

Exploration of electrodeposited platinum alloy catalysts for methanol electro-oxidation in 0.5 M H₂SO₄: Pt-Au system

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ABSTRACT

The electrocatalytic activity of electrodeposited Platinum (Pt)-Gold (Au) alloy layers on an inert substrate electrode for methanol oxidation reaction. Analyses using energy-dispersive fluorescent X-ray analysis and powder X-ray diffractometry confirm alloying of Pt with Au in a range of compositions. Steady-state polarisation measurements in 0.5 M methanol+0.5 M H₂SO₄ solutions clearly show that the onset of electro-oxidation shifts to less anodic potential values (approximately 160 mV), while also exhibiting current enhancements up to 15 times the currents obtained for the pure Pt electrodeposit. A linear relationship between the cyclic voltammetric peak (oxidation) current and [MeOH] is observed at a scan rate of 50 mVs⁻¹, thus indicating reduced influence of adsorbed CO (CO_{ads}) surface poison. A critical composition, Pt (92%)/Au (8%) [denoted Pt-Au(3) alloy] is found to exhibit maximum electrocatalytic activity, beyond which the activity drops, whereas pure Au does not catalyse the reaction. While the promotion of electro-oxidation is understood to be largely due to the alloy catalyst, surface redox species of Au oxide formed during the electro-oxidation process may also contribute to the oxygenation of CO_{ads}, thereby enhancing the oxidation current. Plausible mechanisms of methanol oxidation on Pt/ transition metal alloy electrocatalysts are discussed in terms of electron transfer (in the alloy) and the role of Au oxide species.

Keyword: - Methanol, electro-oxidation

1. INTRODUCTION

Exploration of alloy catalyst combinations for efficient electro-oxidation of small organic molecules, especially methanol, is currently a worldwide activity in the context of direct methanol fuel cells [1, 2, 3, 4, 5, 6, 7, 8, 9]. The role of the secondary metal catalyst (e.g. ruthenium) is to promote oxygenation of the surface poison, adsorbed CO (CO_{ads}), on platinum (Pt) and thus enhance the overall catalytic activity [10, 11, 12, 13, 14]. Recent theoretical calculations have pointed to the possibility of arriving at catalyst combinations alternative to ruthenium along with Pt electrocatalysts [15].

There is considerable current interest in screening of Pt alloys for the electro-oxidation of methanol and related small organic molecules, Pt-Ru being the benchmark alloy electrocatalyst. This is mainly due to the fact that the reasons for the best performance of Ru (along with Pt) have been uncovered only recently [16, 17]. It is now known that Ru does not exist in its zero oxidation state when the alloy is in contact with an electrolyte solution and that it is instead in an oxyhydroxy form [16, 17], while also providing mixed (electronic and ionic) conductivity [16]. These studies open up new avenues for discovering alloying elements equivalent to or better than Ru. Hence, the interest

has shifted to alloys of Pt with other transition metals. The initial attempts in finding alternatives to Ru included a combinatorial approach to screen such alloys and hence, new roles have been assigned to elements like Os and Ir [18]. However, studies on alloying elements other than Ru are scarce. Much lies in the selection of such alloys in identifying transition metals that might provide the same beneficial effect as provided by Ru. The key to such catalytic enhancement is (a) the stability of the transition metal on the surface at methanol oxidation reaction (MOR) conditions, and (b) achieving the optimum surface composition. Prompted by model calculations [19] and bonding energy data, Park et al [20] recently have re-reported studies on Pt-Ni alloy nanoparticle films on a gold electrode surface for methanol oxidation. These particles were synthesised by chemical reduction of Pt and Ni salts in an aqueous medium. The results of these studies were compared with the behaviour of electro-catalysts like Ni-Ti [21], Pt-Au [22], pure Ni [23, 24] and pure Pt [25] in acid and alkaline media, but not with the bulk alloy electrocatalysts (as has been done in the case of oxygen reduction) [26]. However, the issue of explaining the main characteristics of Pt-Ni, (i.e. for systems other than Ru) by the bifunctional mechanism is raised by Park et al [20] considering the differences in the bonding energies of Ru-O and Ni-O vis-a-vis Pt-C. Thus, a study involving bulk alloy electrocatalysts becomes necessary at this juncture and hence forms an important part of our current efforts. For practical reasons, it is preferable to choose a method that affords benefits such as ease of immobilisation on inert surfaces, good adherence and feasibility to control the size and loading particles. Electrodeposition is an established technique for obtaining alloys of different compositions on the electrode surface, and fits into this category of catalyst immobilisation strategies.

