

Electrocatalytic activities of some codeposited binary noble metal surfaces over carbon substrates for anodic oxidation of methanol in alkaline medium: Part I—Platinum-noble codeposits

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Electrocatalytic activities of binary noble metal codeposits Pt-Pd, Pt-Rh, Pt-Ru, Pt-Ir and Pt-Au of different compositions over carbon substrate have been studied for the anodic oxidation of methanol in alkaline medium. Galvanostatic steady state and slow sweep cyclic voltammetric methods in conjunction with chronopotentiometric estimation of roughness factor (R_f) and examination of the geometric properties of the electrodes from scanning electron micrographs (SEM) are employed. Catalytic activities of these binary deposits are better than the Pt-deposited electrode. The electrocatalytic activities reach a maximum at a particular composition depending on the cometal, the order being: Rh > Ru > Pd > Ir > Au. The peak current density (i_p) and roughness factor (R_f) values also exhibit similar type of variations with maxima lying at the composition of maximal activities. The observed enhancement of catalytic activities of C/Pt electrodes with addition of cometals can be explained with the help of well known 'bi-functional theory' of alloy electrocatalysts. A careful analysis of the results, in particular the SEM's, reveal that while the extrinsic geometric properties are very much responsible for the observed activities, intrinsic electronic properties of the codeposits are equally important.

In our previous papers¹, it has been demonstrated that efficient, cost-effective electrocatalysts for methanol oxidation could be developed by coating carbon substrates with a thin layer of the noble metals. It is well known^{2,3,4a} that reaction between the adsorbed CHO and OH species is the rate determining step in the electrooxidation of methanol in alkaline medium and that, whereas Pt and Pd preferentially adsorb^{2,4a} the carbonaceous fragments, Ru, Rh and Ir adsorb^{4b} the OH species better. Hopefully then, codeposits of these two groups of noble metals, should impart enhanced catalytic activity to the electrocatalysts². To provide experimental support to our surmise, we report herein the results of investigation on the anodic oxidation of alkaline methanol on some thinly coated Pt-M (M = Pd, Rh, Ru, Ir or Au) binary codeposits over carbon substrates.

Polarization characteristics of the electrodes for the reaction under study were evaluated from galvanostatic and cyclic voltammetric experiments¹, chronopotentiometric studies¹ were used to find out the 'roughness factor' (R_f) of the electrodes and the nature and size of the polycrystalline growth of the codeposits were examined using a scanning electron microscope (SEM).

Materials and Methods

Methanol (BDH, AR) was purified by the litera-

ture method⁵. The chemicals used were PdCl₂, RhCl₃, AuCl₄ (all Johnson-Mathey) and PtCl₄, RuCl₃ and IrCl₃ (all A M, India) and NaOH (proanalysis, E. Merck). Hg-HgO/OH⁻ (1 M) and the platinized Pt foil (geometric area ≈ 4 cm²) were used as the reference and counter electrodes, respectively¹. Preparation of the carbon base of this working electrode has been given earlier¹. The Pt-M (M = Pd, Rh, Ru, Ir and Au) surfaces of different compositions were deposited on the pretreated carbon substrates (exposed geometric area ≈ 0.1 cm²) electrochemically from baths containing the respective metal chlorides [both 2%, w/v, in 2 N HCl] in appropriate proportions. The compositions of the electrolytes in the baths were varied from 0 to 100 atomic % of the cometals. Actual composition of the codeposits in the electrodes was not estimated (see ref. 6), since codeposits were obtained under identical conditions of codepositions. Such an approach offered a more practical and handy reference⁶. The time and current density employed for such depositions were 30 min and 5 mA cm⁻² respectively, a condition previously found to produce best results¹. The design of the cell used, techniques employed for recording current potential curves by both galvanostatic and cyclic voltammetric methods, the procedure for estimation of roughness factor from chronopotentiometric method have been described

earlier¹. The cyclic voltammograms (CVG's) were taken in the potential range of -500 to $+500$ mV at a scan rate of 50 mV s^{-1} . The surface structure of the codeposits were examined with a scanning electron microscope (model ISI-60A, Akashi Seisakusho Ltd, Japan). Experimental conditions were similar to those described earlier^{4,5}.

Results

Figures 1 and 2 show the galvanostatic steady state current-potential curves for the anodic oxidation of 1 mole dm^{-3} MeOH in 1 mole dm^{-3} NaOH at $\sim 25^\circ\text{C}$ on different C/Pt-M electrodes and the corresponding Tafel plots respectively. The apparent exchange current densities $[(i_o)_{app}]$, i.e. exchange current density per unit apparent area of the electrodes and the Tafel slope (b) values, as obtained from Tafel plots are listed in Table 1.

Typical CVG's for various electrodes are shown in Fig. 3a-c. The peak current densities (i_p) and peak potentials (E_p) are given in Table 1. As in the previous paper¹, the first cycle was always taken as the representative curve⁷.

Figure 4 shows the charging curves for the oxidation of 'assumed' monolayer of adsorbed hydrogen from the surfaces of different electrodes^{1,8-10} at a current of 700 mA . The transition time (τ) and the corresponding quantity of charge ($i\tau = Q_H$) required to oxidize the presumed monolayer¹⁰ of hy-

drogen at different current pulses are quoted in Table 2. The constant values of charge density ($q_H/\text{mC cm}^{-2}$) obtained for higher current values are taken as corresponding to the charge required to oxidize a monolayer of adsorbed hydrogen on different surfaces^{1,8-10} of unit apparent area. All these values along with the roughness factor (R_f) calculated^{1,8-10} ($R_f = q_H/0.23$) are given in Table 2. These electrodes reproduced the R_f values within $\pm 5\%$. The true exchange current densities $[(i_o)_{tr} = (i_o)_{app}/R_f]$ obtained are presented in Table 1.

The scanning electron micrographs of the codeposited C/Pt-M surfaces are shown in Fig. 5(a-e).

