POTENTIODYNAMIC INVESTIGATION OF REDUCTION OF OXIDE LAYER AT PLATINUM AND PALLADIUM ELECTRODES

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Hydrogen could avidly and spontaneously chemisorb dissociatively on platinum group electrodes <1>. The atomic hydrogen chemisorbed could be oxidised either galvanostatically <1-5> or potentiodynamically <2,6,7>. Anodic galvanostatic oxidation of the chemisorbed hydrogen present on the platinum electrode would give the following three specific regions

1) The hydrogen region (about 0 to 350 mV wrt Reversible Hydrogen Electrode,RHE)
2) The double layer region (about 350 mV to 800 mV wrt RHE)
3) The oxygen region (> 800 mV wrt RHE).

Potentiodynamically various information regarding the nature of the hydrogen chemisorption, oxide layer formation, the reduction of the oxide layer and the cathodic deposition of hydrogen could be arrived at very rapidly and in the self same run.

A typical transient obtained with platinum electrode in 0.5 M H_2SO_4 solution is presented in the Fig 1 (a), wherein the three specific regions are also demarcated Oxide layer formed upto about 1.2 V began to get reduced during the cathodic cycle at about 0.8 V wrt RHE at a platinum electrode. The cathodic peak height was found to increase linearly with temperature at constant sweep rate. The peak area in the $i-\psi_r$ plot would furnish the amount of reaction. To a first approximation, the peak heights were found to be directly proportional to the peak area. Hence the peak height would be expected to be proportional to the reaction rate. This suggested that the Arrhenius plots could be constructed for the oxide reduction reactions by constructing the plots of logaritms of peak heights obtained from the transients as a function of temperature. The results of such a study made with platinum and palladium electrodes are presented in this communication.

METHODS AND MATERIALS

A three-compartment cell with about 250 ml working electrode compartment was used in the current study. Palladised-palladium electrode was used as the reference, while the working electrode was either a smooth platinum or palladium electrode. A platinised-platinum electrode was used as a counter electrode. It was found in these experiments at 26° C that the palladised-palladium electrode was anodic by 90 mV wrt RHE in 0.5 M H_2SO_4. Either preelectrolysed 0.5 M H_2SO_4 or prelectrolysed 1 M NaOH was used as the supporting electrolyte. The temperature of working electrode compartment was controlled to ±0.5 C by circulating preconditioned water in the external jacket of the cell.

The electronic set up used for the potentiodynamic investigation consisted of a Hewlett Packard low frequency function generator (Type 202A), a home made potentiostat, a Tektronix Oscilloscope (Type 531A) fitted with a Tektronix camera and a decade resistance box (General Radio Company). This resistance box helped in accurate current measurement. The potentiodynamic transients were obtained at 3 cps. At each one of the selected temperatures, a period of 60 minutes were allowed to efflux towards the attainment of the temperature equilibration. Since a home made potentiostat was also incorporated in the circuit, an attempt was made to check up the reproducibility as well as reliability of the results. This was carried out in the following three ways:

1) The transients were photographed consecutively on the same photo film. The departure noticed between two consecutive transients was ⩽ 5%

2) Since a palladised-palladium reference electrode had been used, the first partial hydrogen oxidation peak (out of the 3 low temperature peaks) noticeable at 26° C in the hydrogen region of the platinum electrode should disappear at elevated temperature. (This is anticipated because the potential of + 90 mV wrt RHE drifted anodically to higher potentials as the temperature of the system was increased<3>. As expected the first hydrogen peak virtually disappered at 80° C (compare Fig. 1a with Id.

3) With a Wenkin potentiostat identical results were registered.