The present work is aimed at studying the role of Ni in the electrodeposited films of Pt-Au on the electro-oxidation of methanol.

2. MATERIALS AND METHODS

Electrodeposition of alloy catalyst catalytic films were electrochemically deposited from a deposition mixture comprising 0.01 M $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and varying concentrations of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01–0.50 M) at 25 °C. Before deposition, the Au electrode was polished with alumina paste and washed ultrasonically in Millipore water (18 MW cm). It was then subjected to electrodeposition at a fixed potential of 1.2 V versus a saturated calomel electrode (SCE) for a duration of 10 min. After deposition, the working electrode was washed thoroughly with Millipore water and dried before further investigation.

The electrochemical cell used in this work was a conventional three-compartment cell. A large surface area Pt sheet and mercury-mercurous sulphate electrode (MSE) ($\text{Hg}/\text{HgSO}_4/0.5 \text{ M H}_2\text{SO}_4$) were used as the counter and reference electrodes respectively. A gold disc electrode of 4 mm diameter (Bioanalytical Systems), which is electrodeposited with Pt/Pt-Au films served as the working electrode. All chemicals were analytical grade and used as obtained without further purification.

Cyclic voltammetry was performed using a potentiostat (PINE, Model AFRDE 5 Bipotentiostat) coupled to an X-Y/t recorder (Rikadenki RW 201T). Polarisation and chronoamperometric experiments were performed with a Solartron Electrochemical interface Model SI 1287.

3. CHARACTERISATION OF CATALYST LAYER

The resulting electrodeposits were analysed using X-ray diffractometry (JEOL 8030 diffractometer with $\text{CuK}\alpha$ (Ni-filtered) radiation ($k=1.5418 \text{ \AA}$) at a rating of 40 kV and 20 mA). The approximate film composition (± 2 atomic%) was analysed with an energy-dispersive fluorescent X-ray analysis (XRF-EDX) (Horiba X-ray analytical microscope XGT-2700). A scanning electron microscope (Hitachi-S3000H) was used to study the morphology of the electrodeposited Pt/Pt-Au films.

4. RESULTS AND DISCUSSION

4.1 Electro deposition of Pt and Pt-Au and characterization

A poly-crystalline Au surface is chosen as the working electrode since (a) it is electrocatalytically inactive towards methanol oxidation and adsorption, and (b) it presents a reproducible signature of its oxidation/reduction in voltammetry. Before plating of Pt or Pt-Au, the cleanliness of the polycrystalline gold electrode was ensured by checking its standard voltammetric response and its associated charge values during oxidation and reduction in the first cycle. Upon the deposition of Pt layers, the standard voltammetric response of Au disappeared and the electrode assumed the response typical of polycrystalline Pt, consisting of the well-known reversible Hupd region (0.65 to 0.4 V versus MSE) and Pt oxidation/reduction (0.0–0.1 V vs MSE). Methanol was found to undergo oxidation at this electrode with voltammetric features similar to those reported in the literature [28].

