Methanol Oxidation on Polycrystalline Pt and Pt + Ru Alloy Electrodes.

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The electrooxidation of methanol in acid was studied on polycrystalline Pt and a Pt-Ru (60-40) alloy prepared by arc-melting. The technique used was an alternative type of pulse voltammetry where voltammograms were constructed by chronoamperometric data collected after the application of a potential program on the electrode. The former was chosen such that before each set of measurements the electrode surface was activated and cleaned from the resulting methanolic poison. It was found that on a surface free of poisonous species dissociative chemisorption involving an electron transfer is the rds over a wide potential region. Also, on a poison-free surface, Pt and Pt-Ru show similar catalytic activities at low polarisations whereas Pt-Ru is a better catalyst at high overpotentials. In situations where contamination is expected to occur (higher concentrations, longer times) Pt-Ru is always a superior catalyst due to the oxidative removal of the adsorbed poison by surface Ru oxides.

The electrooxidation of methanol is one of the most extensively studied oxidations of organic species at electrode surfaces due to the potential use of methanol as a fuel in practical fuel cells designed for terrestrial applications [1-4]. Although numerous fundamental studies on the subject have been carried out since the early 60's [5,6] and the development of methanol-based fuel cells has already reached a pilot stage [7,8], understanding of the reaction mechanism and some practical problems related to fuel cell performance are still open areas for basic and applied research respectively [9].

It is now well established that the electrode gets poisoned by adsorbed intermediates; this problem is minimised when Pt is alloyed with certain metals or when some foreign metal adatoms [10,11,12]) are deposited on a Pt electrode. The most promising of these binary catalysts are Pt-Ru electrodes. The oxide RuO_x is formed at less positive potentials than PtO_x; it is believed that RuO_x facilitates the oxidative removal of the poisoning adsorbate and therefore sustains high rates of methanol oxidation. It has also been established that optimum electrocatalytic activity is exhibited by alloys having a bulk Pt-Ru composition in the 70-30 to 50-50 range [11,13,14].

Wieckowski and co-workers have carried out extensive studies of methanol oxidation on Pt monocrystals [15,16].They used chronoamperometric technique which also

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included a periodic pulsing of the potential to positive values so that any poison accumulated during methanol oxidation is further oxidised and removed: the reaction is always being studied on a clean surface. According to our knowledge such a chronoamperometric technique (which would include an appropriate electrochemical cleaning/activation of the electrode surface) has not yet appeared in the literature for the study of methanol oxidation on Pt-Ru electrocatalysts.

This paper presents a study of methanol oxidation on polycrystalline Pt and Pt-Ru alloy electrodes by means of chronoamperometry, as a function of both electrode potential and time - in the short (ms) and medium range (mins) time scale - under conditions of minimum electrode poisoning. It is our aim to investigate whether the presence of Ru in the electrocatalyst enhances the overall rate of methanol oxidation in a wide potential region, even in the short and medium range time scale, that is before severe ageing/ contamination of the electrode surface occurs.

Mechanistic information has been deduced from pseudo- and near- steady state polarisation curves while the type of the reaction kinetics was investigated based on the chronoamperometric data.

Analysis of Reaction Mechanism and Kinetics

The overall reaction for the complete electro-oxidation of methanol in acid media can be written as

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e \quad \ldots \quad R$$

It should be expected that such an electrochemical reaction involving 6 electrons proceeds *via* multiple steps and pathways each of them involving no more than one or two electron transfers and this is indeed the case. Both the soluble products of the reaction and volatile components (CO_2, HCHO, HCOOH and traces of CH_3COOH) have been determined [18,19,20].

Oxidative removal of both the poison and the reactive intermediate, leading to the completion of methanol oxidation to CO_2, is achieved by oxygen containing species. These can be H_2O coming from the solution [21], or OH_{ads}, or PtO_x, depending on the extent of positive polarisation of the electrode.

Reaction Sequence for Methanol Oxidation

Dissociative chemisorption

$$CH_3OH_{sol} + Pt \longrightarrow Pt\text{-}CH_3OH_{ads} \quad \ldots \text{ R.1.a}$$

and

$$Pt\text{-}CH_3OH_{ads} \longrightarrow Pt\text{-}CH_2OH_{ads} + H^+ + e \quad \ldots \text{ R.1.b}$$

or

$$CH_3OH_{sol} + Pt \longrightarrow Pt\text{-}CH_2OH_{ads} + H^+ + e \quad \ldots \text{ R.1}$$

$$Pt\text{-}CH_2OH_{ads} \longrightarrow Pt\text{-}CHOH_{ads} + H^+ + e \quad \ldots \text{ R.2}$$

$$Pt\text{-}CHOH_{ads} \longrightarrow Pt\text{-}COH_{ads} + H^+ + e \quad \ldots \text{ R.3}$$

Formation of oxygen containing surface species

$$Pt + H_2O \longrightarrow Pt\text{-}OH_{ads} + H^+ + e \quad \ldots \text{ R.4.a}$$

or

$$Pt + H_2O \longrightarrow Pt\text{-}O + 2H^+ + 2e \quad \ldots \text{ R.4.b}$$

Reactive path

At low overpotentials (no oxygen adsorbed on Pt)

$Pt\text{-}COH_{ads} + H_2O_{sol}$ (or H_2O_{ads}) ——>
$Pt\text{-}COOH_{ads} + 2H^+ + 2e^-$ ... R.5.a

