

ELECTROCATALYSIS BY MICROELECTRODEPOSITS

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Glassy carbon disc electrodes were used to deposit micro quantities of Pt and Pd catalysts. Voltammetric studies were made to examine the hydrogen adsorption and oxygen reduction on these model catalysts. Their electrocatalytic activity towards anodic oxidation of methanol, formaldehyde and ethylene glycol in acid and alkaline medium is dependent upon the amount of deposits, their hydrogen adsorption properties and crystallite parameters.

Keywords: Pt and Pd microdeposits, hydrogen adsorption, specific activity, electrooxidation of organics

INTRODUCTION

Platinum group metals are used most frequently as electrocatalysts for fuel cell electrode reactions. These catalysts are dispersed as fine particles on porous active carbon or carbon black support materials [1]. Various reports are available on the crystallite size effects of Pt catalysts on their electrocatalytic properties [2-5]. Depending on the nature of the support the properties and activities of catalysts could differ since the pore structure of the support affects the transport of the reactants, products and electrolyte.

Smooth supports dispersed with micro-quantities of metals are convenient to evaluate the electrocatalytic property without any effect of the pore structure of the support [6-9]. In order to find the effect of size of metal particles on their catalytic properties, the studies on "model catalysts" have been recommended. Vacuum evaporation technique has been employed as standard procedures to prepare model catalysts [10-11]. Takasu et al has investigated the catalytic properties of ultrafine Pt[10, 12-14] and Pd[11, 15-17] deposited on flat glassy carbon substrates by vacuum evaporation method. These catalysts exhibited high catalytic activities towards electro-oxidation of CH_3OH and HCOOH and hydrogen evolution in aqueous medium. Reports are not available on the catalytic properties of electrocatalysts prepared by electrodeposition techniques. It is in this connection the electrocatalytic activity of Pt and Pd electrodeposited in microgram quantities on glassy carbon electrodes was investigated and reported in this paper.

EXPERIMENTAL

Electrodeposition studies

Analytical grade chemicals and triple distilled water were used. The Pt and Pd salts from Ms. Arora Mathey Ltd. were employed. A glassy carbon rod (GC-30 from Ms. Tokai carbon Co. Ltd., Japan) was used as the substrate. The glassy carbon disc was embedded into a copper cup and tight fitted inside a Teflon sleeve. The flat surface was polished with refractory oxides and polishing cloth according to known procedures [18], degreased and the mirror polish surface was cleaned with acetone. A conventional three-compartment glass cell assembly was employed for carrying out the electrodeposition studies from noble metal salts in 1.0 M H_2SO_4 solution (0.05 wt.). The glassy carbon rod was made as the working electrode, a Pt foil as the counter electrode and SCE as the reference electrode. A PAR model 173 Potentiostat was employed. The deposition potential was kept at -0.10 V vs. SCE for different duration. The quantity of the metal deposited (in $\mu\text{g}/\text{cm}^2$) was estimated from the I-t curve by calculating the charge used for the deposition [19].

Electrochemical characterisation of electrodeposits

The electrochemical hydrogen adsorption measurements consisted of recording cyclic voltammograms over a range of potential upto an anodic limit of 500 mV in hydrogen saturated 1.0 M H_2SO_4 solution at 0.1 V/sec. The charge in the cathodic and anodic hydrogen region (Q_H) was calculated by graphical integration. A charge value 210 $\mu\text{g}/\text{cm}^2$ for hydrogen monolayer was used to obtain the surface area of the Pt deposits [20,21]. The specific surface

area of the Pd deposits was calculated using the charge involved in the reduction of the oxide monolayer (Q_o) formed when the Pd/GC electrode was cycled between -0.180 V and 1.35 V vs. SCE in 1.0 M H_2SO_4 . A charge value of 405 ($\mu g/cm^2$) real area for Pd was assumed for the formation of a monolayer [22]. The voltammograms recorded were either the first or second cycle, since Pd was reported to undergo dissolution during cycling [23].