Discussion

The polarization curves (Fig. 1) and also the $(i_o)_{app}$ values (Table 1) clearly demonstrate that electrocatalytic activity of the C/Pt electrode is enhanced by codeposition with other noble metals, viz. Pd, Rh, Ru, Ir and Au. The plots of $(i_o)_{app}$ against the composition of the binary metal deposits (Fig. 6a-c), are all marked by the appearance of a maximum, similar to those observed^{2,10} with binary alloy electrodes. The compositions of electrode having maximal activities (θ_{max}^M) and also the extents of enhancement of the activities at these compositions are different for different binary systems as is evident from Table 3.

These results, and in particular those for Pt-Ru and Pt-Au systems, are similar to those observed^{2,10}

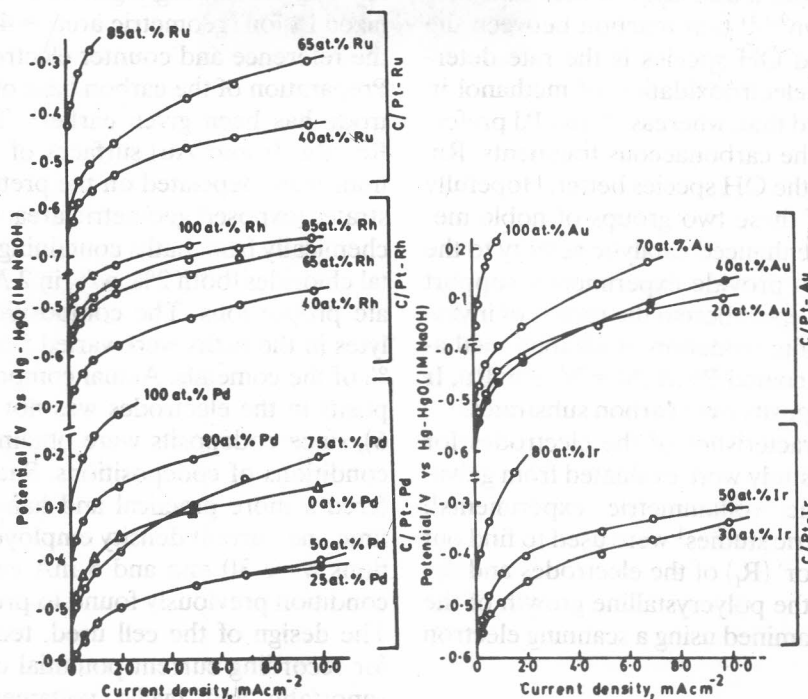


Fig. 1—Steady state current-potential curves for anodic oxidation of MeOH (1M) in 1M NaOH on different Pt-cometal (M) deposited electrodes on carbon substrate (C/Pt-M) at 25°C

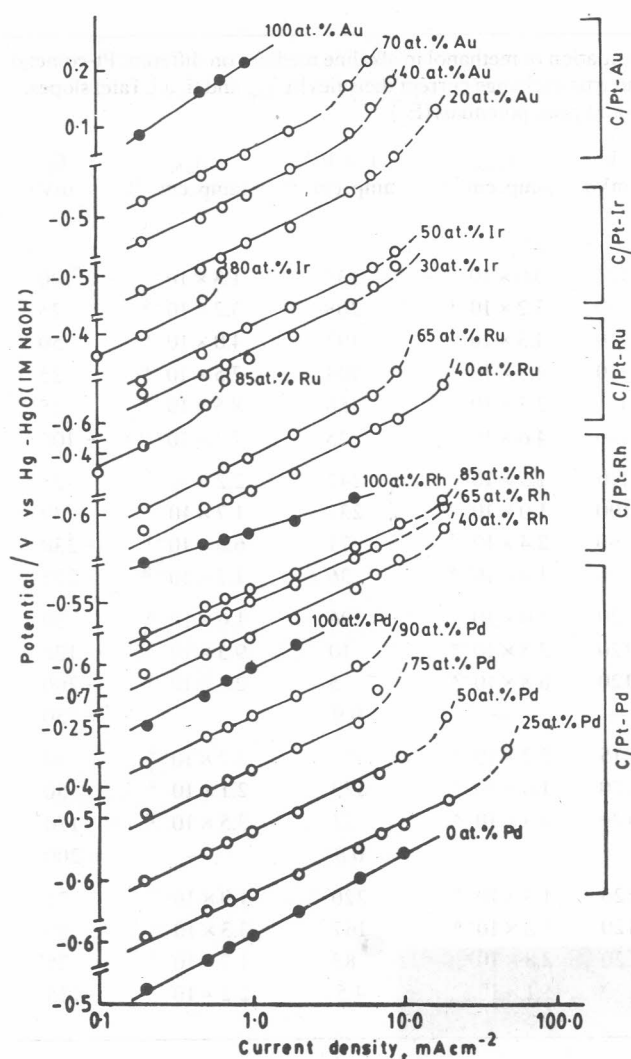


Fig. 2—Tafel plots for the oxidation of 1 M MeOH in 1 M NaOH on Pt-cometal (M) deposited electrodes on carbon substrate (C/Pt-M) at 25°C

for the corresponding binary alloy systems. Thus activities equivalent to those offered by binary alloys of noble metals could be achieved using a thin coating of the codeposits over carbon substrates. This appears to confirm the view⁶ that activity enhancement is caused by the surface of the electrode material and not by the bulk of it.