At higher overpotentials

$Pt\text{-}COH_{ads} + Pt\text{-}OH_{ads}$ ——>
$Pt\text{-}COOH_{ads} + H^+ + e$ ... R.5.b

or

$Pt\text{-}COH_{ads} + Pt\text{-}O$ ——>
$Pt\text{-}COOH_{ads} + Pt$ ... R.5.c

followed by

$Pt\text{-}COOH_{ads}$ ——> $Pt + CO_2 + H^+ + e^-$ ... R.6

Poisoning path and poison removal

$Pt\text{-}COH_{ads}$ ——> $Pt\text{-}CO_{ads} + H^+ + e^-$ ... R.7

$Pt\text{-}CO_{ads} + H_2O_{sol}$ (or H_2O_{ads}) ——>
$Pt\text{-}COOH_{ads} + H^+ + e^-$ ... R.8.a
(followed by R.6)

or

$Pt\text{-}CO_{ads} + Pt\text{-}OH_{ads}$ ——>
$Pt\text{-}COOH_{ads} + Pt$ ... R.8.b
(followed by R.6)

or

$Pt\text{-}CO_{ads} + Pt\text{-}O$ ——> $Pt + CO_2$ ... R.7.c

Although reactions R.1 and R.5 in the above sequence, have been reported to be the slowest, it is worthwhile considering in detail what would be the dependence of the overall reaction rate on the electrode potential and time, if any of steps R.1 to R.6 was the rds. If R.1.a is the rds, then there should be no potential dependence of the reaction rate in the region where no significant amounts of H or O are adsorbed (low overpotentials) and a decrease in the region of surface oxide formation (R.4) which hinders methanol adsorption (high overpotentials).

The reaction rate-current should also obey one of the most commonly encountered kinetic laws for irreversible adsorption of organic molecules on electrodes:

Langmuir kinetics is represented as:

$$i_{ads} = KQ_{ads} \exp(-kt) \quad \ldots (1)$$

Then log i shows linear dependence with time.

Roginskii-Zel'dovich [22], or Elovich[23,27] kinetics are represented by:

$$i_{ads}^{-1} = f(Q_{ads}, t) \quad \ldots (2)$$

where Q_{ads} is the saturation charge on the surface. Then 1/i shows a linear dependence with t.

Rate Determining Reaction

If any of the steps R.1.b, R.2 or R.3 is the rds, then Tafel behaviour should be observed at low overpotentials whereas a decrease in the reaction rate should be expected at high overpotentials due again to the decrease in free Pt sites where $Pt\text{-}CH_3OH_{ads}$ can be formed (methanol does not adsorb at Pt-O sites). No Langmuir or Elovich kinetics should be obeyed since this step is essentially a surface reaction. If R.1 is the rds, then the potential dependence should be similar to that of R.1.b, but the current should follow one of the above mentioned adsorption kinetics.

If the oxidative removal of Pt-COH according to any of the of steps in R.5 is the rds, the rate of the reaction need not follow adsorption kinetics. In particular, R.5.a should lead again to a Tafel behaviour whereas R.5.b and R.5.c should show a more complex dependence on potential since the surface concentration of $Pt\text{-}OH_{ads}$ and PtO increases with electrode potential and also affects (hinders) methanol adsorption on free Pt sites, therefore decreasing the surface concentration of Pt-COH. R.5.c could also lead to a saturation of the current when the saturation coverage for Pt-O is reached.

Finally, if R.6 is the rds, simple Tafel behaviour but no adsorption kinetics are expected. As far as the poisoning of the electrode surface with $Pt\text{-}CO_{ads}$ is concerned, the fact that this is an ageing phenomenon, i.e. it increases with time, implies that the removal of the poison (one of the reactions of R.8) is slower than the rds of the reactive path therefore leading to an accumulation of adsorbed CO. The comments regarding the potential dependence of steps R.6 above, are valid for the oxidative removal step R.8.

EXPERIMENTAL

The Pt - Ru alloy electrode used in this work was prepared by arc melting of Ru powder and Pt wire (Alfa Aesar). The resulting spherical structure was flattened on both sides by polishing on a hard emery paper. Then the face to be used as an anode was further polished on emery papers of decreasing degree of roughness. Finally, the same face of the electrode was polished to a mirror finish with 1, 0.3 and 0.05 μm alumina powder (Micropolish II, Buehler) .

The Pt electrode was a 10 mm diameter platinum disc (Alfa Aesar) and was also polished on alumina powder and cleaned in millipore water under ultrasonic.

All electrochemical measurements were carried out using a Model 273 Potentiostat/ Galvanostat (EG&G Instruments) interfaced to a computer and using Model 270/250 Research Electrochemistry Software.

Model K0105 Flat Specimen Holder Kit was modified in that a teflon washer and an additional O-ring was placed above the Kalrez washer, exposing a geometric area of ca 0.55 cm^2 of the working electrode. The reference electrode was a 0.2 M H_2SO_4 mercury/mercurous sulphate electrode (prepared in the laboratory). Its potential was checked before and after each set of experiments against a SCE (Radiometer). **However, all potentials reported in this work are reported with respect to the Standard Hydrogen Electrode (SHE)** for comparability with the existing literature. The counter electrode was a Pt coil.

Methanol was 99.9+ % pure and Sulphuric Acid (double distilled,PPB/TEFLON grade) both from Aldrich.

All experiments were performed under an Argon blanket in Argon-deaerated solutions and at room temperature (22-25°C).