Determination of the electrochemical activity of the electrodeposits

Linear sweep potentiodynamic voltammograms were obtained in the potential range -0.24 V to 1.35 V vs. SCE in 1.0 M H_2SO_4 and in the range -0.9 V to 0.50 V vs. Hg, HgO/OH- in 1.0 M KOH solutions containing various organics (1.0 M) using PAR Model 370 Electrochemistry System. The results compared are the potentials at which a maximum is obtained during the anodic sweep (E_{peak}) and the current at the maximum (i_{peak}) for various amounts of the catalysts deposited. The intrinsic activity (i_g : the current per unit mass in mA/g) and the specific activity (i_s : the current per unit real surface area) were calculated by known procedures [24].

RESULTS AND DISCUSSIONS

Results of the electrodeposition studies

In the electrodeposition of Pt and Pd from their salts, the current efficiency for the deposition is reported to be greater than 95 % [25] at potentials negative than the normal E^0 values [26]. The quantity of metals deposited at various charge values were calculated and tabulated in Table I. The physical observation of the deposits on the glassy carbon disks has indicated that the Pt deposit is bright, whereas the Pd deposit is black and spongy, as observed in a microscope. The scanning electron microscopic picture of the Pt deposit is shown in Fig. 1. This shows the presence of white globules

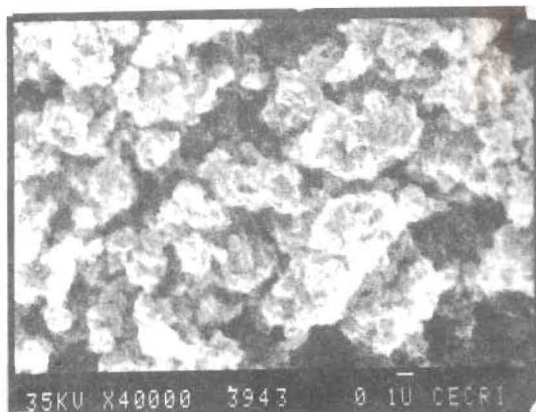


Fig. 1. SEM photograph of the Pt deposit ($242 \mu g/cm^2$) on glassy carbon disk

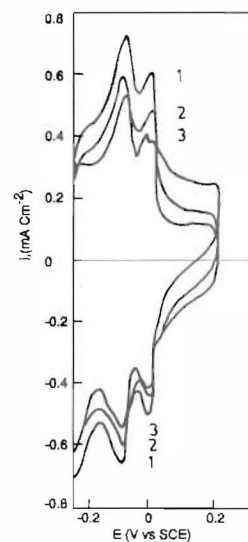


Fig. 2. Cyclic voltammograms of the Pt deposit in 1.0 M H_2SO_4 in the hydrogen region (1) $363 \mu g/cm^2$ (2) $242 \mu g/cm^2$ and (3) $121 \mu g/cm^2$

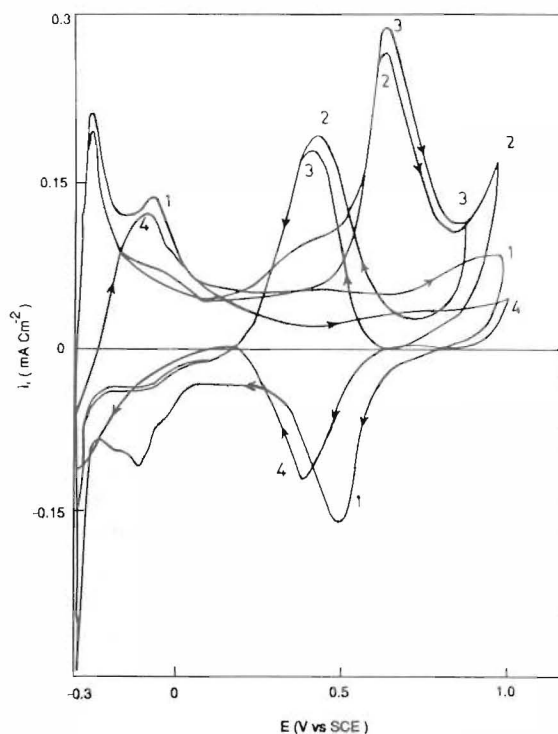


Fig. 3. Cyclic voltammograms for Pt and Pd electrodeposits at 100 mV/sec in 1.0 M H_2SO_4 + 1.0 M CH_3OH .
(1) Pt ($242 \mu g/cm^2$) without methanol
(2) Pt ($120 \mu g/cm^2$) with methanol
(3) Pt ($242 \mu g/cm^2$) with methanol
(4) Pd ($198 \mu g/cm^2$) with methanol

