

PERFORMANCE EVALUATION OF PLATINUM CATALYSED HYDROGEN GAS DIFFUSION ELECTRODES FOR ALKALINE FUEL CELLS

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The porous hydrogen gas diffusion electrodes employ skeletal nickel as catalyst. They show a potential of -800 mV vs Hg/HgO at a c. d. of 30-35 mA. cm⁻². In order to improve their performance platinum is incorporated in the matrix in different quantities ranging from 0.5 to 2.0 mg. cm⁻². The electrochemical behaviour of these electrodes are compared with the method of deposition of platinum. Current densities greater than 50 mA. cm⁻² were achieved and the optimum of platinum catalyst is reported.

Key words: Gas diffusion electrodes, three layer electrodes, alkaline fuel cells, platinum supported catalysts, skeleton nickel matrix

INTRODUCTION

Hydrogen electrodes form one of the essential components of hydrogen-oxygen/air acidic or alkaline fuel cells. Conveniently, porous carbon gas diffusion electrodes containing platinum as electrocatalyst have been employed in these fuel cells [1,2]. They are reported to withstand load currents up to 200 mA. cm⁻². Search for replacement of platinised carbon electrodes has met with considerable success. Among these Raney nickel hydrogen anodes for alkaline systems are worth mentioning [3,4]. These hydrogen electrodes have highly dispersed, high surface area Raney nickel. Though the carbon electrodes can be made as thin as possible, the Raney nickel electrodes had considerable thickness.

A variety of promoter elements to enhance the activity of Raney nickel catalyst have been reported [5], of which 2% titanium has been reported to give maximum activity [4]. Addition of titanium and molybdenum has also been studied [6]. Though the operating life of the electrodes was considerably improved, the long-term performance could not be realised. Further the comparative performance of these electrodes with noble metal catalysed porous sintered nickel electrodes has not been reported.

In this communication the studies conducted on porous gas diffusion electrodes containing sintered nickel as the matrix and platinum as the promoter element to the Raney nickel are reported.

EXPERIMENTAL

Preparation of the skeletal nickel catalyst

The skeletal nickel catalyst was prepared from the Raney nickel (BDH nickel-aluminium alloy 50:50) by the method described elsewhere [7].

Preparation of gas diffusion electrodes

Two layer and three layer gas diffusion electrodes were prepared [8]. The electrode thickness was 1.5 mm of which the supporting layer had a thickness of 0.6 mm and the catalyst layer 0.9-1.0 mm. The geometric area of the electrode was 30 cm².

Catalyst incorporation

Two types of incorporation of the catalyst have been studied. In the post-catalysation technique, the platinum was incorporated in the sintered electrode matrix by the following procedures. In method (a), an aqueous solution of platinum (1% solution of H₂PtCl₆) was dispersed on both layers of the gas diffusion electrodes and air dried. The electrodes were catalysed by repeated paintings with platinum salt solution and then dried at 393K in hydrogen atmosphere for one hour. The catalyst loading was adjusted in the range 2-4 mg. cm⁻².

In method (b), the platinum salt was dissolved in isopropyl alcohol and the electrode was painted with the solution and air dried. The electrode was then immersed in a solution of isopropyl alcohol containing sodium borohydride. The duration of the reduction was varied between 30 minutes and one hour until the gas evolution was complete. The electrodes were washed in the same solution and dried in hydrogen atmosphere as before.

The precatalysation procedure was adopted for depositing platinum on nickel powder, skeletal nickel and activated charcoal and then making the gas diffusion electrodes as per procedure given above. The technique employed usually for the platinisation of carbon black for use in acid fuel cells [9] was followed. After incorporating the platinum into the catalyst powders, they were dried and heat treated in hydrogen atmosphere at 373K for 2 hours. The platinum catalyst loading was 2 mg.g⁻¹ of powder.

