INDUSTRIAL METAL FINISHING

STUDIES ON POTENTIAL FOR IONISATION OF DIFFUSED HYDROGEN AT PALLADIUM/ALKALI INTERFACE

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ABSTRACT

In the potentiostatic charging technique for measurement of permeation current, an anodic potential is applied to the palladium coated side of the steel membrane, to ionise the permeated hydrogen. Different authors have applied different potentials ranging from +200 mV to -550 mV with respect to Hg/HgO electrode. In the studies on the exact range of potentials, two regions of plateau, both in the negative and positive regions were observed in the plotting of permeation current vs. applied potential. In situ cyclic voltammetric studies, carried out at palladium side of steel membrane, in 0.2 M NaOH solution, gave rise to two reproducible humps at -200 mV and -360 mV, indicating the exact range of potentials for the ionisation of permeated hydrogen. This observation was substantiated by measuring the actual quantum of ionisation at intervals of 25 mV, both in the negative and positive plateau regions. Cyclic voltammetric studies with pure palladium, steel and palladised steel in 0.2N NaOH solution are also found to support the finding that the region of -200 mV to -360 mV with respect to Hg/HgO electrode is the most suitable to be adopted for the efficient ionisation of diffused hydrogen in the permeation cell.

Key Words: Potential for ionisation, diffused hydrogen, permeation current, cyclic voltammetry

INTRODUCTION

In electroplating and metal finishing industry, the preparation of steel substrate, involves acid pickling as one of the common methods for the rust and scale removal prior to giving suitable finish to it. Obviously this creates a condition favourable for hydrogen entry into the metal, leading to hydrogen embrittlement and lowered ductility of the metal. Similarly, during electroplating, the substrate entraps hydrogen giving rise to hydrogen embrittlement.

In potentiostatic charging method [1] for measuring permeation current, one side of a thin steel membrane is cathodically polarised to charge the surface with hydrogen and its permeation rate is determined from the ionisation current on the reverse side, palladium coated side. To ionise hydrogen at palladium/0.2 N NaOH solution interface, different authors have applied different potentials, ranging from +200 to -550 mV with respect to Hg/HgO electrode. The present study makes an attempt to define clearly the range of potentials for the instantaneous ionisation of hydrogen at the palladium coated steel surface, using various techniques like in situ cyclic voltammetry, cyclic voltammetry and the permeation current measurement at different potentials.

EXPERIMENTAL

Materials and preparation

Mild steel specimens of thickness 0.4 mm, and of composition C = 0.063%., Mn = 0.23%, S = 0.03%., P = 0.011% were used for permeation studies as well as for cyclic voltammetric studies. Specimens of size 5cm x 2 cm were mechanically polished and degreased with trichlorethylene. These specimens prepared from cold rolled sheets were not given any heat treatment. G.R. grade sodium hydroxide and BDH grade palladium chloride were used. 0.2N NaOH solution prepared using conductivity water was preelectrolysed.

Measurement of permeation current

The cell used for electropermeation study was similar to one described earlier [1]. The glass cell has provision for circulating water. The cell has two arms and they are connected through teflon bushings, clamped between two stainless steel sheets, suitably held intact. The right arm of the permeation cell has two inlets, one for the platinum auxiliary electrode and the other for Hg/HgO/0.2 NaOH reference electrode. The left arm has provision for keeping a reference electrode of the same type. The palladised steel membrane is placed between teflon bushings and clamped tightly.

The steel membrane was made to function as a bipolar electrode in the cell. The anode side of the membrane was electroplated with a thin layer of palladium ('palladised') from a solution of palladium chloride (0.8 g/l) and NaOH (60 g/l) at a current density of 12 mA.cm^{-2} for 2 minutes at ambient temperature. Both the compartments of the cell were filled with preelectrolysed 0.2N NaOH solution. A constant cathode current density of 100 μA.cm^{-2} was impressed at the steel side of the membrane in the left arm of the cell. An anodic potential was applied to the palladium side. During cathodic charging, hydrogen ions are discharged and a small fraction of hydrogen atoms adsorbed on the membrane penetrated inside. On the arrival at the exit side of the membrane (i.e. palladium coated side) the hydrogen atoms are ionised by the applied potential. The hydrogen ionisation current was monitored on a recorder.