Table I: Characteristics of the Pt and Pd electrodeposits

Deposit	Charge for deposition (mC/cm ²)	Amount deposited (μg/cm ²)	charge (hydrogen region)(mC/cm ²)	H/M %	Crystallite size (C _s)nm	Electrochemical Surface area (m ² /g)	Number of surface atoms X 10 ⁷ /cm ²	peak ratio (i _{p111})/(i _{p100})
Pt	30	62	19.06	64	1.7	164.7	1.22	3.5
Pt	60	121	30.86	51	2.1	133.3	1.92	2.7
Pt	120	242	46.3	39	2.8	100.0	2.20	2.0
Pt	180	363	43.2	24	4.5	62.2	2.69	1.7
Pt	240	485	49.8	21	5.2	53.0	3.11	1.1
Pd	30	33	17.05	57	1.9	263.0	1.06	-
Pd	60	66	25.92	43	2.5	200.0	1.61	-
Pd	120	132	41.80	35	3.1	161.0	2.61	-
Pd	180	198	51.15	28	3.8	132.0	3.19	-
Pd	240	264	57.60	24	4.5	111.0	3.99	-

and colonies of Pt particles. The bright image shows that the Pt particles grow at the surface of the glassy carbon disks. It is reported in literature that when the loading level is less than 40 (μg/cm²) (geometric area), the particles are almost spherical and randomly distributed [27]. At high loading greater than 100 (μg/cm²) the distribution becomes wider. The SEM picture of the Pd deposit was found to be shabby. Fig.2. shows the current potential profile obtained with Pt/GC electrode at 100 mV/sec. in 1.0 M H₂SO₄ solution. The main features of the profile are the presence of two symmetric hydrogen adsorption and desorption peaks in a similar way reported for bulk Pt sheet electrode [28,29]. The hydrogen adsorption region was in the potential range -0.05 V to -0.20 V vs. SCE and the charge are used to calculate the real surface area of the catalyst [22]. As the amount of the deposit increases, the peak heights for the weakly adsorbed hydrogen at -0.15 V (i_{p111}) and the strongly adsorbed hydrogen at -0.20 V (i_{p100}) increase. The electrochemical surface area of the Pt crystallites (S in m²/g) and the crystallite size (C_s) values were determined from the Q_H values, as reported in Ref. 30 and given in Table I. It is also noted that the ratio of i_{p111}/i_{p100} also decreases at high Pt amounts. From the table, it is clear that as the amount of the Pt deposit increases the electrochemical surface area decreases and consequently the crystallite size increases. It is apparent that the crystallite size values are considerably smaller than that observed under SEM. This suggests that the particles formed as coalesced ultra micro Pt clusters are observed under SEM [31]. For the Pd deposits on glassy carbon disks, the crystallite size and the electrochemical surface area values were determined from the charge values for the reduction of the oxide monolayer and also reported in Table I.

Electro-oxidation in acid medium

The electrooxidation of the three organic compounds namely methanol, formaldehyde and ethylene glycol are studied by cyclic voltammetry and the results are presented below. Fig. 3 shows the voltammograms in 1.0 M H₂SO₄ + 1.0 M CH₃OH. Curve 1 represents the behaviour of Pt deposits in H₂SO₄ in the absence of CH₃OH. Curves 2 and 3 represent the behaviour in the presence of CH₃OH. The pattern is quite similar to the behaviour reported for a Pt wire electrode [32]. The methanol oxidation starts around 0.3 V, a peak is observed at around 0.7 V during the anodic scan (P_{a1}) and

