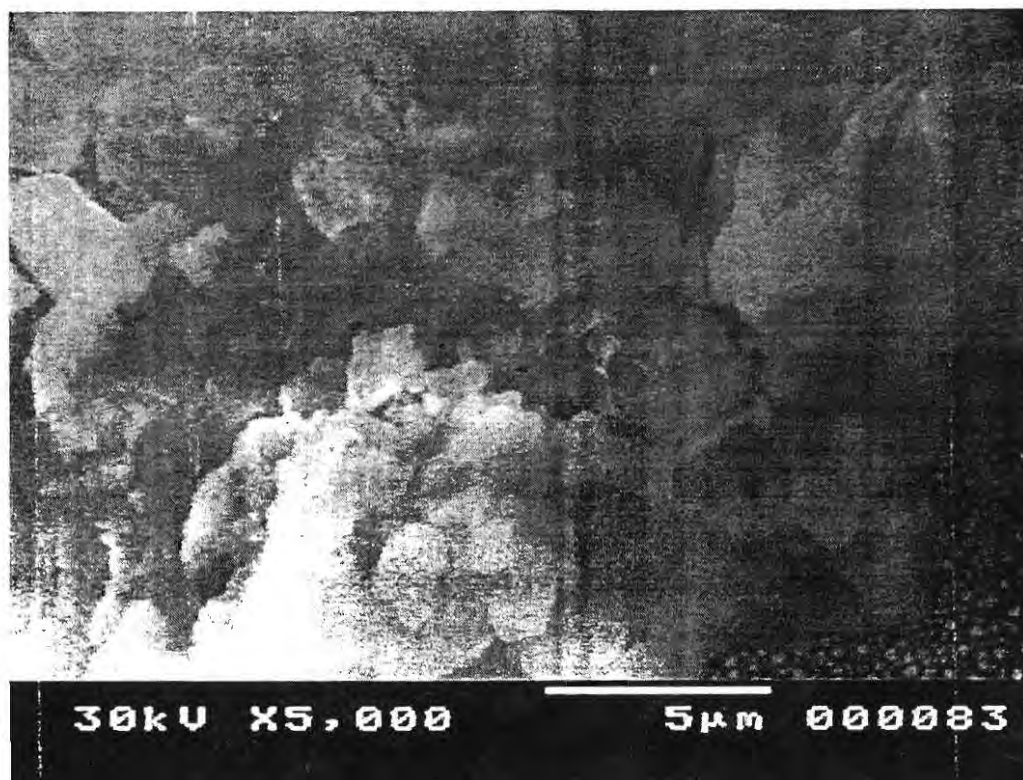

Fig 2a

30kV X3,500 5μm 000082

(B)

Fig 2 b

30kU X5,000 5μm 000083

(C)

Fig 2c

Fig.(2): Scanning electrone 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.