RESULTS

Potential Program for Electrochemical Cleaning / Activation

In the case of Pt-Ru, the choice of the potential program to be applied before the collection of each set of

chronoamperometric data should be done very carefully. The upper potential pulse has to be positive enough to oxidise any adsorbed poison but below the value of the anodic dissolution of Ru (0.8-0.9V *vs* SHE) [17]. In addition to this moderate anodic pulse, a negative pulse (at the onset of hydrogen evolution) should also be incorporated in the potential program.

After a series of preliminary experiments it was decided that the following potential program should be applied on both the Pt and Pt-Ru(60-40) electrodes:

Negative pulse : -0.05 V *vs* SHE for 2 s

Positive pulse : +0.75 V *vs* SHE for 2 s

This was chosen just below the onset of Ru anodic dissolution (0.8 - 0.9V [17]) but in a region that CO is readily oxidised on both Ru and Pt [24].

Waiting pulse : +0.25 V *vs* SHE
120 ms or 1000 mS

The waiting pulse was included to reduce any oxides formed during the positive pulse. Its value (0.25 V) lies between the hydrogen adsorption region (to avoid the interference of hydrogen desorption with methanol oxidation during the potential step of interest) and that of significant methanol adsorption. Duration of transients was chosen such that it is the minimum value (*ca* 120mS) required for almost complete reduction of any residual oxides irreversibly formed during the many of the activation sequences (*ca* 30) and also ensuring minimum adsorption of methanol prior to the potential pulse experiment. The residual current that is present thereafter, if any, is only due to any incompletely reduced oxides on the surface.

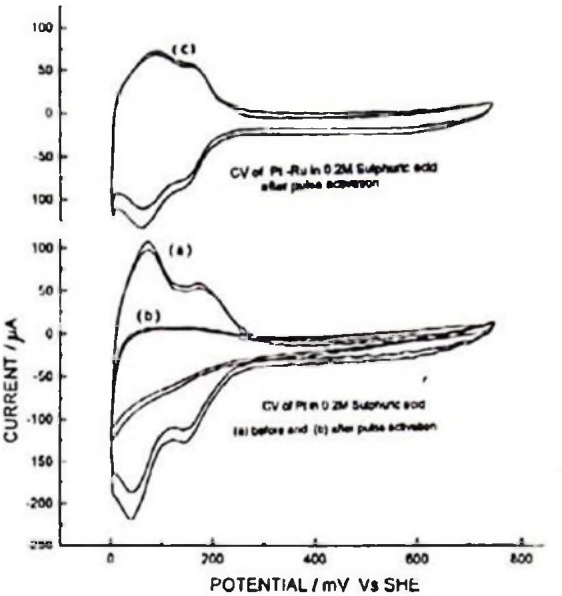


Fig 1 CV in 0.2 M Sulphuric acid
Scan rate 200 mV/sec.
a First cycle on Pt
b After application of 30 activation pulses on Pt
c After application of 30 activation pulses on Pt - Ru

Potential of interest: +0.45 to +0.75 V *vs* SHE for 100 ms or 180 s

Curve (a) in Figure 1 shows the very first voltammogram recorded for Pt in 0.2 M H_2SO_4 while curve (b) shows the voltammogram recorded after the potential program described above had been applied for 30 times (the potential of interest being 0.25 V i.e. in the double layer region). It can be seen that the application of the potential program is essential for the electrochemical activation of the surface and the development of the voltammetric characteristics of pure polycrystalline Pt. The same effect was also observed in the case of the Pt-Ru alloy.

Therefore the protocol was applied before each set of experiments and repeated as many times as necessary for the H-adsorption/desorption envelope to attain a steady state size. CVs 1(b) and 1(c) show the voltammetric picture of the Pt and Pt-Ru (60-40) electrodes in the supporting electrolyte. The shape and definition of the latter resembles the picture reported in the literature for Pt-Ru alloys of similar compositions [14,15].

The true surface area of the electrodes was calculated each time from the charge corresponding to the adsorption of H based on the 210 $\mu C/cm^2$ related to the phenomenon and all currents were normalised accordingly [14].

It should also be pointed out that when the negative pulse (which lies in the onset of H_2 evolution region) was not applied, not only did the hydrogen adsorption/ desorption envelope decrease in size, but also the corresponding methanol oxidation currents recorded during the chronoamperometric experiments appeared

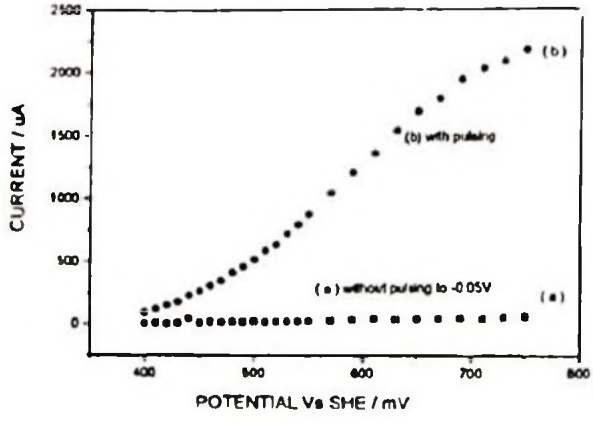


Fig 2 Effect of pulsing to -0.05 V vs SHE (the Potential Corresponding to H_2 Evolution Reaction)
I-E Plot for Pt - Ru in 0.05 M MeOH + Sulphuric acid Constructed from Chronoamperometry data at 50 ms of the 100 ms Transient.
a without Pulsing b after Pulsing

to be substantially smaller, even if one accounts for the difference in surface area (Figure 2, 50 ms, logi-E curves). Therefore it seems that hydrogen adsorption/ evolution does not merely clean the surface from additional impurities but also plays an active part in removal of the methanol oxidation poison.