Cyclic voltammetric studies

A H-cell having a platinum counter electrode, Hg/HgO/0.2N NaOH reference and working electrodes of pure palladium, pure steel or palladised steel was used in the cyclic voltammetric study. Preelectrolysed 0.2N NaOH was the electrolyte. The potential range used was from +500 mV to -800 mV at a sweep rate of 1 mV/sec. This experiment was carried out both in the presence and absence of dissolved oxygen.

In situ cyclic voltammetric studies were also carried out using the electropermeation cell, described earlier. But in this study, as and when hydrogen permeated through the steel membrane and arrived at the palladium side, its ionisation was carried out by sweeping of the potential of the palladised side of the steel membrane, from +500 mV - 800 mV with respect to Hg/HgO/0.2N NaOH electrode at a sweep rate of 1 mV.sec.$^{-1}$ and 100 mV.sec.$^{-1}$ both in the presence and absence of dissolved oxygen.

RESULTS AND DISCUSSION

Potential for ionisation of diffused hydrogen

Table 1, gives values of potentials, used by different authors for the ionisation of hydrogen, permeated through the membrane. In general, potentials

Table I : Potential values reported by various authors for the ionisation of diffused hydrogen

Sl. No.	Reference	-E (mV) vs Hg/HgO/ 0.1 N or 0.2N NaOH
1.	M.A.V. Devanathan and Z. Stachurski [1]	-152 mV (0.2N NaOH)
2.	M.A.V. Devanathan Z. Stachurski and W. Beck [2]	-145 mV (0.2N NaOH)
3.	M.A.V. Devanathan and Z. Stachurski [3]	+353 mV (0.2N NaOH)
4.	R. Subramanian, S. Venkatesan and M.A.V. Devanathan [4]	-150 mV (0.2N NaOH)
5.	R. Subramanian [5]	+150 mV (0.2N NaOH)
6.	N. Subramanian, S.K. Rangarajan, K. Balakrishnan, S. Venkatakrishna Iyer, S. Venkatesan and B. Sathianandham [6]	-150 mV (0.2N NaOH)
7.	S. Venkatesan and S.K. Rangarajan [7]	not mentioned
8.	K. Balakrishnan and G. Devarajan [8]	+150 mV (0.2N NaOH)
9.	G. Devarajan [9]	+150 mV (0.2N NaOH)
10.	N.V. Parthasaradhy [10]	-150 mV
11.	N.J. Paul and H.V.K. Udupa [11]	
12.	N.J. Paul and S.K. Rangarajan [12]	Not mentioned
13.	N.J. Paul, H.V.K. Udupa and Prasannakumar [13]	Not mentioned
14.	T.K.G. Namboodiri and Leonard Nanis [14]	-84 mV to -234 mV(0.2N NaOH)
15.	T.K.G. Namboodiri [15]	-84 mV to -234 mV (o.2N NaoH)
16.	H.O.'M. Bockris, M.A.Genshaw, and P.K. Subramanian [16]	-550 mV (0.1N NaOH)
17.	P.K. Subramanian [17]	-452 mV (0.1N NaOH)
18.	M. Veerashanmughamani and P.L. Joseph [18]	+210 mV (0.1N NaOH)
19.	T. P. Radhakrishnan and B.S. Chaudhari [19]	-300 mV (0.1N NaOH)
20.	A.E. Yaniv, T.P. Radhakrishnan and L.L. Shreir [20]	-300 mV (0.1N NaOH)
21.	T.P. Radhakrishanan and L.L. Shreir [21]	-158 mV (0.1N NaOH)
22.	R.F. Bhundy and L.L. Shreir [22]	+254 mV (0.1N NaOH)

ranging from +200 mV to — 500 mV with respect to Hg/HgO electrode have been reported [2-22] . It is seen that there is uncertainty with regard to the selection of anodic potential, applied for causing the ionisation of permeated hydrogen.