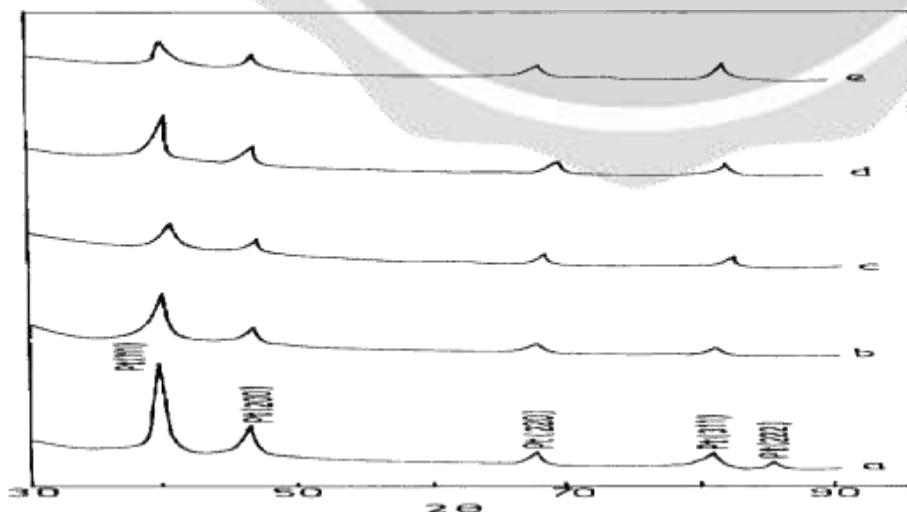
The electrodeposited layers were subjected to characterisation by XRF-EDX to find out the approximate Pt:Au ratio. Different ratios of Au could be deposited along with Pt by keeping the concentration of H₂PtCl₆ constant and varying that of NiCl₂ in the plating bath.

The electrodeposited Pt and PtAu matrix that clearly show the characteristic peaks of Pt fcc structure. The intensity of the Pt characteristic peaks such as (111), (200), (220), and (311) decreases as the Ni content increases in the film. As can be noted from the [27] diffractograms, no characteristic lines of Ni fcc structure are observed.

4.2 XRF-EDX analysis of electrodeposited Pt Au catalytic surface films

Description	Platinum (%)	Nickel (%)
Pt	100	—
Pt-Ni(1)	95	4
Pt-Ni(2)	94	7
Pt-Ni(3)	92	8
Pt-Ni(4)	90	10

Pt peak clearly shows alloy formation between Pt and Au [29, 30]. Further, the lattice parameters increase up to Pt-Au(3), and afterwards decrease. The decrease in the lattice constants can be accounted for by the segregation of the alloying elements in the matrix. The substitution of Pt by Au in the matrix becomes increasingly difficult and hence the decrease in 'd' value may be due to the limited miscibility of Pt with Au



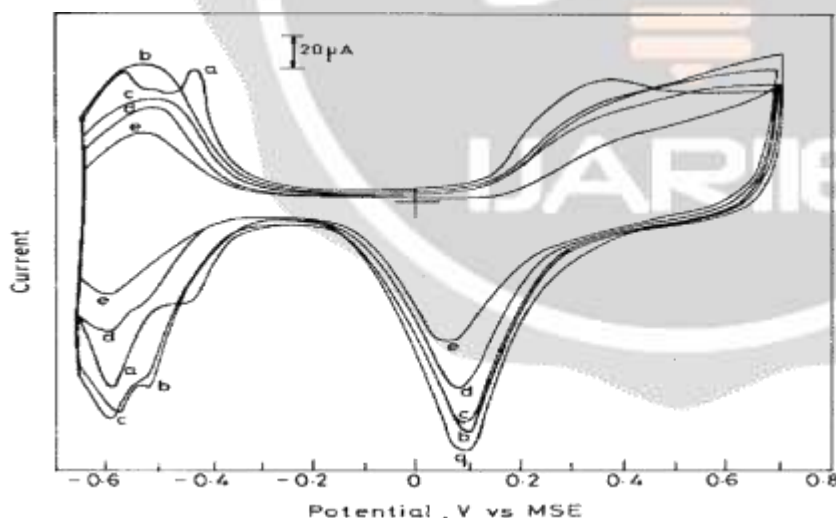
The cyclic voltammetric (first cycle) responses of electrodeposited films of Pt and Pt-Au in 1 M H₂SO₄ solution at $v=50$ mVs⁻¹ in a potential window of 0.66 to 0.70 V versus MSE. It can be seen from the voltammograms (Fig. 1a–e) that the charge densities associated with the reversible hydrogen adsorption-desorption region decrease to a considerable extent upon the inclusion of Ni in the Au matrix due to the site blocking effect. Inclusion of any foreign metal in the Pt matrix will bring down the charge densities in the H_{upd} region [32], similar to the metal up behaviour. This feature forms the basis for voltammetrically confirming the presence of the metal that alloys with Pt.