The nearly constant b values of 120 ± 10 mV for all the codeposits, except that containing 85% Ru, (see Table 1), and similarities in the nature of the CVG's on these electrodes (Fig. 3a-c) and those obtained with C/Pt¹ and C/Pd^{1b} electrodes are indicative¹¹ of a common mechanistic pathway. As pointed out earlier, the reaction between adsorbed CHO and OH species is the rate-determining step in the electrooxidation of methanol in alkaline media and while Pt and Pd fall in one group^{2,3,4a} and preferen-

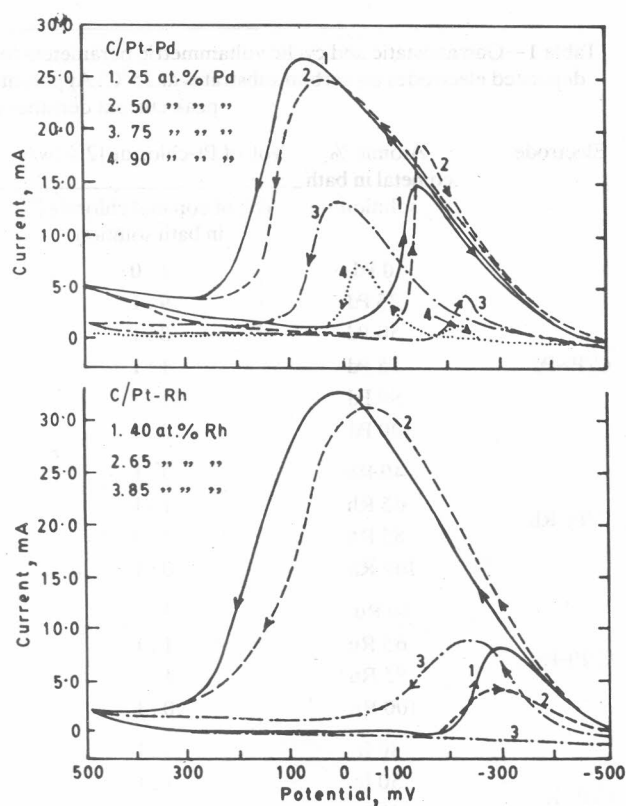


Fig. 3a—Typical cyclic voltammograms on different platinum-cometal (M) (Pd, Rh) electrodes in 1 M MeOH-1 M NaOH at a sweep rate 50 mV s^{-1}

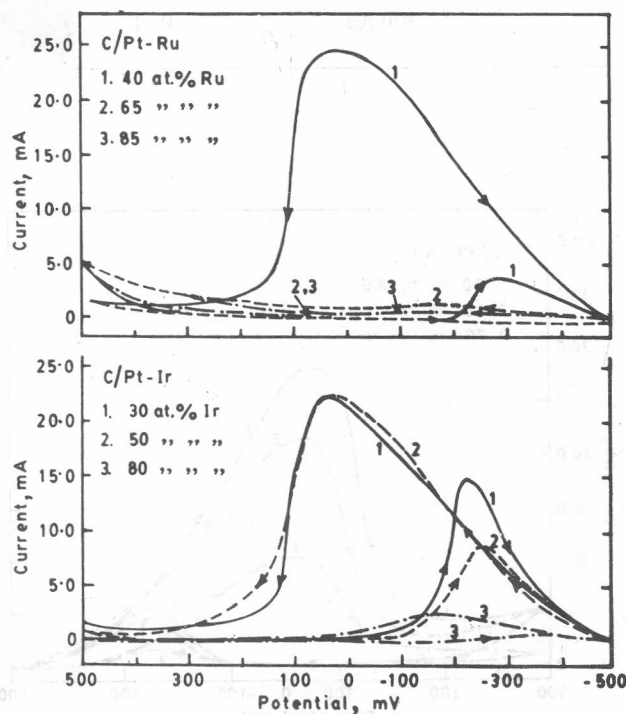


Fig. 3b—Typical cyclic voltammograms on different C/Pt-M (M = Ru and Ir) electrodes in 1 M MeOH-1 M NaOH at a sweep rate 50 mV s^{-1} at 25°C

Table 1—Galvanostatic and cyclic voltammetric parameters for oxidation of methanol in alkaline medium on different Pt-cometal deposited electrodes on carbon substrates at 25°C: Apparent and true exchange current densities [$(i_o)_{app}$ and $(i_o)_{tr}$], Tafel slopes, peak current densities (i_p) and peak potentials (E_p)

Electrode	Atomic % cometal in bath solution	Vol. of Pt-chloride [2% (w/v)]	b (mV)	$(i_o)_{app}$ (amp. cm ⁻²)	$i_p \times 10^3$ (amp. cm ⁻²)	$(i_o)_{tr}$ (amp. cm ⁻²)	E_p (mV)
		Vol. of cometal chloride [%] in bath solution					
C/Pt-Pd	0 Pd	1:0	125	6.0×10^{-7}	135	1.3×10^{-9}	100
	25 Pd	9:1	110	3.2×10^{-6}	208	3.2×10^{-9}	75
	50 Pd	3:1	110	3.5×10^{-6}	192	4.0×10^{-9}	50
	75 Pd	1:1	110	4.3×10^{-7}	104	7.5×10^{-10}	25
	90 Pd	1:3	110	2.3×10^{-8}	58	8.5×10^{-11}	-25
	100 Pd	0:1	120	4.6×10^{-9}	25	7.7×10^{-11}	-100
C/Pt-Rh	40 Rh	3:1	110	1.5×10^{-5}	242	2.2×10^{-8}	25
	65 Rh	1:1	100	1.0×10^{-6}	237	1.7×10^{-9}	-30
	85 Rh	1:3	90	2.4×10^{-7}	71	6.5×10^{-10}	-230
	100 Rh	0:1	90	1.4×10^{-8}	36	1.3×10^{-10}	-275
C/Pt-Ru	40 Ru	3:1	120	1.0×10^{-5}	196	1.6×10^{-8}	30
	65 Ru	1:1	120	3.5×10^{-6}	10	9.5×10^{-9}	-120
	85 Ru	1:3	120	6.8×10^{-8}	5	2.5×10^{-10}	-200
	100 Ru	0:1	—	—	0.9	—	-350
C/Pt-Ir	30 Ir	3:1	115	2.2×10^{-6}	173	3.7×10^{-9}	40
	50 Ir	1:1	120	1.0×10^{-6}	173	2.1×10^{-9}	50
	80 Ir	1:3	120	8.3×10^{-8}	21	3.5×10^{-10}	170
	100 Ir	0:1	—	—	0.8	—	-200
C/Pt-Au	20 Au	3:1	125	1.3×10^{-6}	220	1.9×10^{-9}	75
	40 Au	1:1	120	1.3×10^{-6}	167	3.3×10^{-9}	50
	70 Au	1:3	120	3.8×10^{-7}	83	1.3×10^{-9}	25
	100 Au	0:1	170	1.1×10^{-9}	4.5	2.2×10^{-11}	-125

