A new method of Fabricating Flexible Polymer Electrode and its application to Hydrogen Evolution Reaction

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A flexible polymer electrode has been fabricated using silver epoxy coated PVC sheet coated with thin layer of conducting polypyrrole. This electrode is extremely light and shows better performance for hydrogen evolution reaction as compared to bare silver electrode. Thus this may have potential application in fuel cells for Space Craft.

In the recent years increasing attention has been focused on electrocatalytic studies of conducting polymer coated modified electrodes [1-5]. These electrodes are easily fabricated using low cost materials and simple techniques.

So far, the studies on modified electrodes are mainly confined to electrodes where polymer are deposited electrochemically either on a metal or graphite substrate [6-9]. We have recently reported [10] fabrication of polymer coated modified electrodes on flexible plastic support painted with a thin film of suitable metallic paint like silver paint. We have also studied [10] the behaviour of these electrodes towards oxygen reduction reaction (ORR) in alkaline medium. We are reporting here another such electrode where flexible PVC sheet coated with silver paint is further modified by a thin layer of electrodeposited polypyrrole and applied to hydrogen evolution reaction (HER).

Admittedly, polypyrrole coated semiconductor and other electrodes have been studied earlier [11] for hydrogen evolution reaction and very recently polypyrrole coated modified electrodes have been studied for oxygen reduction reaction [12]. The primary objective of the present research is not to emphasis on mechanistic aspects of HER on modified electrodes but to develop new method of fabrication of such electrodes on light flexible support so that the latter may have an application in fuel cells for space craft [13].

EXPERIMENTAL

A PVC sheet of appropriate size (1 cm^2) (from sheet used for separator in Exide lead acid battery, thickness 0.5 mm) with a connector strip was covered with a thin layer of conducting silver epoxy (Ted Pella, USA) using an applicator. Only front side of this electrode is conducting and the other side is nonconducting.

The surface of the silver coated PVC electrode was further modified by forming a very thin layer of conducting polypyrrole by electropolymerisation technique using pictrate ion as doppant.

Electrolytic solution was prepared by dissolving 1 ml pyrrole (Merck, Germany) in 200 ml saturated solution of pictric acid (Glaxo, UK) in aqueous DMF (10% v/v). (DMF was distilled as that of DMSO [14]). 20 ml of this solution was taken in one

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compartment cell where Ag coaed PVC sheet (1 cm^2) was used as anode. The counter electode was a Pt wire and saturated calomel electrode (SCE) was the reference. Electrolysis was carried out for different periods (50 sec. 150 sec.) so as to get different thickness of deposited polymer. After polymerisation, the polymer electrodes were washed repeatedly with distilled water and kept in deareated distilled water for few days.

Electrochemical parameaters for HER had been studied on the pure Ag electrode, Ag coated flexible polymer electrode and conducting polymer coated modified electrodes in 1 N H_2SO_4 solution. Tafel studies was made with a sweep rate of 0.5 $mV.s^{-1}$ in the potential range -300mV to + 300mV using three electrodes and a computerised potentiostat galvanostat (Vibrant model VCS-30) coupled with interface and data acquisation software.

RESULTS AND DISCUSSION

The fabricated electrodes are chemically stable when dipped in deareated distilled water and also stable in H_2SO_4 medium (upto 1M). The film conductivity was found to be 5-20 $S.cm^{-1}$. Though cyclic voltammetric studies using those electrodes at different scan rate exhibit some noise peaks - particularly with polymer coated electodes - the prominant cathodic and anodic peaks can be identified and typical results are shown in Table 1.

Interesting enough, while cathodic peaks for metallic silver and silver-expoxy electrodes are in the same position, those for polypyrrole coated electrodes are shifted to higher negative direction (independent of thickness). This may simply be due to the shifting of equilibrium potential in the cathodic direction with modified electodes. Plot of E_p vs log n (plot not shown) shows

Table 1

Electrochemical Parameters for HER in 1 M Sulphuric acid Medium

scan rate 40 $mV.s^{-1}$

Parameter	Ag	Ag Epoxy on PVC	PVC-Ag-PPY	
			50 sec	150 sec
E_p (mV)	219	219	259	259
i_p (mA)	1.9	0.6	5.6	2.5
Tafel slope (mV/dec)	125	125	38	61
Transfer Coeff. α	0.5	0.5	1.5	1
$(k_s)_{app} \times 10^3$ (cm/sec)	3.7	3.7	6.9	5.6
$i_o \times 10^4$ ($A.cm^{-2}$) at $E = E_o$	0.4	1.2	6.9	7.5*
$i \times 10^4$ ($A.cm^{-2}$) at η = 100 mV	0.8	2.1	5.8	6.7*

*Parameters derived from linear Polarization; Apparent area of the electrode = 1 cm^2

* i_o on Ag = 1.25×10^{-6} [19] 3×10^{-6} [20]

quasi-reversible nature of HER on all these electrodes.

For quasireversible system, the apparent rate constant can be calculated using the following equation [15].

$$\log k_s = 0.52 - 1/2 \log \frac{b}{D} + 1/2 \log v_c - 1.1 \frac{RT}{bnF} \quad ...(1)$$

where b= Tafel slope. The critical scan rate (n_c) is obtained from the intersections of the linear plots of E_p vs log at slow and high sweep rate region [15]. The value of diffusion coefficient (D) of the reductant (H_3O^+) is taken from literature [16].

Apparent rate constant values are shown in Table 1. The apparent rate constants are very important parameters for practical uses, because rapid evolution of hydrogen can be achieved on such electrodes compared to the unmodified electrodes. This may be due to the increase in active surface area of the modified electrodes.

Mechanistic aspects of HER on different metal surfaces in different media had been studied exhaustively [17].

The transfer coefficient values suggest that the mechanism of HER of Ag and Ag-epoxy coated electrodes differ from that of polymer coated modified electrodes. In polmer the desolvation process is accelerated and thus accelarates discharge and desorption process.

The apparent exchange current values and exchange current at overvoltage 100 mV obtained from linear polarisation are shown in Table 1. These values are coroborating well with the predicted trends of these electrodes towards HER.

The behaviour of light deposited (50 sec) and thick deposited (150 sec) polymer electodes are also very interesting. It is seen that catalytic activity gradually drops down for thick deposited polymer electrode. Similar behaviour of catalytic activity of modified electrodes has also been noted earlier [18] and explained in terms of decrease in transport of both electrons and subtrate through the thick film.

Thus, the present result suggests that the catalytic activity of this extremly light and flexible Ag electrode towards HER is further enhanced by modification of the electrode through thin conducting polypyrrole layer but this gradually decreases with increasing thickness of the polymer film. Potential application of such electodes in hydrogen generation seems to be promising.

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