Characterisation of electrodes and the electrocatalysts

The pore volume and pore size distribution of the electrodes were obtained from the mercury penetration porosimeter. The internal surface area of the pores was calculated by processing the data as reported earlier [10]. The surface area of the catalyst was measured by nitrogen adsorption technique. The porosity of the electrodes was determined by liquid absorption technique using dioxan as the medium. The thickness of the various reaction layers was found to be uniform as determined through the microscope. The presence of platinum in the various layers was confirmed by electron microprobe analysis in SEM.

Electrochemical measurements

The electrochemical testing assembly has been described previously [11]. The electrolyte used was 6.0 M KOH. A Hg/HgO reference electrode was employed and the potentials are referred to this reference electrode. Each experiment was repeated with different electrodes of the same type. The steady state galvanostatic polarisation data were recorded at 303, 333, and 353K. All tests are reported at a gas pressure of 1.0 kg. cm⁻².

RESULTS AND DISCUSSION

The characteristics of the electrocatalysts and electrodes are reported in Table I (A) and I (B). Electrodes 1 to 10 employ skeletal

TABLE-I(A): Characteristics of the hydrogen electrodes

Supporting layer	: Carbonyl nickel 255 powder
Catalyst layer	: 255 nickel + catalyst
Catalyst (electrodes 1-10)	: Skeletal nickel
Amount	: 150 mg. cm ⁻²
Electrode 11-13	: Activated charcoal (heat treated in NH ₃ at 1273K for 100 hrs)
Amount	: 38mg. cm ⁻²

TABLE-I (B): Amount of noble metal promoter in the electrodes

Electrode No.	Promoter metal employed	Supporting layer		Catalyst layer		Method of incorporation
		(mg. g ⁻¹)	(mg. cm ⁻²)	(mg. g ⁻¹)	(mg. cm ⁻²)	
1	--	--	--	--	--	--
2	Pt	0.5	0.5	1.0	1.0	a
3	Pt	1.0	1.0	1.0	1.0	a
4	Pt	-	-	2.0	2.0	c
5	Pt	1.0	1.0	1.0	0.5	c
6	Pt	1.0	1.0	2.0	1.0	c
7	Pt	1.0	1.0	1.0	1.0	b
8	Pt	1.0	1.0	2.0	2.0	b
9	Pd	1.0	1.0	1.0	1.0	a
10	Pt + Pd	1.0	1.0	2.0	2.0	a
11	Pt	2.0	2.0	--	--	c
12	Pt	--	--	1.0	0.5	c
13	Pt	1.0	1.0	1.0	0.5	c

nickel obtained from Raney nickel and 11 to 13 employ activated charcoal as electrocatalysts. The activated charcoal has been activated by heat treatment in ammonia and carbon dioxide atmospheres at 1273K for 100 hours [12].

Figs. 1 (a,b,c,d) show the scanning electron micrographs of microtone cut of the hydrogen electrode. Fig.1(a) shows the cross

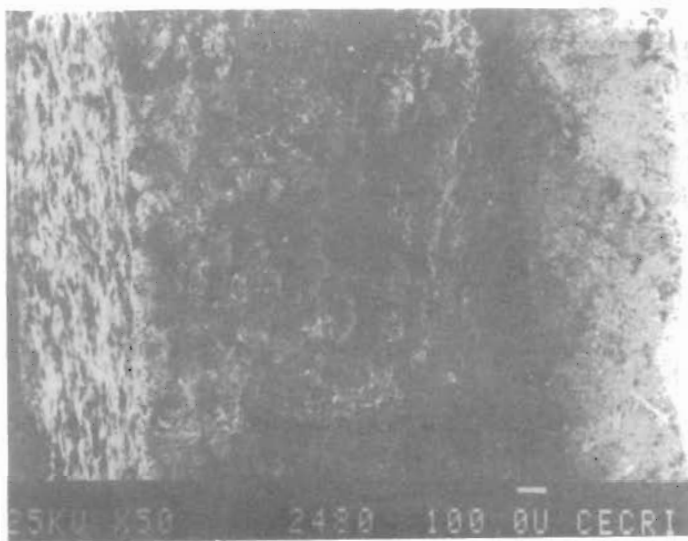


Fig. 1 (a): SE micrograph of the cross section of the three layer hydrogen gas diffusion electrodes

section of the electrode and junction of the layers. It can be seen that the layers have fairly uniform thickness and are well united with each other. Figs. 1 (b) and 1(c) are the micrographs corresponding to the catalyst layer and gas supporting layer respectively. The pores are fairly uniform in size and the catalyst particles are well mixed with supporting nickel matrix. Fig. 1 (d) shows the pore structure of the nickel matrix catalysed with platinum.