Potentiostatic ionisation of hydrogen

A plot of permeation current vs potential is shown in Fig.1, which shows a plateau region between —200 mV to —400 mV, with respect to Hg/HgO/0.2N NaOH electrode, when the potential of the palladium/0.2 N NaOH solution interface is changed from —100 mV to —600 mV. The
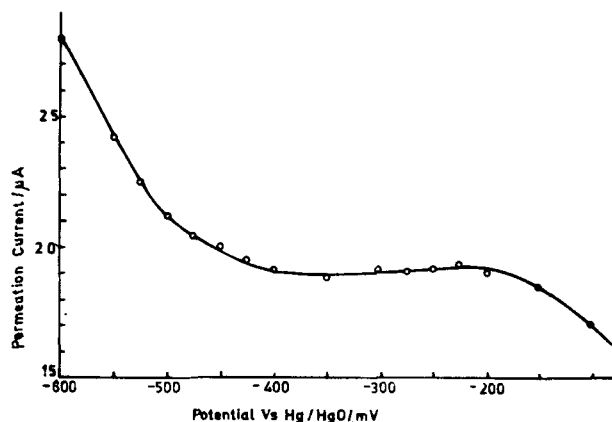

Fig.1. A plot of permeation current vs potential, for potentials ranging from —100 to —600 mV.

current for ionisation of hydrogen is independent of potential in this plateau region. A similar plateau in the range of +250 mV to +500 mV was observed when the experiments were carried out in the region from +100 mV to +700 mV.
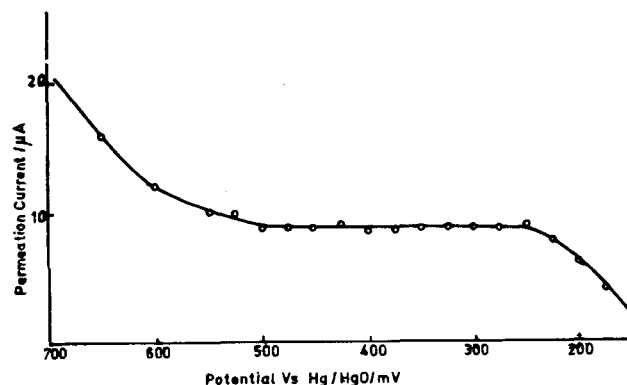

Fig. 2. A plot of permeation current vs potential, for potentials ranging from +100 to +700 mV

The choice between the two plateau regions has to be made on the basis of quantum of diffused hydrogen. This can be done by choosing the plateau which gives maximum quantum of ionisation of diffused hydrogen.

Table 2, gives quantum of ionisation expressed in microcoulombs for a fixed duration of 5 minutes, at two ranges of potential, i.e. (i) -200 mV to -400 mV and (ii) +250 mV to +500 mV with respect to Hg/HgO electrode. It is found that ionisation current is almost the same in the positive

Table 2 : Quantum of hydrogen ionisation at different potentials

Positive plateau region		Negative plateau region	
Potential (mV) vs Hg/HgO	Microcoulombs	Potential (mV) vs Hg/HgO	Microcoulombs
+ 250	356.8	—200	2640
+ 300	204.0	—225	489
+ 325	139.2	—250	448
+ 350	208.8	—275	448
+ 375	168.0	—300	1128
+ 400	216.0	—325	96
+ 425	252.0	—350	82
+ 450	312.0	—375	77
+ 475	204.0	—400	76
+ 500	384.0		

plateau region, whereas in the negative plateau region maximum quantum of ionisation takes place in the potential region between -200 mV and -300 mV. So on this basis, the region of potentials between -200 mV and -400 mV can be chosen for the permeation current measurements. The plateau obtained in the positive region may be due to some other reactions like chemisorption of oxygen or oxide formation over palladium and definitely not due to ionisation of hydrogen.