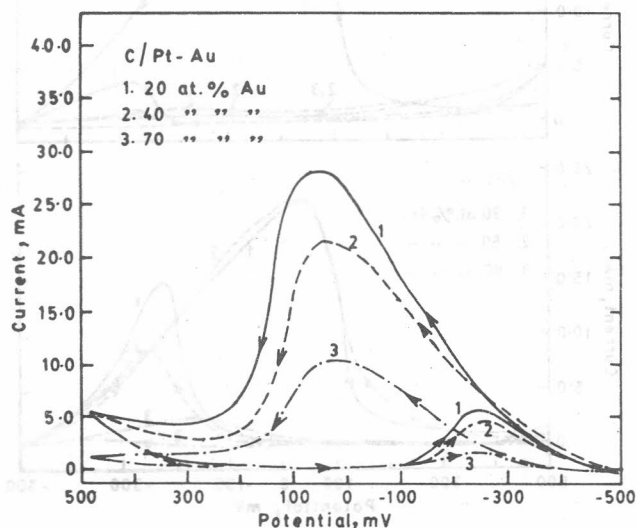


Fig. 3c—Typical cyclic voltammograms on different C/Pt-M (M = Au) electrodes in 1M MeOH-1M NaOH at a sweep rate 50 mV s⁻¹ at 25°C

tially adsorb the carbonaceous CHO fragment due to their lower % *d*-band character, Rh, Ru and Ir with 1.7-2 unpaired *d*-electrons per atom³ get almost covered with oxygen or the like species at a lower anodic potential as compared to Pt and Pd^{4b}. The graded variation of E_p values (Table 1) with the addition of the cometals to Pt suggests that whereas Pt atoms still remain the seat of CHO adsorption, the added cometal offers sites for preferential adsorption of OH radicals. Since the adsorption of OH radicals requires lesser energy in the case of Rh, Ru and Ir², the overall oxidation process occurs at a lower overpotential and hence at less anodic E_p values. Thus one is led to the 'bi-functional theory' of Watanabe and Motoo² and accordingly the general scheme for the electrooxidation of methanol over the codeposited surfaces C/M₁-M₂ (where M₁ = Pt or Pd and M₂ = Rh, Ru or Ir) may be represented as shown in Scheme 1.

Table 2—Chronopotentiometric data for different Pt-cometal deposited electrodes on carbon substrates: Transition time (τ), charge required for the oxidation of monolayer of adsorbed hydrogen (Q_H), limiting charge density (q_H) and roughness factor (R_f) values

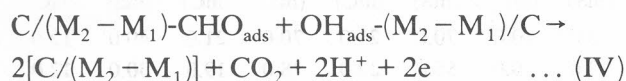
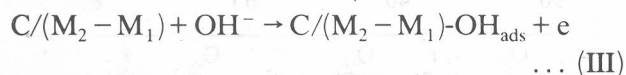
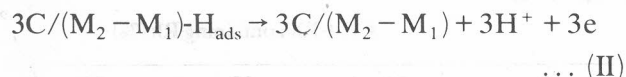
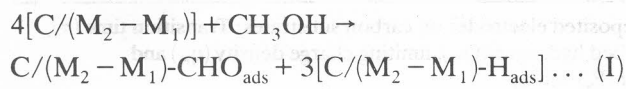
Current $\times 10^3$ / amp	C/Pt-Pd containing Pd (%)								C/Pt-Rh containing Rh (%)					
	25		50		75		90		40		65		85	
	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)
300	107.0	32.0	90.0	27.0	60.0	18.0	33.0	10.0	70.0	21.0	70.0	21.0	40.0	12.0
400	80.0	32.0	68.0	27.0	45.0	18.0	23.0	9.0	55.0	22.0	48.0	19.0	30.0	12.0
500	62.0	31.0	54.0	27.0	34.0	17.0	16.0	8.0	42.0	21.0	36.0	18.0	22.0	11.0
600	52.0	31.0	43.0	26.0	28.0	17.0	13.0	8.0	35.0	21.0	30.0	18.0	18.0	11.0
700	44.0	31.0	37.0	26.0	24.0	17.0	11.0	8.0	30.0	21.0	26.0	18.0	16.0	11.0
q_H :	239		200		131		62		161		138		85	
R_f :	1040		870		270		270		700		600		370	

Current $\times 10^3$ / amp	C/Pt-Ru containing Ru (%)						C/Pt-Ir containing Ir (%)					
	40		65		85		30		50		80	
	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)
300	70.0	21.0	40.0	12.0	30.0	9.0	63.0	19.0	50.0	15.0	30.0	9.0
400	50.0	20.0	30.0	12.0	23.0	9.0	48.0	19.0	38.0	15.0	20.0	8.0
500	38.0	19.0	24.0	12.0	16.0	8.0	36.0	18.0	28.0	14.0	14.0	7.0
600	32.0	19.0	18.0	11.0	14.0	8.0	30.0	18.0	24.0	14.4	12.0	7.2
700	27.0	19.0	16.0	11.0	12.0	8.0	26.0	18.0	20.0	14.0	10.0	7.0
q_H :	146		85		62		138		108		54	
R_f :	636		370		270		600		470		235	

Current $\times 10^3$ / amp	C/Pt-Au containing Au (%)					
	20		30		70	
	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)	τ (mS)	Q_H (mC)
300	70.0	21.0	47.0	14.0	36.0	11.0
400	50.0	20.0	35.0	14.0	25.0	10.0
500	40.0	20.0	24.0	12.0	18.0	9.0
600	34.0	20.0	20.0	12.0	15.0	9.0
700	28.0	20.0	17.0	12.0	13.0	9.0
q_H :	154		92		69	
R_f :	670		400		300	

Table 3—Compositions of electrodes having maximal activities and the extent of enhancement of activity

	Pd	Rh	Ru	Ir	Au
$\theta_{\max}^M$ (atomic % cometal)	35	45-50	50	35	35-40
$[(i_0)_{\text{app}}]$ C/Pt-M	9	35	22	5	3
$[(i_0)_{\text{app}}]$ C/Pt					



Scheme 1

The indicated preferential adsorption of the reaching species in the neighbouring sites (M_1 , M_2) leads to the enhanced catalytic activities², as observed.