Analysis of Chronoamperometric Transients

During blank experiments in 0.2 M H_2SO_4 (over the entire potential region of interest - 0.25 to 0.75 V) it was found that the current reached a near steady-state value after *ca* 30 ms. This indicates that after this period, the surface is free of any capacitive and pseudo capacitive contributions; only the current due to the reduction of any residual oxides irreversibly formed during the many pulse activation sequences (ca 30) exist. The increase in current for a potential step thereafter can be safely attributed to methanol oxidation. The blank currents decaying close to zero after ca 10-20S. indicate an oxide free surface. However at short times, there is a negative residual currents due to the slow reduction of irreversibly formed oxides mentioned above.

Figure 3 shows a typical current-time response of the Pt electrode in 0.5 M of methanol after a potential step from 0.25 to 0.55V.

The above mentioned potential program was applied and the current transients were recorded during the potential pulse of interest. The plots 1/i vs t, log i vs t and i *vs* $t^{1/2}$ were made to check whether the reaction follows Elovich [27], Langmuir or Koryta (diffusion) adsorption kinetics [25].

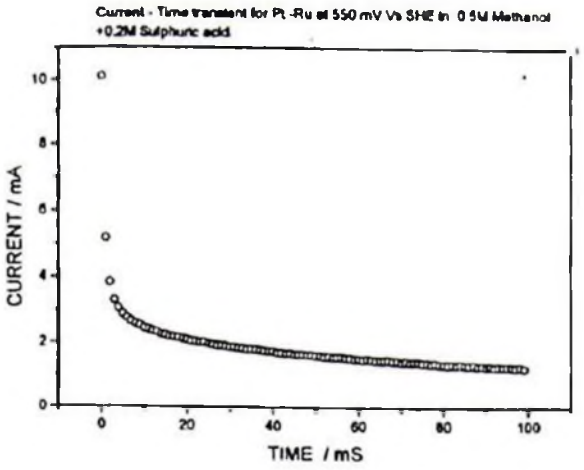


Fig 3 Current Time Transients
Pt-Ru at 550 mV *vs* SHE in 0.5 M MeOH + 0.2 MSulphuric acid

The results of this fitting, given as linear regression coefficients, are presented in Tables 1 for both Pt and Pt-Ru, at 0.5M MeOH, for short (up to 100 ms) times, for different applied potential values.

The 1/i *vs* t plot (Figue 4) shows the behaviour corresponding to the Elovich

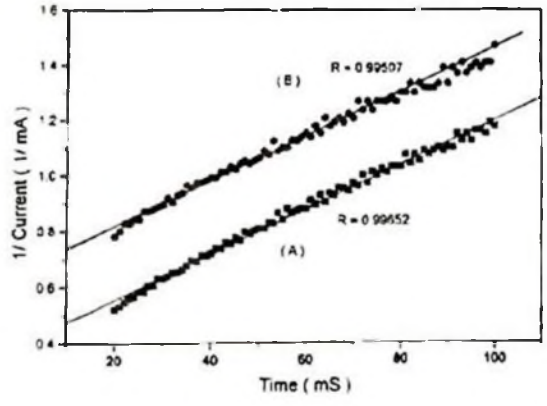


Fig 4 1/i vs t Plots in in 0.5 M MeOH + 0.2 MSulphuric acid
a Pt at 550 mV *vs* SHE
b Pt-Ru at 500 mV *vs* SHE

Table 1

Analysis of chronoamperometric transients - Correlation coefficients of Fitting

Medium: 0.5M Methanol + 0.2M Sulphuric acid
100mS transients plotted with the data points from 20 mS - 100mS

Potential	I^1 vs t	log I vs t	I vs $t^{1/2}$
Pt electrode			
450	0.990	0.984	0.985
500	0.995	0.986	0.987
550	0.996	0.985	0.983
590	0.995	0.987	0.985
630	0.995	0.987	0.989
650	0.988	0.996	0.976
750	0.982	0.966	0.971
Pt- Ru (60-40) electrode			
450	0.986	0.980	0.984
500	0.995	0.991	0.989
550	0.996	0.991	0.993
590	0.995	0.987	0.992
650	0.995	0.989	0.992
750	0.986	0.979	0.984

kinetics [27]. The data in the table shows that on the whole, the kinetics of adsorption follows the Elovich kinetics. We find similar behaviour at 0.05M Methanol also. However, the 180S transients do not follow any of the three functions. This indicates that the surface is atleast partially covered with poison and inhibits methanol oxidation.

Based on the electrochemical data, Wieckowskii *et.al.* found that methanol oxidation follows Langmuir kinetics at longer times (although at somewhat lower potential of 0.4V). But both Langmuir and Elovich Kinetics could be speculated on the

basis of radiotracer data [28]. However, the majority of available data support the idea of Elovich Kinetics [26,27]. It is interesting to note that we also find Elovich behaviour at potentials below *ca* 650mV; but above these potentials, the transients do not fit to any of the three fits showing an apparent deviation from purely chemisorption mechanism.

Cyclic Voltammetry

Figure 5A shows the cyclic voltammograms for methanol oxidation on the Pt (curve a) and Pt-Ru (curve b) electrodes from a 0.05 M methanolic solution, recorded at a 20 mV/s potential sweep rate. Figure 5B shows the result of the same experiment in a 0.5 M methanolic solution. The voltammograms were obtained after the application of the activation potential program for several times and the electrode potential was swept first from 0.25 to 0 V before the positive going scan was recorded.