'In situ' cyclic voltammetric studies

Fig.3 and Fig.4 depict the 'in situ' cyclic voltammograms of Pd/0.2 N NaOH in the presence of dissolved oxygen and in the absence of dissolved oxygen.
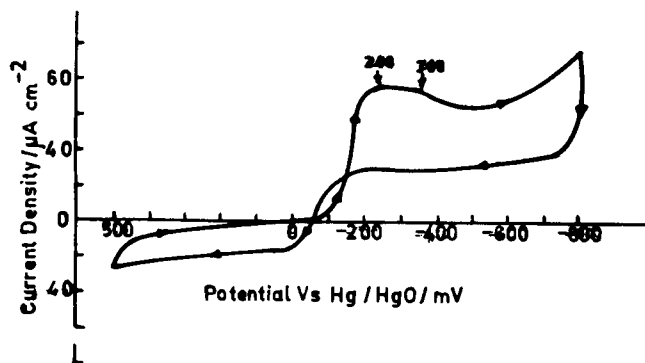

Fig. 3. In situ cyclic voltammogram for the system Pd/0.2 N NaOH in the presence of dissolved oxygen at a scan rate of 1 mV sec⁻¹
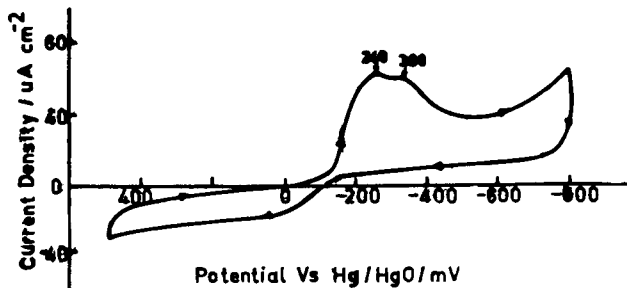

Fig. 4. In situ cyclic voltammogram for the system Pd/0.2 N NaOH in the absence of dissolved oxygen at a scan rate of 1 mV sec⁻¹.

Two humps are noticed in the curve, during the forward scan both in the presence and absence of dissolved oxygen, at the same potentials. By increasing the scan rate, in the presence of dissolved oxygen a new curve (Fig. 5) is obtained, where the forward and backward voltammograms do not cross each other, as in Fig.3. Yet the two humps in the forward cyclic voltammogram occur almost at the same potentials, namely, -260 mV and -350 mV (as in Fig.3).
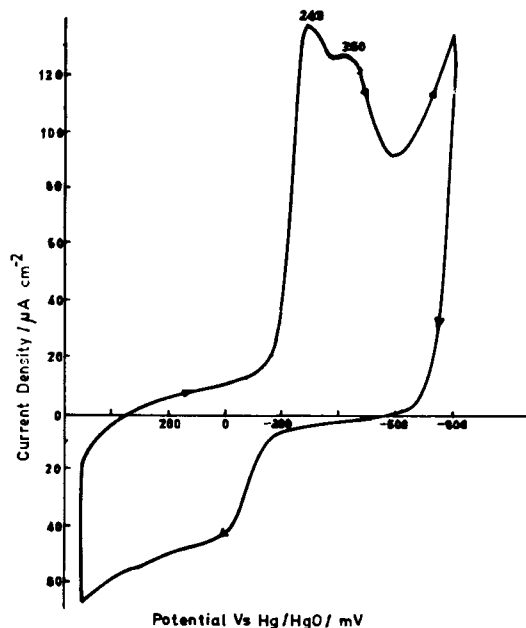

Fig. 5. In situ cyclic voltammogram for the system Pd/0.2 N NaOH in the presence of dissolved oxygen at a scan rate of 10 mV/sec⁻¹.

Fig.6, gives the voltammogram of the system Pd/0.2 N NaOH in the absence of dissolved oxygen at the enhanced scan rate, namely, 10 mV/sec and here too the two humps occur almost at the same potential values as in Figures 3, 4 and 5. The two humps indicate higher currents in the presence
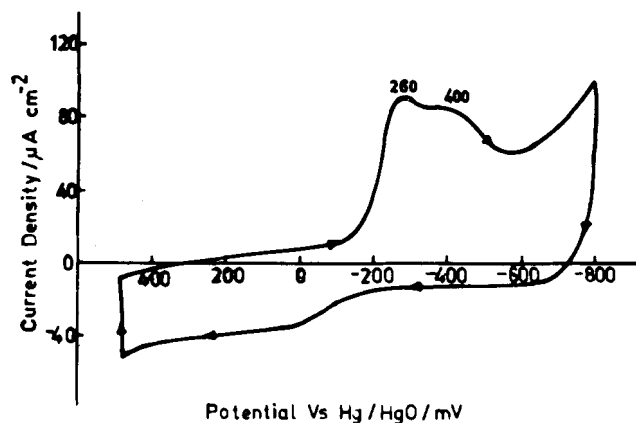
Fig. 6. In situ cyclic voltammogram for the system Pd/0.2N NaOH in the presence of dissolved oxygen at a scan rate of 10mV sec^{-1}.