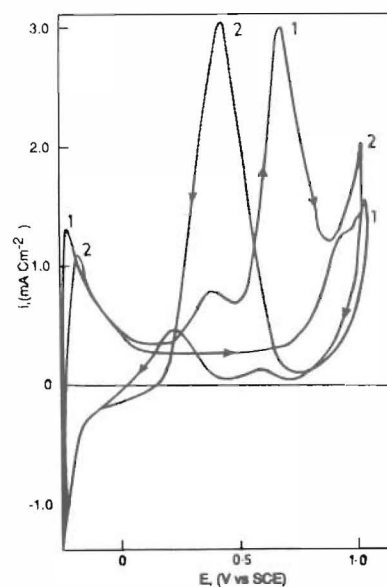


Fig. 4. Cyclic voltammograms for Pt electrodeposits (242 μg/cm²) at 100 mV/sec in (1) 1.0 M H₂SO₄ + 1.0 M HCHO: (2) 1.0 M H₂SO₄ + 1.0 M GLYCOL

Table II: Electrocatalytic activity of Pt and Pd deposits in acid medium

Catalyst	Amount ($\mu\text{g}/\text{cm}^2$)	E_{peak} (V)	CH_3OH I_{peak} (mA/cm^2)	Specific activity (A/m^2)	Peak ratio ($i_{\text{p1}}/i_{\text{p2}}$)	Ethylene glycol		Specific activity (A/m^2)
						E_{peak} (V)	I_{peak} (mA/cm^2)	
Pt	62	0.64	0.19	0.012	1.1	0.67	0.20	0.015
Pt	121	0.68	0.24	0.015	1.5	0.68	0.40	0.020
Pt	242	0.70	0.38	0.017	1.9	0.69	0.50	0.030
Pt	363	0.71	0.40	0.019	2.7	0.70	0.60	0.040
Pt	485	0.72	0.50	0.019	3.0	0.71	0.65	0.050
Pd	33	-	-	-	-	0.68	0.20	0.005
Pd	66	-	-	-	-	0.89	0.25	0.007
Pd	132	-	-	-	-	0.70	0.28	0.009
Pd	198	-	-	-	-	0.70	0.30	0.010
Pd	264	-	-	-	-	0.71	0.31	0.011

during the reverse scan at 0.5 V (P_{a2}). However, the peak potential values are found to shift in the positive direction, by 20 to 50 mV, depending upon the amount of the catalyst. The peak height values also differ accordingly. The ratio (P_{a1})/(P_{a2}) also decreased continuously with the decrease in the particle size. The peak potential, peak current and the specific activity values of the catalyst for the different amounts of Pt deposits on GC are tabulated in Table II. The hydrogen region is not completely suppressed by methanol adsorption, since the oxidation - reduction peaks of hydrogen

are still visible. However, the peak due to strong adsorption of hydrogen is absent in the presence of methanol [33].

The curve 4 represents the behaviour of Pd deposit on GC. The current voltage pattern does not indicate any peak for methanol oxidation. The fact that Pd does not chemisorb CH_3OH is reflected from the fact that the peak height for the hydrogen oxidation does not change in the presence of methanol. Because of this the palladium oxide reduction peak is also observed at +0.44 V, which is absent for the Pt deposits in the presence of CH_3OH in 1.0 M H_2SO_4 .

Fig. 4 shows the linear sweep voltammograms for the Pt deposited catalysts for the oxidation of formaldehyde and ethylene glycol in 1.0 M H_2SO_4 . During the anodic scan the oxidation of formaldehyde (curve 1) starts at 0.60 V when the Pt surface is partially covered with an oxide layer. A peak is observed at 0.90 V, thereafter the current decreases. In the cathodic scan, two anodic peaks at 0.40 and 0.25 V are noticed even after the Pt-O reduction region. The oxidation is reported to proceed through a path, which involves the formation of formic acid radical as the intermediate [34]. This intermediate is strongly adsorbed on the surface, which is hardly oxidised at all during the anodic sweep. However, the current due to oxidation of strongly adsorbed hydrogen is completely absent indicating that the intermediates are strongly adsorbed.