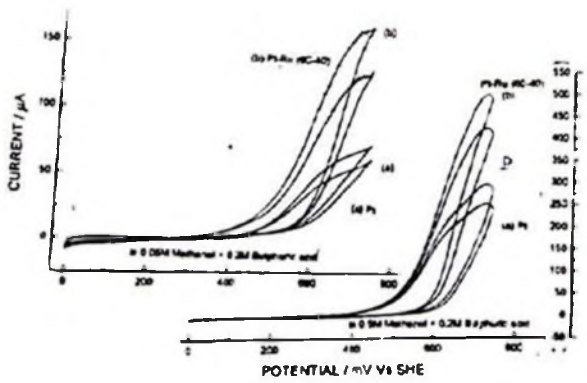


Fig 5 Cyclicvoltammograms
Scan Rate 200 mV/Sec
A in 0.05 M MeOH + 0.2 M Sulphuric acid
B in 0.5 M MeOH + 0.2 M Sulphuric acid
a Pt b Pt-Ru

It is clear that during these potentiodynamic experiments, the oxidation of methanol occurs at higher rates on the Pt-Ru (60-40) alloy than on pure Pt, at both concentrations of methanol and over the entire potential region under study. However, closer observation reveals that the potential difference for the onset of the oxidation during the forward scan between the two electroded is smaller for the lower concentrations (*ca* 50 mV) than that for the higher concentration (*ca* 100 mV). The potentials where methanol starts to oxidise are very close [29] to the values corresponding to the beginning of formation of measurable OH_{ads} on the electrode surface i.e. ca 0.50 - 0.55 V for Pt-Ru and 0.55 - 0.60 V for Pt (However, oxygenated Ru species are known to be present on the surface from potentials as low as 0.2 V [30]). In the same potential region, CO adsorbed from solution is completely oxidised / stripped from Ru and Pt electrodes respectively [24]. This implies the significant role of adsorbed oxygenated species in removing the poison Pt-CO (removal *via* R.8.b) formed during the slow scan starting at 0 V or/and facilitating the reactive path by oxidising the reactive intermediate Pt-COH (*via* R.5.b). This idea is also supported by the shape of the cyclic voltammograms in which the forward and reverse scans form a loop. This is characteristic of nucleation processes; in this case the loop is due to the nucleation of $M\text{-}OH_{ads}$ species and its positive effect on methanol oxidation.

Comparing the currents obtained at 0.75 V in the 0.05 M solution and 0.5 M solution, it follows that a 10-fold increase in methanol concentration results in a 2.5-3 - fold increase in the current. These values correspond to a reaction order of *ca* 0.5 for

Pt-Ru and *ca* 0.4 for Pt. Chu *et.al.* [13] have also reported a reaction order of 0.5 at 0.5 V . (The fact that the reaction orders at high and low overpotentials seem to coincide and follow the same type of adsorption kinetics, shows that the mechanism of methanol oxidation remains the same through a wide potential region studied).

However Tafel analysis at the foot of the voltammetric waves (between 0.40 and 0.55 V) led to Tafel slopes 170 mV/decade for Pt-Ru and 250 mV/decade for Pt - much higher than those reported in the literature [15,16,32]. This should be due to the accumulation of poisonous Pt-CO during the positive going scan and demonstrates the necessity for a periodic cleaning of the electrode surface from the poison.

Pulse Voltammetric and Polarisation Curves constructed from Chrono-amperometric Data :

In this work we have used a modified method of obtaining a pseudo-steady state I *vs* E curve; we have applied the previously mentioned potential program for cleaning / activation followed by various potentials of interest in the 0.35 to 0.75 region - spaced at 10 mV between 0.35 and 0.55 V and 20 mV between 0.55 and 0.75 V and collected current data as a function of time. We could then construct I *vs* E curves for a given time, by plotting the currents sampled at that particular time against the corresponding applied potential pulse.

Figure 6 presents voltammetric curves for the oxidation of corresponding to 50 ms data, for Pt and Pt-Ru using 0.05 M CH_3OH, and 0.5M CH_3OH solution. Figure 7 presents curves corresponding to 180 S

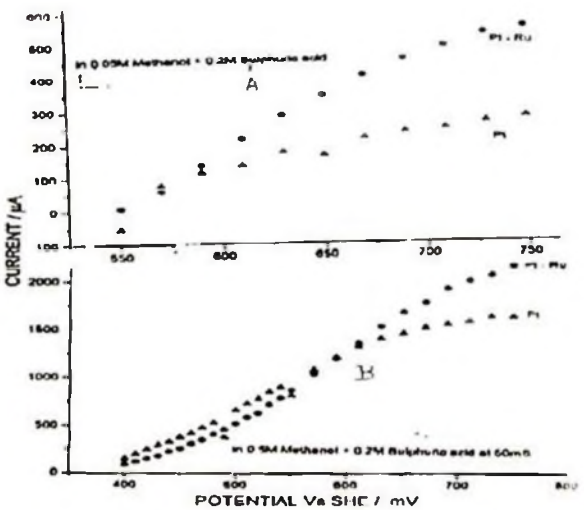


Fig 6 I-E Plots at 50 ms
A in 0.05 M MeOH + 0.2 M Sulphuric acid
B in 0.5 M MeOH + 0.2 M Sulphuric acid
a Pt b Pt-Ru