4.3 Methanol oxidation at electrodeposited Pt-Au catalysts on Ni

The catalytic activity of the Pt-Au binary alloy decreases remarkably when the Au content exceeds 8%. As the Au composition increases, the number of active Pt sites (Pt*) available for the dissociative chemisorption of the methanol molecule is reduced which causes a reduction in the oxidation current.

Polarisation curves were analysed using the Tafel relationship and the slope values calculated from the linear region are given in Table 4. The observed Tafel slope values, viz., 74 (Pt-Au-1), 69 (Pt-Au-2), 90 (Pt-Au-3) and 78 (Pt-Au-4) mV decade⁻¹ are lower than the value known for pure Pt surface, i.e. 126 mVdec⁻¹ (potential-dependent coverage by CO). A value of 120 mVdec⁻¹ is associated with a mechanism in which the oxidative removal of CO_{ads}, in the case of Pt electrodes, is typically an electrochemical rate-determining step. The lower slope values show a potential-independent nature of CO coverage, conforming to the earlier observation that the adsorbed CO is susceptible to consumption by nucleophilic attack (the nucleophiles being OH radicals or any species partially arising out of oxidised Au that may form in the alloy during the methanol oxidation).

It is noteworthy that with Pt-Au(3), the peak current increases linearly with [MeOH], whereas such a relationship is not observed with polycrystalline Pt. Unfortunately, there are no reports in the literature, to our knowledge, to compare these results. The linear relationship indicates the reduced influence of any adsorbed surface poison on Pt-Au(3). As methanol oxidation reaction (MOR) is a multistep reaction with possible poisoning of the electrode surface during its oxidation, the peak current is not expected to scale linearly with [MeOH], unless the reaction rate depends linearly on methanol concentration.



The OH_{ads} chemistry (on Pt or Pt-Au sites) is known to play a key role in promoting methanol oxidation. The interplay between the contributions from (a) electron transfer from Ni to Pt and thus the OH_{ads} reactivity (towards the consumption of CO), and/or (b) the “ensemble” effect, is not currently understood, and has intrigued many researchers in this field. Certainly, this aspect needs more detailed experiments wherein a perfect control over the surface sub-structure (e.g. surface segregation) can be exercised. The recent work of Paulus et al. [35] in the context of oxygen reduction reaction clearly emphasises this point. In our opinion, any ideal electrocatalyst candidate should be in a position to bring about the merger of these two peaks (E_{p_f} and E_{p_r}).

5. CONCLUSIONS

Using electrodeposition, smooth deposits of Pt-Au alloys of various compositions were obtained on Au substrate. The elemental analysis (XRF) and powder X-ray diffraction studies showed the formation of Pt-Au alloys (solid solutions). These electrodeposited alloy films were evaluated for oxidation of methanol in 1 M H₂SO₄ solutions, using (a) steady-state polarisation, (b) cyclic voltammetry, and (c) chrono-amperometry

From the steady-state polarisation studies in 1 M methanol in 1 M H₂SO₄ solutions, it is clear that with increase in the Au content of the Pt-Au alloy: The onset of electro-oxidation shifts to less anodic potential values (by ~160 mV). Current enhancements up to ~15 times on compared with the currents observed for the pure Pt electro-deposit and the following observations confirm the electrocatalytic activity of the deposited layers.

The normalised current measured after 1 h in chrono-amperometry experiments is 3 orders of magnitude higher for the Pt-Ni(3). A linear relationship between the oxidation current and [MeOH] was observed, thus indicating reduced influence of CO ads surface poison. A critical composition, Pt (92%)/Au (8%) [PtAu(3) alloy] was found to exhibit maximum electrocatalytic activity (based on the shift in onset potential), beyond which the activity drops whereas pure Ni did not catalyse the reaction, as observed by us and Park et al. [20].

Since the current work and work carried out elsewhere confirms that the electrochemical promotion of oxidation of small molecules (specifically, methanol) is likely a general behaviour of the transition metal alloys of Pt, it now remains to be seen if the catalytic activity can be increased by using supported (e.g. on carbon) nanoparticle films. A comparison of the behaviour of these nanoparticle films versus atomically smooth [41] alloy deposits will be able to reveal the true power of nanoparticles as electrocatalysts.

6. REFERENCES

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