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RESULTS AND DISCUSSIONS

The oscilloscopic traces registered for platinum electrode in 0.5 M H_2SO_4 at 4 selected temperatures are presented in Fig. 1. It is evident from this figure that the peak height for cathodic oxide reduction at platinum electrode increased linearly with increasing temperatures. The results obtained in a similar study made with palladium electrode is also furnished in the Table 1. The dependence of the peak height on the reciprocal temperature is presented in the Fig. 2

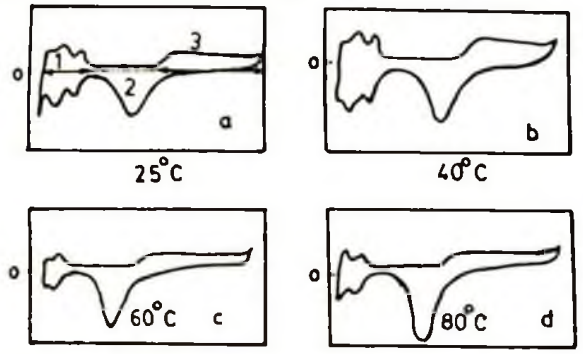


Fig.1 Potentiodynamic transients at smooth platinum electrode in 0.5 M H_2SO_4 at (a) 26° C (b) 40° C (c) 60° C (d) 80° C Y axis (current) X axis time or emf.

TABLE 1
ENERGY OF ACTIVATION

Electrode	Electrolyte	Ea Kcal/mol	Remarks
Pt	H_2SO_4	3.09	-
Pt	NaOH	5.01	-
Pt	NaOH	3.95	(with CH_2O film)
Pd	H_2SO_4	2.78	-
Pd	NaOH	1.50	-

The energy of activation, Ea, for the oxide reduction noticed with NaOH and H_2SO_4 solutions are presented in the Table 1. It becomes apparent from the table that the Ea values observed are very small viz. 1.5 to 5.01 Kcal/mole Such a low value would be indeed anticipated for the spontaneous catalytic reaction like dissociative chemisorption of hydrogen. Elsewhere also such low values were recorded by Sidheswaran when the Temkin model for the oxidation of hydrogen chemisorbed was considered <7>.

The Ea values for platinum was found to be slightly larger than that of palladium. A slightly lowered Ea value for pd is understandable in view of the existence of some intertitial hydrogen in the matrix of the electrode. Even in the presence of chemisorbed organic, the Ea noticed was about 4 Kcal/mole, sugesting the apparent insignificant influence of the chemisorbed organic compound on the oxide reduction reactions. However, it should be remembered that the water discharge on the chemisorbed organic had been identified to be the slow step in the case of oxidative cleavage of the chemisorbed radical.

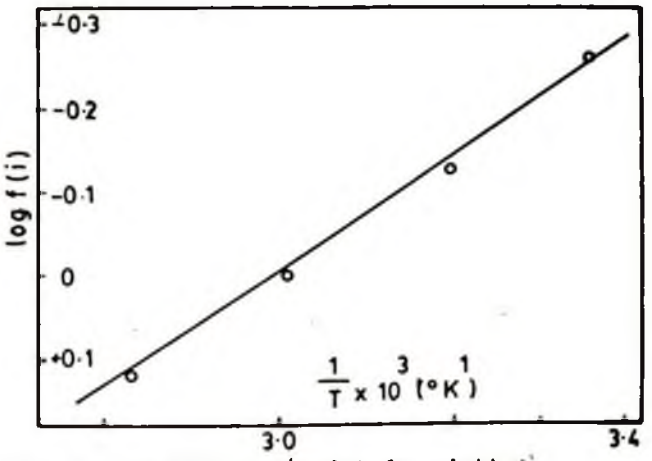


Fig. 2 log f(i) vs 1/T plot for platinum electrode and palladium electrode.

REFERENCES

1. B.B. Damaskin, O.A. Petril, and V.V. Batrakov, *Adsorpion of organic compounds on electrodes* (Plenum Press, New York), 1971.

2. V.N. Kamath, *A study of intermediates absorbed on platinum electrodes from methanol, formic acid and carbon dioxide solutions'* Ph.D. thesis, Indian Institute of Technology, Bombay (1968).

3. P. Sidheswaran, *Anodic oxidation of chemisorbed formaldehyde and related studies* Ph. D.thesis, Indian Institute of Technology, Bombay, 1971.

4. V.N. Kamath and Hira Lal, *J. Electroanal Chem* , 19 (1968) 137; 249.

5. P. Sidheswaran and Hira Lal, *Electroanal. Chem.*, 34 (1972) 173.

6. M.V.Breiter, *Electrochemical Process in Fuel Cells'* (Springer-Verlag Inc New York) 1969.

7. P. Sidheswaran,' *J. Scientific and Ind Res.*, 33 (1974) 240.