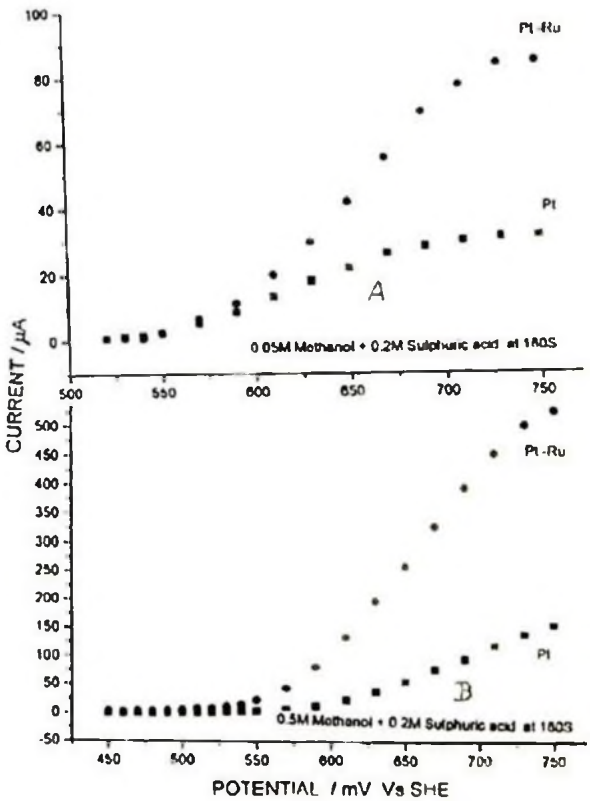


Fig 7 I-E Plots at 180 ms
A in 0.05 M MeOH + 0.2 M Sulphuric acid
B in 0.5 M MeOH + 0.2 M Sulphuric acid
a Pt b Pt-Ru

data.The curves are plotted from the potential at which significant oxidation current is obtained in each case.

It can be seen that all the voltammograms show the same qualitative features. That is, at low positive overpotentials (below 0.55 V) the Pt and Pt-Ru electrodes show the similar catalytic activity within the experimental error. In the case of higher concentration and short time (Fig 6B) where the accuracy is better, Pt seems to be a slightly better electrocatalyst - a situation that is different from the one encountered in the potentiodynamic voltamogramms of Figure 5. This has to be attributed to the activation effect of the positive potential pulse at 0.7 V. For high overpotentials Pt-Ru is again superior to Pt. Also, for the same cases, the voltammograms show an S-shaped pattern; they tend to a plateau at high potentials. Tthis trend is more pronounced for the Pt electrode.

In contrast, the voltammogram corresponding to high methanol concentrations and long times (Figure 7B) exhibits a continuous almost linear increase with electrode potential and the activity of the Pt-Ru electrode is higher than that of pure Pt throughout the entire potential range.

Figure 8 is the log i *vs* E curve, corresponding to that of Fig. 6B. Tafel slopes as calculated for the 50mS transients at 0.5M methanol in the potential region *ca* 0.40-0.50 are 115 mV for Pt and 110 mV for Pt-Ru. Similarly for 180S transients (Fig 8B) a Tafel slope of *ca* 100 mV is obtained at 0.5M methanol.

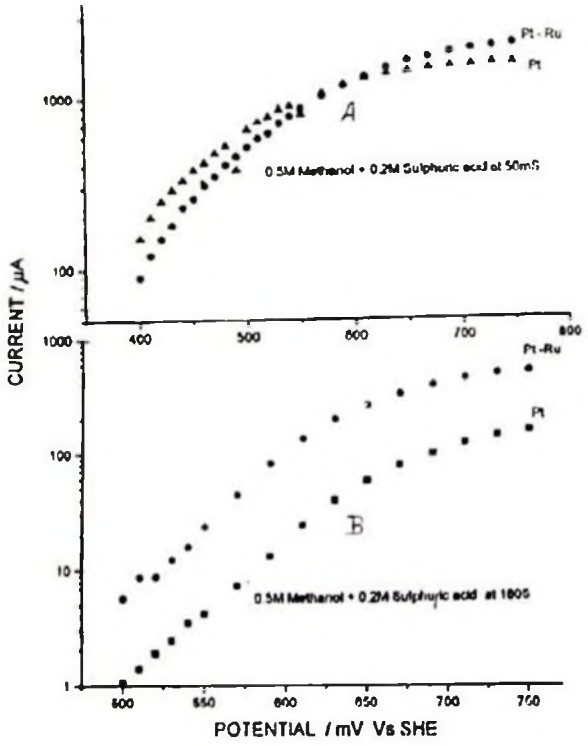


Fig 8 Tafel Plots
A in 0.5 M MeOH + 0.2 M Sulphuric acid at 50 ms
B in 0.05 M MeOH + 0.2 M Sulphuric acid at 180 ms
a Pt b Pt-Ru

DISCUSSION

In short time experiments (in the ms range) methanol adsorption does not reach its equilibrium [29,33]; But during longer experiments (in the mins range), the current decay has been attributed to the continuous formation of a poisonous reaction intermediate. Therefore, in both cases the results do not correspond to a steady-state situation but to a pseudo steady state.

In short time transients it can be asssumed that after the poison is oxidised at positive pulse at +0.75 V, no significant quantity of the latter has been formed during the 120 ms at +0.25 V and the 50 ms at the

potential of interest. It is also known that for low methanol concentrations it takes at least 500 ms for the coverage of adsorbate methanolic residues to reach a significant value [33], even at a potential of 0.4 V which is that of maximum adsorption [34].