of oxygen, than in its absence at both the scan rates of 1 mV sec^{-1} and 10 mV sec^{-1}. All these voltammograms clearly bring out the fact that humps obtained both in the presence and absence of oxygen are not oxygen reduction peaks. Moreover, the constancy of their respective potential values, clearly indicates that some characteristic electrochemical reactions, other than the reduction of oxygen are occurring at these fixed potentials. The potentials at which humps occur, may probably represent the onset and end of the ionisation of diffused hydrogen, thereby forming the boundaries for the region of hydrogen ionisation, namely, —250 to —350 mV. Incidentally, this region falls within the plateau region obtained during the potentiostatic ionisation experiments (Fig.1) on the negative side, namely, —200 mV to —400 mV and also coincides to a large extent with the region of potentials where high quantum of hydrogen ionisation is obtained. Further the values of potential corresponding to the humps are independent of the presence and absence of dissolved oxygen. All these observations clearly show that the potentials corresponding to the two humps (i.e. —240 mV and —340 mV) represent the region of ionisation of hydrogen. Moreover, the backward scan does not give rise to any peak, indicating the absence of oxidation of any reduced species, obtained during the forward scan. The hydrogen ionisation reaction (i.e. H ⟶ H$^+$ + e) at the palladium/NaOH solution interface, takes place at a potential anodic, to the equilibrium potential of NHE in 0.2 M NaOH i.e. —1.020 V vs SCE [23]. So hydrogen can be ionised at any potential anodic to —1.020 V vs SCE at the Pd/0.2N NaOH interface.

Cyclic voltammetric studies

To explain the formation of a plateau region in the positive region between + 250 mV to + 500 mV, cyclic voltammetric behaviour of pure palladium membrane, steel membrane, and 'palladised' steel membrane in 0.2N NaOH have been studied.

Fig.7 gives the cyclic voltammogram of pure palladium foil in 0.2N NaOH in the absence of oxygen at a scan rate of 1 mV sec^{-1} with the potential being swept from + 500 mV to —800 mV with respect to Hg/HgO. A well
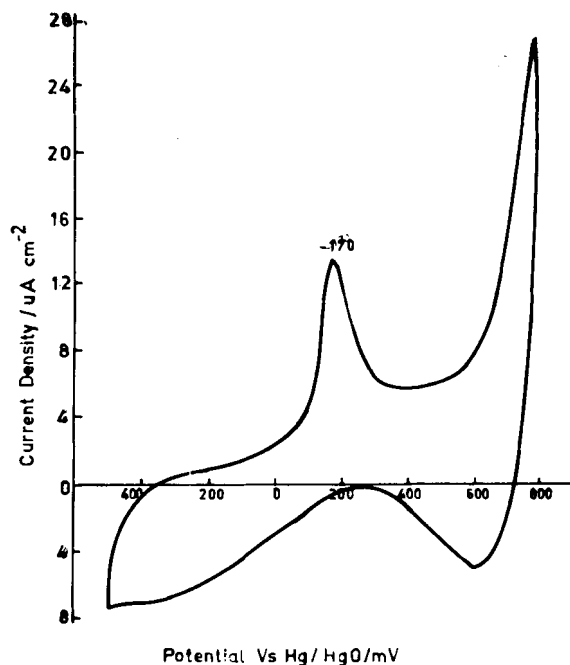

Fig. 7. Cyclic voltammogram of pure palladium foil in 0.2N NaOH, in the absence of dissolved oxygen at a scan rate of 1 mV sec^{-1} and at potentials ranging from + 500 to - 800 mV.

defined peak is observed at -170 mV in the forward scan and a hump at -600 mV in the reverse scan, which may be due to adsorption of hydrogen and reduction of adsorbed OH$^-$ ions respectively