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 (fig.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 from this table, composite electrode with different composition can be prepared by changing the "bath solution" composition.
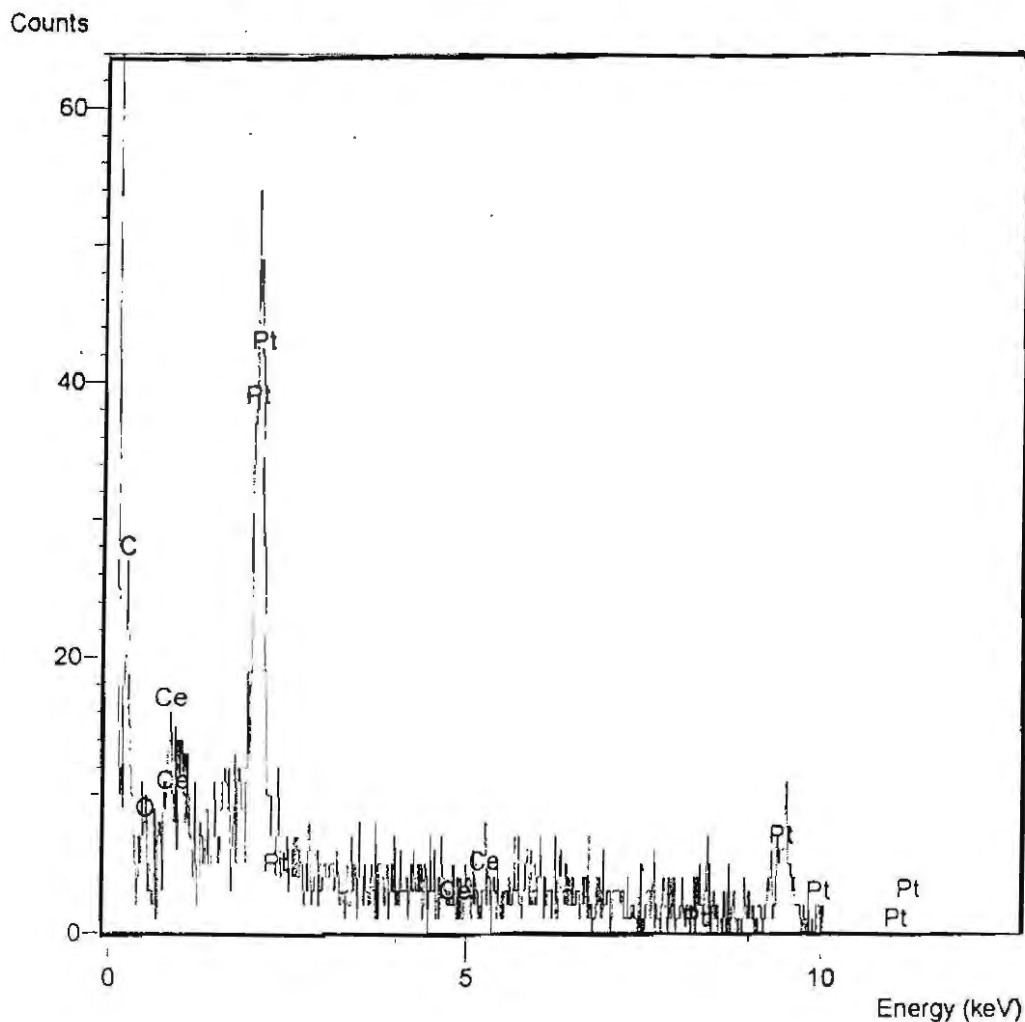
Counts

Fig.(3). EDAX image of Pt/CeO₂/GC composite electrode.

Table (1): Pt/M ratios obtained by EDAX of modified glassy carbon electrode.

Deposition bath	0.24g CeO₂ + 0.3mM H₂PtCl₆ in 25 ml H₂SO₄	0.24g SnO₂ + 0.3mM H₂PtCl₆ in 25 ml H₂SO₄	0.24g WO₃ + 0.3mM H₂PtCl₆ in 25 ml H₂SO₄
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 vs SCE.

3.2. Cyclic voltammetry experiments

Fig. (4) shows the cyclic voltammograms of various modified $Pt/MO_x/GC$ in 0.1M H_2SO_4. Peaks observed below 0.1V are due to hydrogen adsorption/desorption process. During the forward potential scan, the increase in current at potential > 0.5V are due to the oxidation of Pt surface which reduce in the reverse scan forming a reduction peak between 0.5 and 0.4 V depending on the type of the electrode composition. 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 (fig. 5). However, careful examination to these voltammograms indicates that there is 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 **[Elshafei et al., (1994)]**. So, increasing the height of peak (II) as in case of $Pt/CeO_2/GC$ and $Pt/WO_3/GC$ indicates that the Pt surface is more rich in Pt(100) site more than in $Pt/SnO_2/GC$ electrode. As a result of the increase in the Pt(100) site on the surface of the first 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.
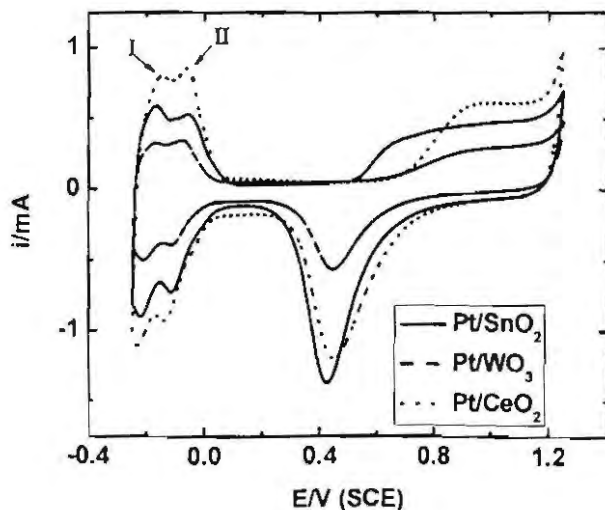