Wieckowski and co-workers [15,16] subtracted the background chronoamperometric transient recorded in the supporting electrolyte from that obtained in the methanolic solution and then extrapolated the resulting curve to zero time so as to get a current value free from any contamination effect. We find such an approach is questionable as it ignores any pseudo capacitance involved with the oxidation of methanol at very short times. As such we have not resorted to the background correction using pure sulphuric acid data.

Therefore, by choosing the sampling time of 50 ms we not only ensured that there will be no charging current contributions but, most important, that any pseudocapacitance contributions will have decayed too; at the same time, no severe contamination should occur within those 50 ms. For 0.5M methanol shown in Figure 6B, it can be seen that at polarisations below ca 0.55 V (which is the potential for the onset of significant OH_{ads} formation on Ru. Both Pt and Pt-Ru electrodes show almost similar currents for methanol oxidation. Furthermore, as the analysis of the chronoamperometric results showed (Table 1) the current transients fit better into the expression for Elovich adsorption kinetics.

From the potential dependence and from the adsorption kinetics, it is evident that dissociative chemisorption (reaction R.1) is the most likely the rds in this potential region. If this is the case, and since no Pt-CO_{ads} poison should be present within 50 ms, one should expect Pt to be a better catalyst because chemisorption of methanol is very limited on Ru at room temperature [24]. This trend is probably offset by the presence of traces of oxygenated species [30] present on the surface which shift the equilibrium of reaction R.5.c (involving the reactive intermediate Pt-COH_{ads}) to the right, thus creating more free Pt sites available for methanol chemisorption. At potentials above 0.60 V, for both 0.05M and 0.5M methanol, the slope of the polarisation curves (Figure 6) increases and Pt-Ru becomes superior to Pt and the current starts to plateau. This does not imply any change in the mechanism: Table 1 shows Elovich adsorption kinetics are followed over a wide range of potentials, and this is a strong evidence that the rds of methanol oxidation on an activated, poison-free Pt or Pt-Ru surface is the same for both low and high polarisations atleast upto *ca* +650mV. Therefore, it seems that dissociative chemisorption is the rds over a wide potential region studied. Again, Pt-Ru shows better catalytic activity than pure Pt since in the potential region above 0.55 V there is much more Ru than Pt oxygenated species on the surface [29] and therefore steps R.5.b or R.5.c have their equilibrium shifted to the right. Consequently, the rate of R.1 (rds) should increase accordingly.

We find that the presence of Ru oxides at high overpotentials has a beneficial effect on methanol oxidation even on a poison-free electrode. The tendency of the current to plateau, which is higher in the case of Pt, could also be attributed to the potential dependence of Pt and Ru oxide formation

and its effect on the availability of Pt sites for chemisorption. The increase of both Ru and Pt oxides with increasing polarisation results in the creation of free Pt sites by means of reactions R.5.b or R.5.c. However, methanol cannot adsorb anymore on the already formed $Pt\text{-}OH_{ads}$ and PtO_{ads} sites. Hence the tendency of the current to saturate with electrode potential is an apparent effect resulting from two opposite changing effects. This also explains the deviation from the adsorption kinetics at higher polarisations >650mV.

In the case of higher methanolic concentrations (0.5 M) and longer times (180 s) the effect of poison accumulation is demonstrated in the pulse voltammograms of Figure 7B where it is seen that no significant current is observed even for the Pt-Ru electrode below 0.55V i.e. before significant quantities of $Ru\text{-}OH_{ads}$ is formed. This is because unless the removal of the $Pt\text{-}CO_{ads}$ species starts to occur at a significant rate via R.8.b or R.8.c, methanol oxidation cannot proceed . As it is shown clearly in the polarisation curves of Figure 8B, the Pt-Ru alloy is superior to pure Pt at all potentials. Furthermore, the ratio of the current at +0.75 V for the two materials ($i_{Pt\text{-}Ru}/i_{Pt}$) is much higher than in the case of short times -low concentrations.

The saturation of the logi-E curves can again be explained as a consequence of the two opposite effects : $Pt\text{-}OH_{ads}$ or $Pt\text{-}O_{ads}$ formation (Pt-CO removal-freeing of Pt sites and Pt-O formation-blocking of Pt sites). It can be seen that these curves have a linear region extending to a very wide potential range (from 0.50 to 0.65) and covering over two orders of magnitude of current.

The fact that the apparent Tafel slope is nearly 100 mV/decade and the very poor correlation coefficients of the fitting of the current transients to the adsorption kinetics mentioned above, is a strong indication that chemisorption is not the sole step determining the reaction rate in this case. Instead, one could propose that methanol oxidation is in this case under mixed control by both chemisorption and the oxidative removal of the poison via one of reactions R.8. The latter are also expected to show a potential dependence due the corresponding dependence of the concentration of surface oxygenated species on electrode potential.