Fig.8 gives the cyclic voltammogram, of pure mild steel in 0.2N NaOH in the absence of dissolved oxygen. A well defined peak is observed at a

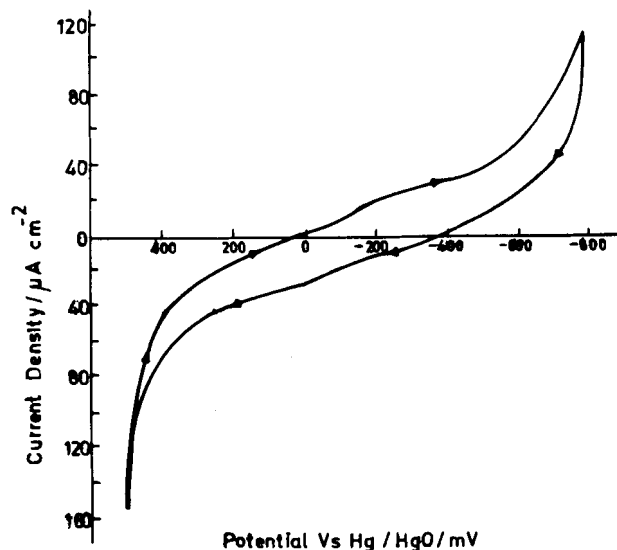Fig. 8. Cyclic voltammogram for pure mild steel in 0.2N NaOH in the absence of dissolved oxygen at a scan rate of 1 mV sec^{-1} and for potentials ranging from + 500 to - 800 mV

potential of + 400 mV with respect to Hg/HgO. According to potential pH diagram [24] the potential of iron is in the corrosion domain in the absence of dissolved oxygen at pH above 12.5. It means that iron corrodes with the evolution of hydrogen and dissolves at a higher valency state to form ferrate ions. The pH of 0.2N NaOH is 13.1 and the peak obtained may be attributed to the transpassive dissolution of mild steel.

Fig.9 shows the cyclic voltammetric behaviour of the 'palladised' phase of the 'palladised' steel in 0.2N NaOH, in the absence of dissolved oxygen. As in the case of forward scan of 'in situ' studies, two humps are observed at almost the same potentials of - 200 mV and - 360 mV in this case also. These potentials as before may represent the region of hydrogen ionisation. In the reverse scan, a hump is observed at a potential of - 300 mV, which may be attributed to the ionisation of residual hydrogen. It was also observed that during subsequent cycles, the depth of this hump decreases with number of cycles.

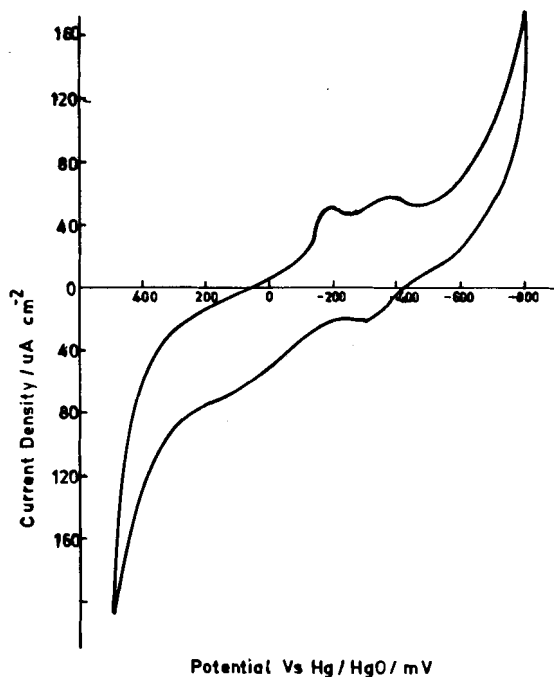**Potential Vs Hg / HgO / mV**

Fig. 9. Cyclic voltammogram of palladium phase of 'palladised' steel in 0.2N NaOH in the absence of dissolved oxygen and for potentials ranging from + 500 to - 800 mV

Fig.10, gives the cyclic voltammogram of palladium phase of the 'palladised' steel in 0.2N NaOH in the presence of dissolved oxygen, which is quite similar in shape to that in the absence of dissolved oxygen. Humps were found to occur in both the cases at the same potentials, both in the forward and reverse scans. These observations clearly point out to the fact that oxygen has practically no part to play in the cyclic voltammetric behaviour of the palladium phase of 'palladised' steel in 0.2N NaOH. The cyclic voltammograms obtained by the 'in situ' method and in the usual way are quite similar, except for the fact that normal cyclic voltammogram has an additional hump of - 300 mV in the reverse scan.