Compared with HCHO, the electrooxidation of ethylene glycol (curve 2) starts at 0.2 V. A shoulder at 0.4 V is also noticed. The initial decrease corresponds to the start of the oxidation of the surface. The current rises at 0.55 V, reaches a maximum at 0.7 V and then decreases similar to the behaviour observed for methanol. During the negative sweep, no oxidation of ethylene glycol occurs until the surface oxide gets reduced. A peak at 0.45 V ($0.7 \text{ mA}/\text{cm}^2$) appears, which corresponds to the shoulder observed during the anodic

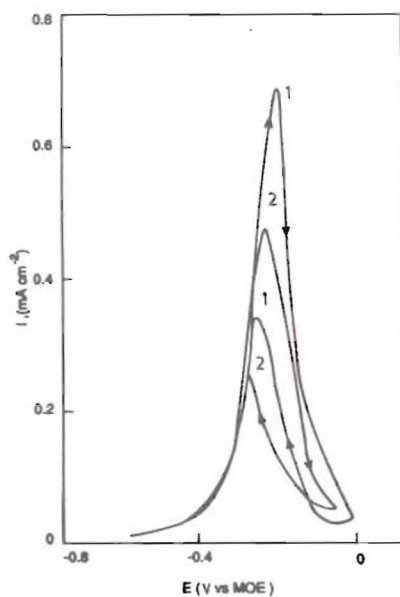


Fig. 5. Cyclic voltammograms for Pt electrodeposits at 100 mV/sec in 1.0 M KOH + 1.0 M CH_3OH (1). Pt ($485 \mu\text{g}/\text{cm}^2$); (2). Pt ($242 \mu\text{g}/\text{cm}^2$)

Table.III:Electrocatalytic acitivity of Pt and Pd deposits in alkaline medium

Catalyst	Amount ($\mu\text{g}/\text{cm}^2$)	CH_3OH			Formaldehyde			Ethylene glycol		
		E_{peak} (V)	I_{peak} (mA/cm^2)	Specific activity (A/m^2)	E_{peak} (V)	I_{peak} (mA/cm^2)	Specific activity (A/m^2)	E_{peak} (V)	I_{peak} (mA/cm^2)	Specific activity (A/m^2)
Pt	62	-0.25	0.35	0.030	-0.25	0.80	0.050	0.05	0.80	0.100
Pt	121	-0.22	0.44	0.034	-0.22	1.00	0.065	0.08	1.00	0.110
Pt	242	-0.20	0.57	0.035	-0.20	1.20	0.070	0.10	1.20	0.120
Pt	363	-0.17	0.64	0.040	-0.18	1.22	0.075	0.12	1.30	0.140
Pt	485	-0.15	0.76	0.050	-0.15	1.25	0.090	0.15	1.40	0.150
Pd	33	+0.01	0.10	0.003	-0.15	0.09	0.020	0.09	1.00	0.035
Pd	66	0.00	0.12	0.004	-0.14	1.00	0.035	0.09	1.10	0.040
Pd	132	+0.02	0.15	0.005	-0.10	1.00	0.040	0.10	1.30	0.050
Pd	198	+0.01	0.16	0.006	-0.12	1.30	0.060	0.10	1.40	0.060
Pd	264	+0.01	0.20	0.007	-0.10	1.10	0.043	0.10	1.98	0.071

sweep [35]. Here again, the formation of strongly adsorbed hydrogen is suppressed. The peak potential values shifted in the positive direction by 10 to 40 mV only, as the amount of the Pt deposit increases for both HCHO and ethylene glycol, compared to a larger shift observed for CH_3OH . The peak current and specific activity values increase as the amount of deposit increases.

In the case of Pd deposits only the oxidation current for ethylene glycol is noticed. Here also the peak potential shifts towards positive direction as the amount of the Pd deposit increases. Both the peak current and specific activity values increase with the deposit amount. Both Pt and Pd deposits exhibit higher activity for the oxidation of ethylene glycol

than HCHO or methanol. However the specific activity values of the Pd deposits were lower than Pt deposits.