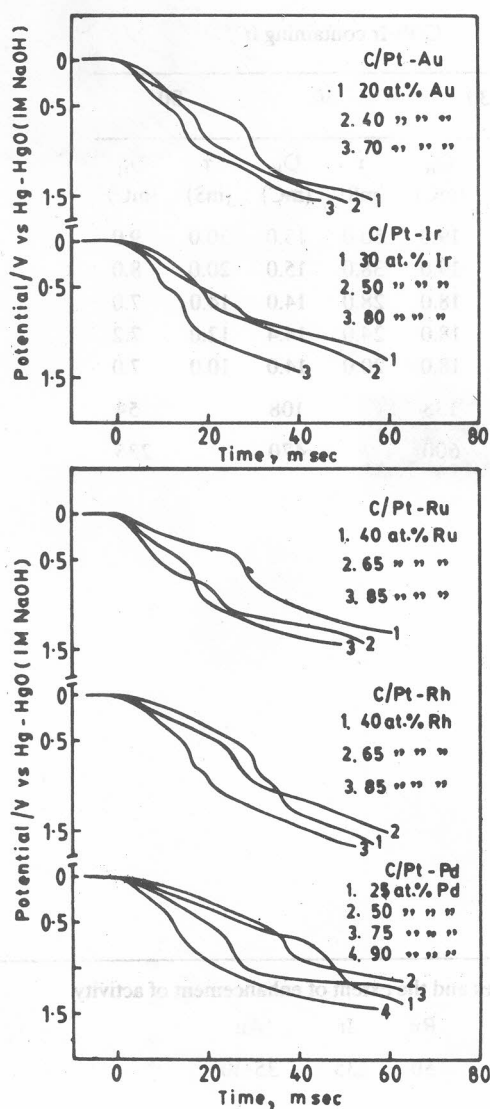


Fig. 4—Typical chronopotentiometric charging curves for oxidation of monolayer of adsorbed hydrogen in 1M NaOH on different C/Pt-M at 25°C (current = 700 mA; area of the electrodes = 0.13 cm²)

However, since adsorption of CHO and OH by M_1 and M_2 sites of the codeposit $C/M_1 - M_2$ are mutually exclusive, at low M_2 content the rates of the reaction and hence i_0 values increase with increasing M_2 . At high M_2 content, since increased extent of surface blocked by the adsorbed OH radical makes the adsorption of organic fragment difficult⁴, the rates of the reaction and hence the i_0 values decrease, though the peaks in CVG's appear earlier in the anodic scale. The composition of maximum activity for any binary codeposit is then the composition where M_1 and M_2 are present in neighbouring sites in such an optimum ratio that the product of θ_{CHO} and θ_{OH} is maximum^{1,2,4}. As for the enhancement of catalytic activities of Pt by Au, it may be noted that though the cometal does not adsorb organic fragment^{2,10}, it does adsorb oxygen or the like species in alkaline medium at a more negative potential range than Pt does^{2,10}.

The peak current (i_p) values also pass through maxima at the corresponding θ_{max}^M (Fig. 6a-c). Since i_p values are dependent on the surface concentrations of the reactants, possibly in neighbouring sites at appropriate distances, it is once again established that the most ideal distribution of M_1 and M_2 sites and hence optimization of the product $\theta_{COH} \cdot \theta_{OH}$ is reached at θ_{max}^M .

The R_f -composition profiles are also almost similar to those for $(i_0)_{app}$ and i_p in respect of nature of variation and peak positions. While this appears to suggest that the enhanced catalytic activities of the codeposits are merely the effect of increased number of active sites¹², appearance of broad humps in $(i_0)_{tr}$ versus composition curves at the respective θ_{max}^M indicate that the variation of R_f alone is not re-

Table 4—Extent of increment of $(i_0)_{app}$ and $(i_0)_{tr}$ values on C/Pt-M electrode

	Pd	Rh	Ru	Ir	Au
θ_{max}^M (at % cometal)	35	45-50	50	35	35-40
$[(i_0)_{app}] C/Pt-M$	9	33	22	5	3
$[(i_0)_{app}] C/Pt$					
$[(i_0)_{tr}] C/Pt-M$	4	22	19	3	3
$[(i_0)_{tr}] C/Pt$					
$(i_p) C/Pt-M$	1.7	1.9	1.6	1.5	1.7
$(i_p) C/Pt$					
$(R_f) C/Pt-M$	2.4	1.6	1.4	1.4	1.6
$(R_f) C/Pt$					