The following reactions are said to take place at positive regions of potentials [23]

i) Pd $\longrightarrow$ Pd$_2$O at + 0.15 V w.r. t. NHE
ii) Pd $\longrightarrow$ Pd$_2$O at + 0.95 V "
iii) Pd $\longrightarrow$ PdO$_3$ at + 1.22 V "
iv) Pd $\longrightarrow$ PdO$_3$ $\longrightarrow$ PdO$_2$ + O$_2$
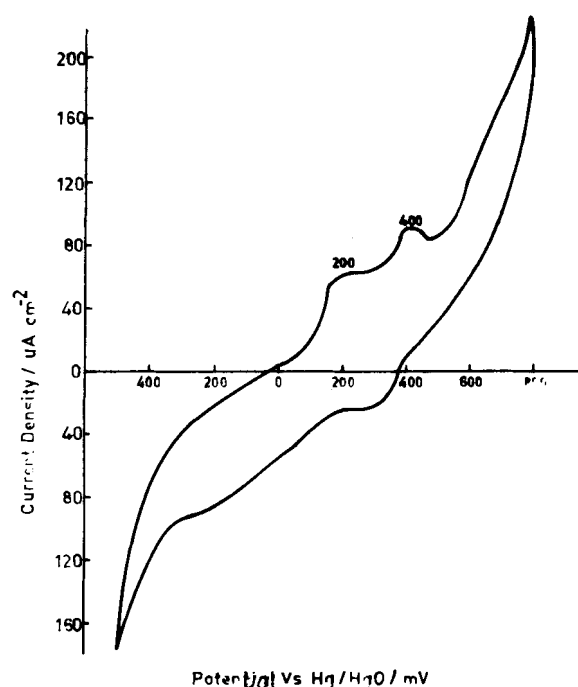   (unstable)

Potential Vs Hg / HgO / mV

Fig. 10. Cyclic voltammogram of palladium phase of 'palladised' steel in 0.2N NaOH in the presence of dissolved oxygen and for potentials ranging from + 500 to - 800 mV

So the formation of oxide over palladium takes place in 0.2N NaOH even at + 0.038 V vs Hg/HgO (i.e. 0.15 V vs NHE). Hence the plateau observed between + 250 mV and + 500 mV over palladium of the 'palladised' steel in 0.2N NaOH during the potentiostatic ionisation experiments is only due to the formation of PdO$_2$. The formation and removal of monolayer of oxide films on palladium under cyclic voltammetric conditions was discussed recently by several authors [25-27] . So the possibility of ionisation of hydrogen in the positive regions of plateau can be ruled out.

CONCLUSIONS

i) Two plateau regions namely (a) 200 mV to - 400 mVs and (b) + 250 mV to + 500 mV with respect to Hg/HgO are obtained, when permeation current is plotted against potential, during potentiostatic ionisation studies at the palladium/0.2N NaOH interface.

ii) The plateau between - 200 mV to - 400 mV with respect to Hg/HgO represents the region of ionisation of diffused hydrogen. At the positive regions of plateau, only oxide formation is possible and not the ionisation of diffused hydrogen. Higher quantum of ionisation of diffused hydrogen is found to occur only in the region - 200 mV to - 400 mV at Pd/0.2N NaOH interface. So a potential of - 300 mV, which corresponds to the midpoint of the plateau is the most suitable potential for ionising the diffused hydrogen, rapidly and efficiently at Pd/0.2N NaOH interface.

iii) Both 'in situ' and normal cyclic voltammetric experiments of Pd/0.2N NaOH interface of the 'palladised steel', give rise to two characteristic humps at - 200 mV and - 350 mV, which may be taken as the onset and ending of ionisation of diffused hydrogen.

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