Fig.(4): Cyclic voltammograms for $Pt/MO_x/GC$ electrodes in 0.1M H_2SO_4. (———) $Pt/SnO_2/GC$, (------) $Pt/WO_3/GC$ and (.......) $Pt/CeO_2/GC$. Scan rate: 50 mV s^{-1}.
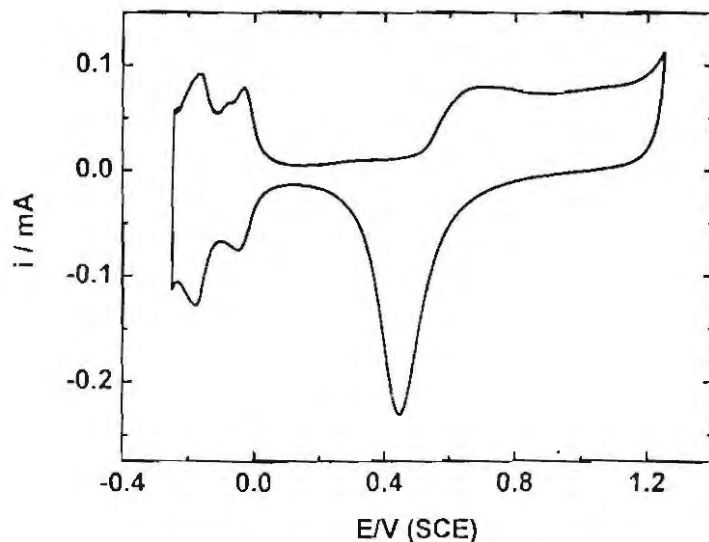
Fig.(5): Cyclic voltammograms for polycrystalline Pt electrode in 0.1M H_2SO_4. Scan rate: 50 mV s^{-1}.

The catalytic activity of the composite electrodes for the electrooxidation of ethylene glycol in acidic solution has been examined. Fig. 6 represents 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 anodic 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 $Pt/SnO_2/GC$ 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 [**El-Shafei et al., (2004); Gasteiger et al., (1995); Grgur et al., (1998) and Watanbe & Motoo (1975)**] together with the modification of the electronic properties of Pt via ligand effect [**Liu & Norskov (2001); Frelink et al., (1995) and**

Frelink et al., (1996)]. However, the role of particle size effect as well as crystallographic ordination of deposited Pt cannot be excluded.
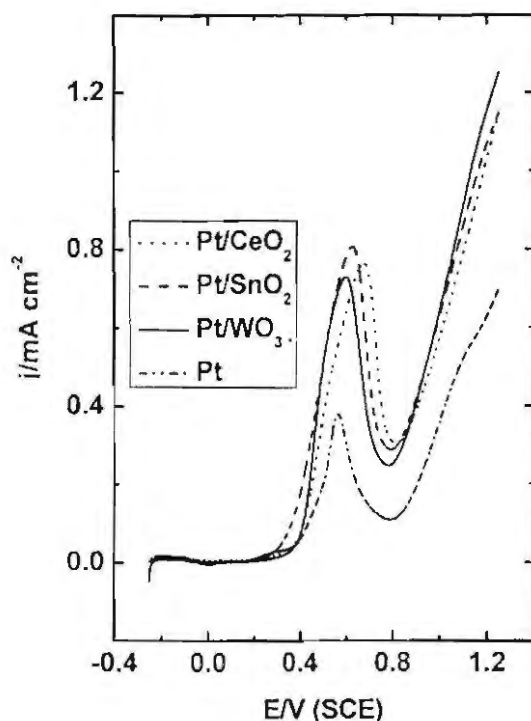

Fig.(6): Current-potential curves for EG electro-oxidation on (———) Pt/SnO$_2$/GC, (--------) Pt/WO$_3$/GC, (..........) Pt/CeO$_2$/GC and Pt (····) in 0.1M H$_2$SO$_4$ + 0.5M EG. Scan rate: 50 mV s^{-1}.