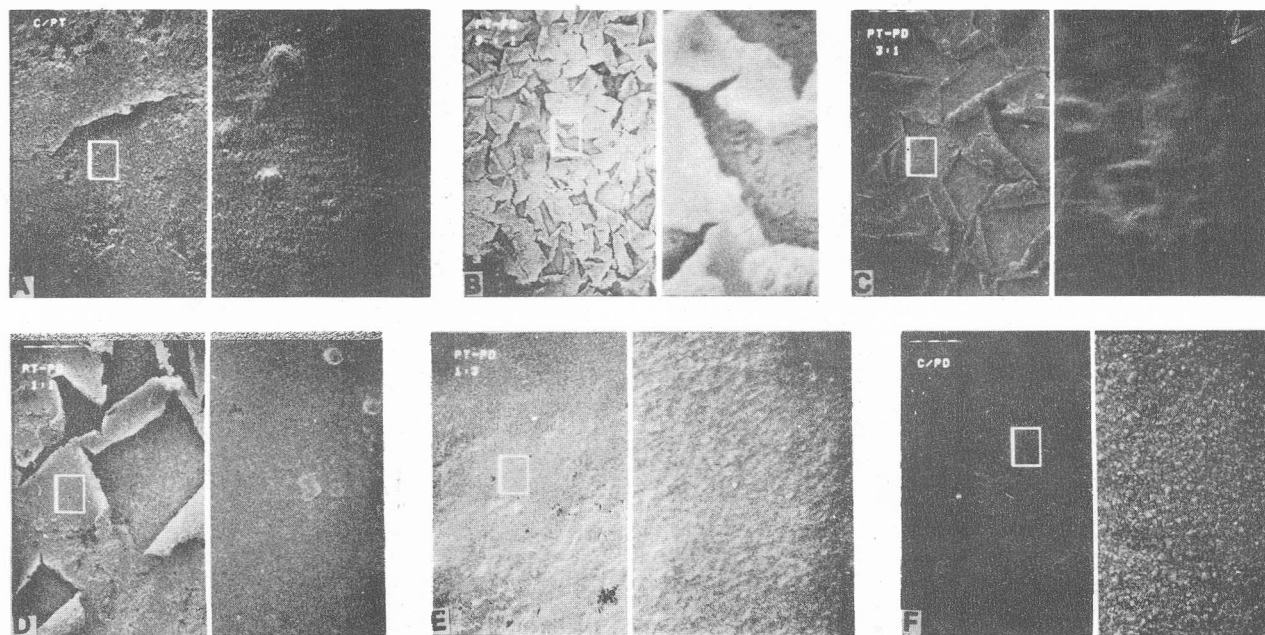


Fig. 5a—Scanning electron micrographs (SEM) of the C/Pt-Pd electrodes: [(A) 0 atomic % Pd; (B) 30 % Pd; (C) 50 % Pd; (D) 70 % Pd; (E) 90 % Pd and (F) 100 % Pd. Magnification: Length of the right marker is 10 μm and right hand part is 10 times enlarged image of the marked region. Tilt position: 0° and acceleration voltage; 25 kV]

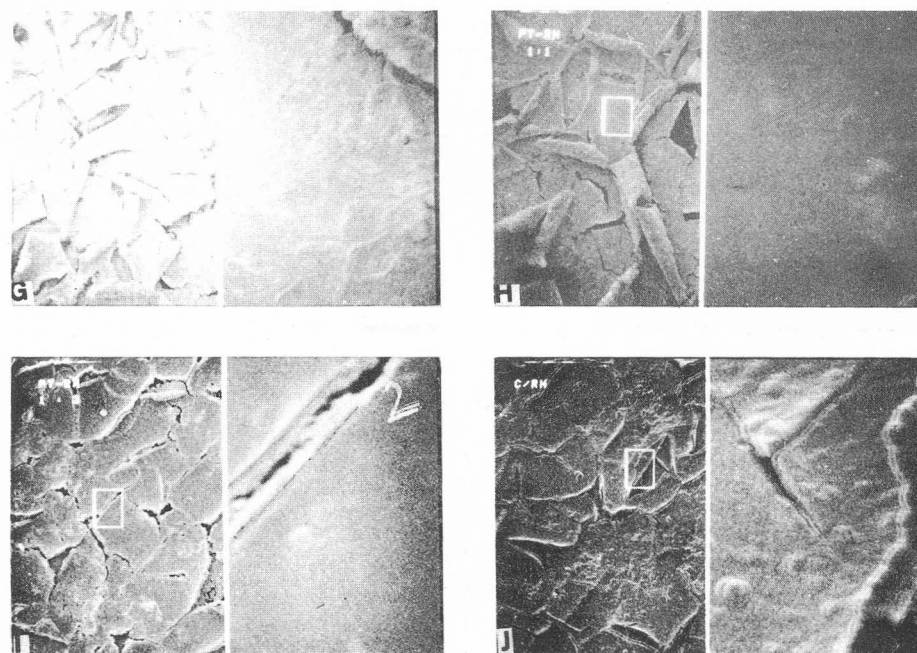


Fig. 5b—Scanning electron micrographs (SEM) of C/Pt-Rh electrodes: [(G) 40 atomic % Rh; (H) 65%; (I) 85% and (J) 100% Rh. Magnification: Length of the right hand marker is 10 μm and right hand part of 10 times enlarged image of the marked region. Tilt position: 0° and acceleration voltage: 25 kV]

sponsible for the observed maximal activities. This is also borne out by the fact that the extent of increment of $(i_o)_{\text{app}}$ and $(i_o)_{\text{tr}}$ values on C/Pt-M electrodes with respect to that on C/Pt surfaces are much different from those obtained for the R_f values as can be seen from Table 4.

That the ratios for peak current densities are almost equal for all the codeposits and for the increment ratios of R_f 's are same, except for C/Pt-Pd system, suggest that for most of the binary deposits an increment in R_f is associated with an increment in the extent of adsorption of CHO and OH species