Electro-oxidation in alkaline medium

The general shape of the voltammograms in 1.0 M $\text{CH}_3\text{OH} + 1.0 \text{ M KOH}$ (Fig.5) is quite similar to the pattern reported for a Pt sheet [36]. The anodic peak current density values increase with the amount of Pt on the glassy carbon substrate. The overpotentials at which the current maximum occurs is very close to the values observed in acid media. The hydrogen adsorption region is also suppressed. The observed peak characteristics and the specific activity values are tabulated in Table III. The current density and activity values are generally higher in alkaline medium than in acid medium. For Pd deposits, the peak potential was anodic ($\sim 0.0 \text{ V}$) than observed with Pt deposits. Little or negligible shift of the peak potentials are noticed at various amounts of the deposit. The peak current values were lower than Pt catalysts and the specific activity values were much lower.

Similarly, the peak current values for the oxidation of formaldehyde are higher than those observed for methanol and for HCHO in acid medium. Two anodic peaks during the anodic and reverse scans were noticed as in acid medium. The pattern for Pd was found to be quite different. Only one anodic peak was observed at -0.10 V during the forward scan and at -0.30 V during the reverse scan. The peak potential values for Pd/GC were more positive than that observed for Pt/GC by about 50 - 100 mV. The peak potentials shifted in the anodic direction for both Pt/GC and Pd/GC as the amount of the deposit increases. It can be seen from Table III that the difference was larger at low catalyst amounts. The peak height values are of the same order as Pt/GC. But the specific activity values were lower than Pt/GC. This behaviour is in contrary to the expectation that

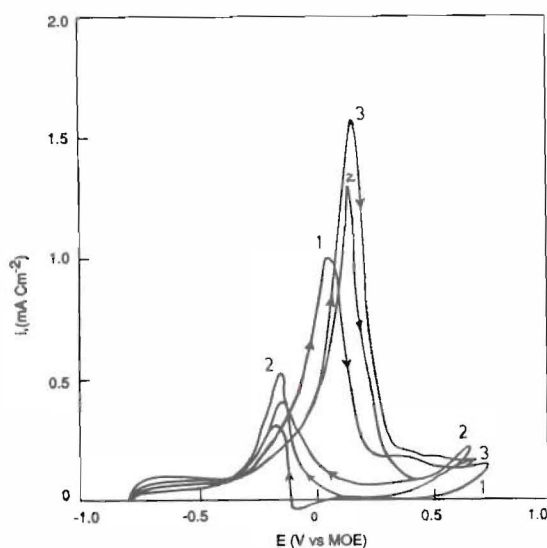


Fig. 6. Cyclic voltammograms for Pt and Pd electrodeposits at 100 mV/sec in 1.0 M KOH + 1.0 M GLYCOL

Pd is a better catalyst than Pt for HCHO oxidation in alkaline medium.

Fig. 6 represents the typical voltammograms in 1.0 M KOH + 1.0 M ethylene glycol. In all the cases the initial oxidation due to adsorbed hydrogen is suppressed. The oxidation of ethylene glycol starts at -0.25 V and reaching a maximum at 0 V. During the cathodic sweep, the peak is observed at -0.20 V. For Pd deposits, the oxidation starts even earlier at -0.35 V and a peak is observed at +0.10 V with a higher current density than Pt, but the specific activity values were lower than Pt/GC. This behaviour is also contrary to the behaviour reported for bulk catalyst [13]. The peak current during the reverse scan is also higher as in the case of HCHO. But no shift of peak potentials was noticed at different Pd contents as observed with CH₃OH unlike Pt deposits. For both Pt/GC and Pd/GC catalysts a shift of the peak potential towards the positive values was noticed, from CH₃OH to HCHO and then ethylene glycol.

CONCLUSION

The microdeposits of Pt and Pd on glassy carbon disk show similar voltammetric pattern as bulk electrodes for the oxidation of methanol, formaldehyde and ethylene glycol in acid and alkaline medium. The oxidation starts earlier at low overpotentials at low catalyst amounts due to the absence of strong adsorption of hydrogen or intermediates. The shift of peak potential in the positive potential region is an indication of the presence of strong adsorption of the organic or intermediates at high catalyst amounts. The size and the electrochemical surface area bear direct relevance to the activity of the catalysts. The activity values are the highest for the oxidation of ethylene glycol in alkaline medium for both Pt/GC and Pd/GC than other organics.

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