CONCLUSIONS

The main findings of the present work for methanol oxidation could be summarised as follows:

a. When an appropriate potential program that ensures the electrochemical cleaning/activation of the electrode from the resulting methanolic poison is used, both at the Pt and at the Pt-Ru electrodes dissociative chemisorption of methanol with the simultaneous transfer of one electron is the rds. The chemisorption follows Elovich adsorption kinetics over a wide potential range .The apparent deviation at potentials above +0.650V appears to be due to opposing effects of surface oxide formation (which inhibits chemisorption) and oxidative removal of poisons (which provides vacant Pt sites helping chemisorption) leading to saturation of the current.

b. On a poison-free surface Pt shows an activity comparable with Pt-Ru alloy, at lower overpotentials (0.40-0.55V)

c. At higher overpotentials and even on a clean surface, the presence of Ru oxygenated species enhances the current, probably by removing the reactive intermediate $Pt\text{-}COH_{ads}$ and therefore creating more free Pt sites for the chemisorption of methanol.

d. In cases that the rate of the reaction and the accumulation of adsorbed poisons is considerable (eg. high concentrations-long times), Ru oxides facilitate the oxidative removal of the poison and therefore the Pt-Ru alloy sustains higher currents for methanol oxidation than polycrystalline Pt.

REFERENCES

1. Fuel Cells Handbook. A.J.Appleby and F.R.Foulkes (Eds.). **Van Nostrand Reinhold** (1989)
2. S.Srinivasan. *J.Electroanal.Chem.*, **118** (1981) 51
3. S.Surampudi, S.R.Narayanan, E.Vamos, H.Frank, G.Halpert, A.LaConi, J.Kosek,R.K.SuryaPrakash and G.A.Olah, *Journal of Power Sources*, **47** (1994) 377
4. B.D.McNicol, *J.Electroanal.Chem.*, **118** (1981) 71
5. J.O'M.Bockris, B.E.Conway, E.Yeager and R.E.White, *Comprehensive Treatise of Electrochemistry*, Vol.3, **Plenum Press, NY** (1981)
6. V.S.Bagotskii and A.M.Skundin, *Chemical Power Sources*, **Academic Press, NY** (1981)
7. G.A.Hards, *Platinum Metals Rev.* **39(1)** (1995) 9
8. D.S.Cameron, G.Hards, B.Harrison and R.J.Potter, *Plat. Metals Rev.*, **31(4)** (1987) 173
9. R.Parsons and T.Vandernoot, *J.Electroanal.Chem.*, **257** (1983) 9
10. H.Binder, A.Kohling and G.Sandstede, in *From Electrocatalysis to Fuel Cells*, (Ed.) G.Sandstede, **University of Washington Press, Seattle WA** (1972) pp. 43-58
11. M.R.Andrew, J.S.Drury, B.D.McNicol, C.Pinnington and R.T.Short, *J.Appl.Electrochem.*, **6** (1976) 93
12. R.R.Adzic, *Isr.J.Chem.*, **18** (1979) 166
13. D.Chu and S.Gilman, *J. Electrochem. Soc.*, **143(5)** (1996) 1685
14. H.A.Gasteiger, N.Marcovic, P.N.Ross and E.J.Cairns, *J.Phys.Chem.*, **97** (1993) 12020
15. K.Franaszczuk, E.Herrero, P.Zolenay, A.Wieckowski, *J. Phys. Chem.*, **96** (1992) 8509
16. E.Herrero, K.Franaszczuk, A.Wieckowski, *J.Phys.Chem.*, **8** (1994) 5074
17. V.S.Entina, O.A.Petrii, *Electrochimiya*, **4** (1968) 678
18. E.M.Belgsir, H.Huser, J.M.Leger and C.Lamy,*J. Electroanal. Chem.*, **225** (1987) 281
19. K.I.Ota, Y.Nakagawa, M.Takahashi, *J. Electroanal. Chem.*, **179** (1984) 179
20. T.Iwasita and W.Vielstich, in *Advances in Electrochemical Science and Engineering*, Vol.1, H.Gerischer and C.W.Tobias (Eds), **VCH Verlagsgesell Weinheim,** (1990) p.127
21. M.Beltowska-Brezinska, *Electrochim. Acta*, **30** (1985) 1193
22. S.Z.Roginskii, in *Adsorption and Catalysis on Heterogeneous Surfaces*, **Izd.Akad.Nauk,SSSR,** (1948)
23. S.Y.Elovich and G.M.Zhabrova, *Zh. Fiz. Khim.*, **13** (1939) 1761, 1765
24. H.A.Gasteiger, N.Marcovic, P.N.Ross and E.J.Cairns, *J. Phys. Chem.*, **98** (1994) 617
25. A.K.N.Reddy, in *Electrosorption*, (Ed.) E.Gileadi, **Plenum Press, NY** (1967) p.53
26. V.S.Bagotskii and Y.B.Vasilev, *Electrochim.Acta.*, **11** (1966) 1439
27. T.Biegler and D.F.Koch, *J. Electrochem. Soc.*, **114** (1967) 904
28. A.Wieckowski and J.Sobkowski, *J.Electroanal.Chem.*, **63** (1975) 365
29. P.S.Khuranen, E.Skou and J.Munk, *J. Electroanal. Chem.*, **404** (1996) 1
30. E.Ticanelli, J G.Beery, M.T.Paffett and S.J.Gottesfeld, *J. Electroanal. Chem.*, **258** (1989) 61
31. V.S.Bagotzky and Y.B.Vassilyev, *Electrochim.Acta*, **12** (1967) 1323
32. O.A.Petry, B.I.Podlovchenko, A.N.Frumkin and H.Lal, *J. Electroanal. Chem.*, **10** (1965) 253
33. B.B.Damaskin, O.A.Petrii, V.V.Batrakov, *Adsorption of Organic Compounds on Electrodes*, **Plenum Press, NY, London,** (1971) Ch.10, p.451
34. *ibid*, p.439