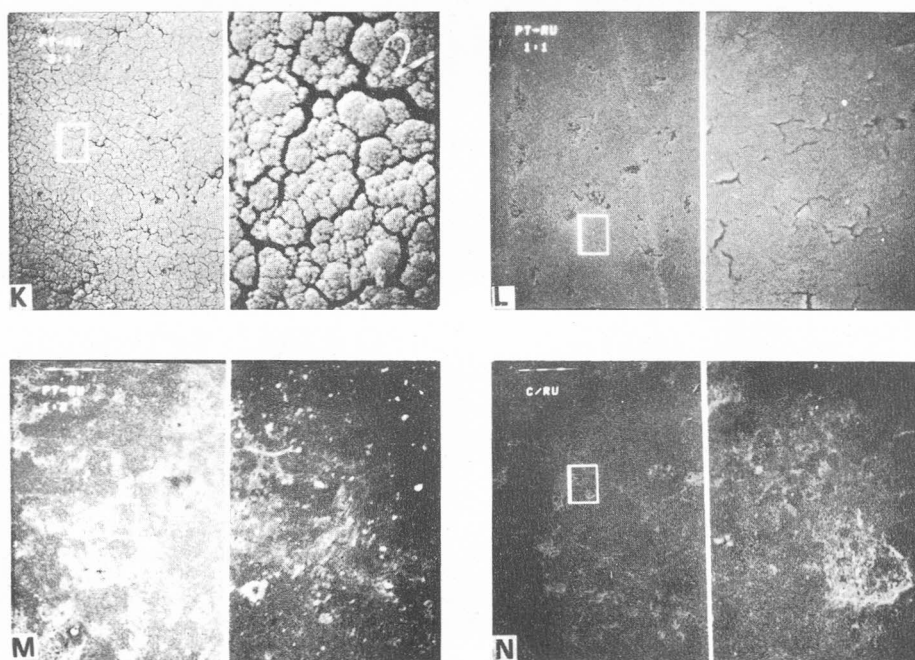


Fig. 5c—Scanning electron micrographs (SEM) of the C/Pt-Ru electrodes [(K) 40 atomic % Ru; (L) 65%; (M) 85%; and (N) 100% Ru. Magnification: Length of the right hand marker is 10 μ M and right hand part is 10 times enlarged image of the marked region. Tilt position: 0° and acceleration voltage: 25 kV]

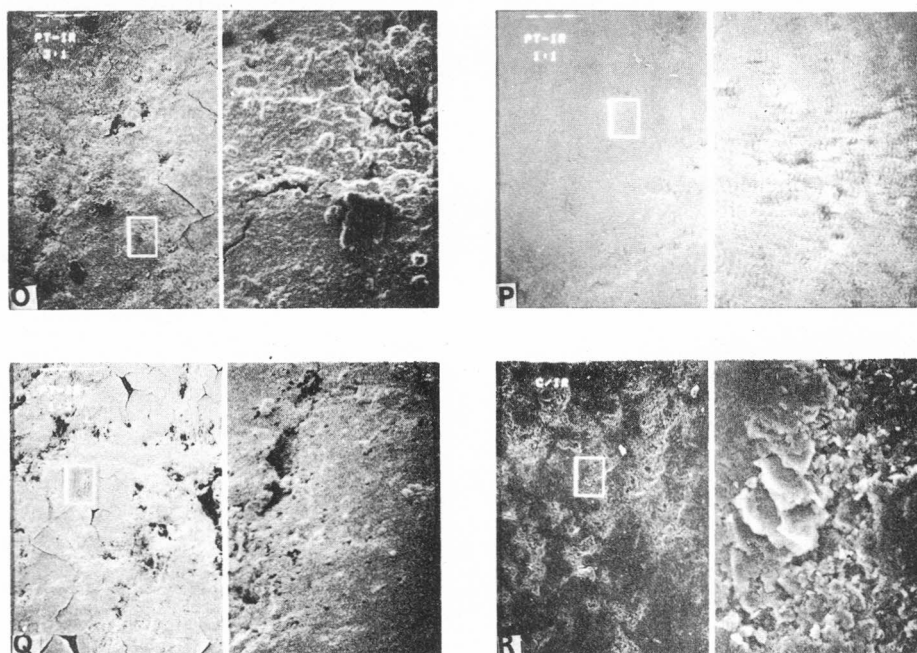


Fig. 5d—Scanning electron micrographs (SEM) of the C/Pt-Ir electrodes: [(O) 30 atomic % Ir; (P) 50%; (Q) 80% and (R) 100% Ir. Magnification: Length of the right hand marker is 10 μ M and right hand part of 10 times enlarged image of the marked region. Tilt position: 0° and acceleration voltage: 25 kV]

over these surfaces. Moreover, the observed lack of parallelism between $(i_o)_{ir}$ ratios and R_f ratios indicates that geometric factors apart, the intrinsic properties of the codeposits are also responsible for the observed overall catalytic effect. Unfortunately, the electronic properties of the codeposited surfaces

are not known and hence the dissection of the effects of the intrinsic and extrinsic properties is not feasible.

Lastly, a perusal of the scanning electron micrographs (Fig. 5a-e) indicates that the distribution of the catalyst materials over the carbon electrodes are

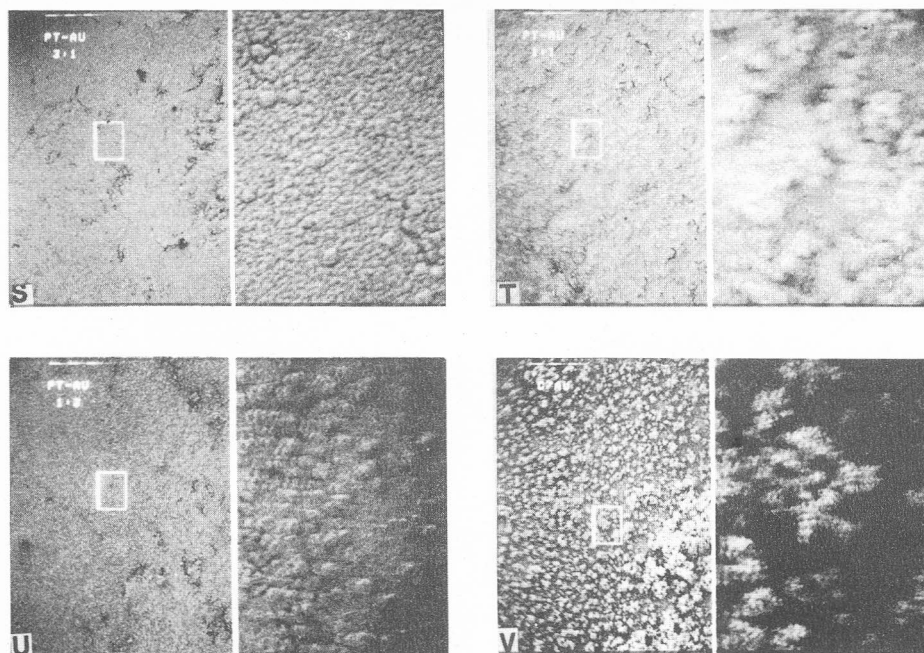


Fig. 5e—Scanning electron micrographs (SEM) of the C/Pt-Au electrodes: [(S) 20 atomic % Au; (T) 40%, (U) 70%; and (V) 100% Au. Magnification: Length of the right hand marker is 10 μm and right hand part of 10 times enlarged image of the marked region. Tilt position: 0° and acceleration voltage: 25 kV]