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 ethylene glycol oxidation has been recorded as a function of time at 0.5V vs SCE over more than 15 min. The resultant curves are shown in fig.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/CeO$_2$/GC modified electrode. The enhancement factor (ratio of oxidation currents for Pt with and without modification) obtained for CV at 0.5V vs SCE 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/SnO$_2$/GC $\approx$ Pt/WO$_3$/GC > Pt/CeO$_2$/GC > Pt. On the other hand, the tolerance against poisoning accumulation was found to decrease in the order: Pt/CeO$_2$/GC > Pt/WO$_3$/GC > Pt > Pt/SnO$_2$/GC.
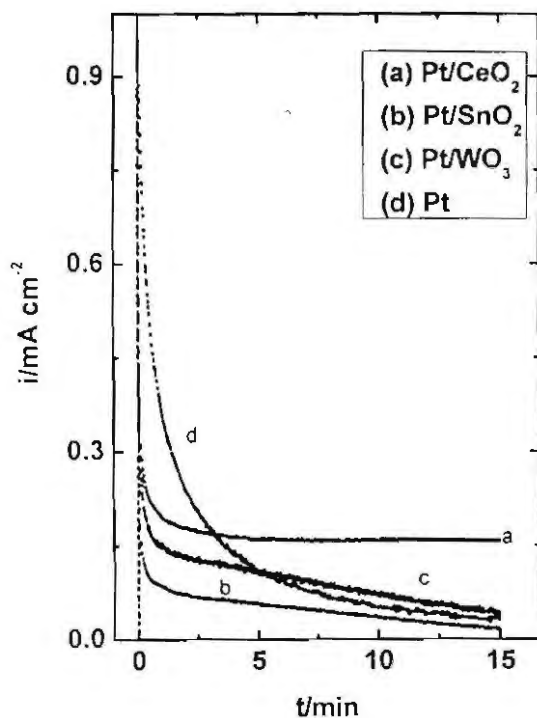

Fig.(7): Chronoamperometric curves recorded at 0.5V vs. SCE for
(———) Pt/SnO$_2$/GC, (-------) Pt/WO$_3$/GC, (........) Pt/CeO$_2$/GC
and Pt ($\cdots$) in 0.1M H$_2$SO$_4$ + 0.5M EG.

Tabel (2): Current density and catalytic factor of EG oxidation at Pt and Pt/MOx/GC electrodes at 0.5V/SCE.

Electrode	Catalytic factor[a]	j ($\mu A\ cm^{-2}$)[b]
Pt/SnO2/GC	2.6	160
Pt/WO3/GC	2.4	40.2
Pt/CeO2/GC	1.8	16.2
Pt	1	33

[a] Ratio of oxidation currents of (Pt/MOx/GC) / (pt) obtained from CV at 0.5Vvs SCE.

[b] Current density of (Pt/MOx/GC) / (pt) obtained from i-t at 0.5V vs SCE after 15 min electrolysis.

4. 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 values. Pt/CeO$_2$/GC electrode exhibited the best tolerance behavior against poisoning process.

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نشاط قطب الكربون الزجاجى المعدل بفلز-اكسيد فلز على أكسدة الإيثلين جلايكول

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تم تحضير بعض أكاسيد الفلزات عديمة الزوبان فى الوسط الحمضى ودراسة خصائصها. تم أيضا دراسه تأثير نوع الأكسيد على النشاط الحفزى للبلاتين تجاه أكسدة كحول الإيثلين جليكول فى الوسط الحمضى. إتضح أن الأقطاب المعدلة المكونة من البلاتين/أكسيد فلز/الكربون الزجاجى تعطى نشاطا أعلى كفاءه من قطب البلاتين عديد التبلور. بينما يعطى قطب البلاتين/أكسيد القصدير/الكربون الزجاجى أكبر قيمة لتيار التأكسد وعلية فإن قطب البلاتين/أكسيد السيريوم/الكربون الزجاجى /أعلى الأقطاب كفاءه على تحمل عملية التسمم.