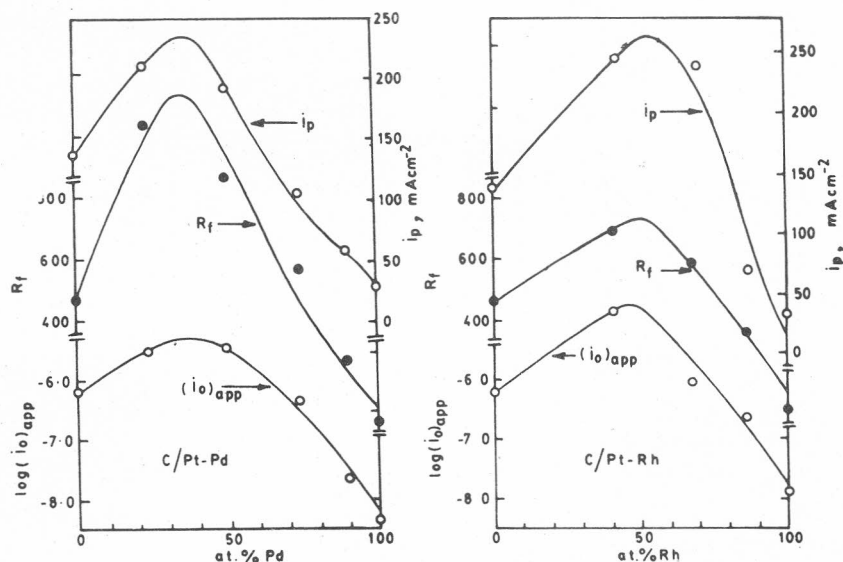


Fig. 6a—Variation of $(i_o)_{app}$, R_f and i_p with cometal (M) composition for C/Pt-M electrodes (M = Pd or Rh) in 1M MeOH-1M NaOH at 25°C [$(i_o)_{app}$ in amp cm^{-2}]

essentially uniform and the 'island growth' present in the cases of pure noble metals Pd, Rh, Ir and especially Au, are almost absent on the codeposited surfaces, with the lone exception of Au, where existence of clusters are once again found. The carbon bases are thus found to be fully covered with the codeposited polycrystals. There is, however, differences to the extent of heterogeneity of the surfaces within a particular group of codeposit (Pt-M) as also

between different cometal deposited surfaces. Though it is not possible to exactly define the composition of maximum heterogeneity of the surface for a particular cometal, it appears to lie in the Pt-rich side in every case. The extent of apparent heterogeneity for the various cometals in the Pt-M codeposits increases in the order: $\text{Rh} < \text{Pd} < \text{Ir} \approx \text{Ru} < \text{Au}$. Lesser heterogeneity and hence more homogeneity for Rh appears to partly

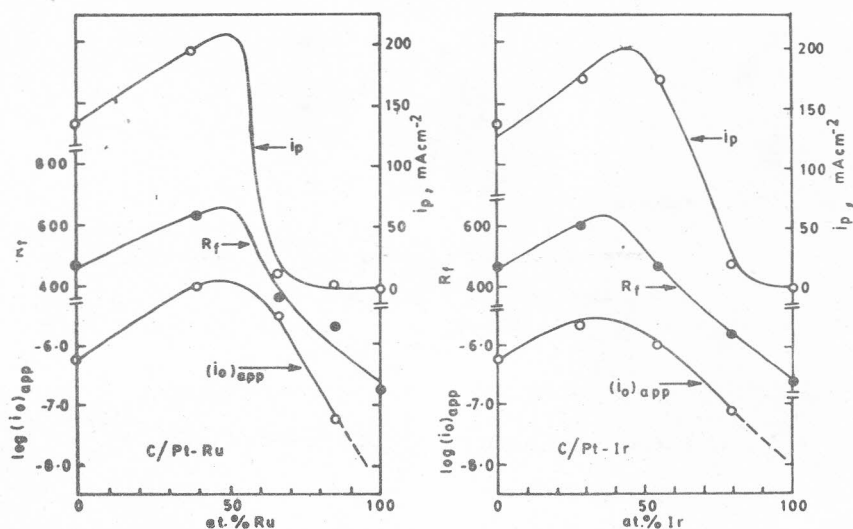


Fig. 6b—Variation of $(i_o)_{app}$, R_f and i_p with cometal (M) composition for C/Pt-M electrodes (M = Ru or Ir) in 1M MeOH-1M NaOH at 25°C [$(i_o)_{app}$ in amp cm⁻²]

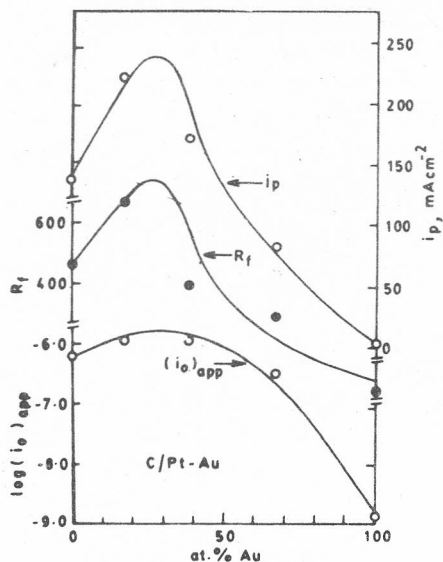


Fig. 6c—Variation of $(i_o)_{app}$, R_f and i_p with cometal (M) composition for C/Pt-M electrodes (M = Au) in 1M MeOH-1M NaOH at 25°C [$(i_o)_{app}$ in amp cm⁻²]

dictate its higher electrocatalytic activity. The observed higher (≈ 1.5 times) R_f values in the case of deposits with Pd as cometal are possibly due to the well known larger H₂-occlusion propensity of Pd rather than the topography of the polycrystallites of Pt-Pd codeposited systems.

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