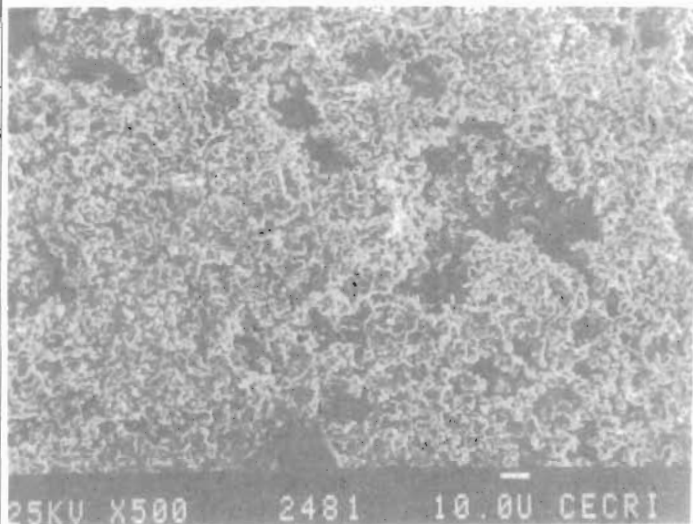


Fig. 1 (b): SE micrograph of the catalyst distribution layer

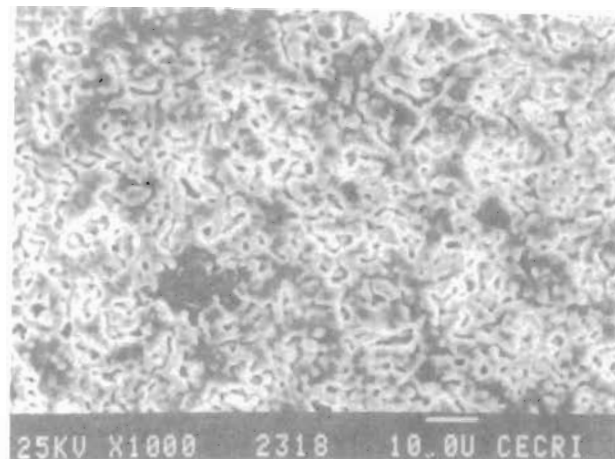


Fig. 1 (d): SE micrograph of the nickel matrix after Pt incorporation

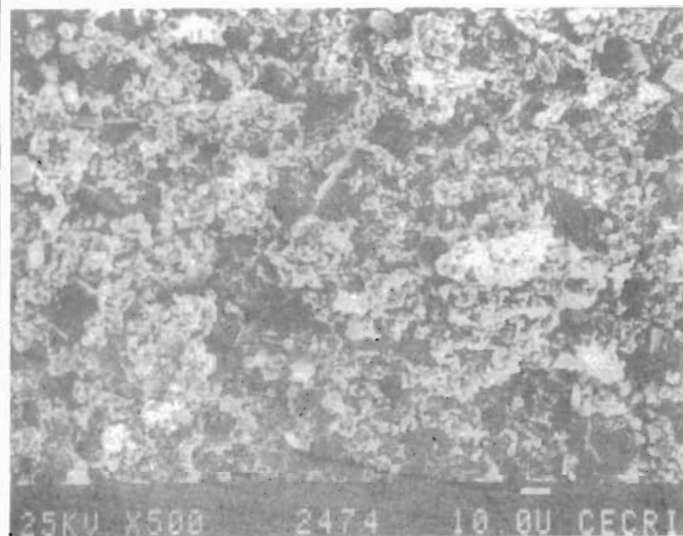


Fig. 1 (c): SE micrograph of the gas supplying layer

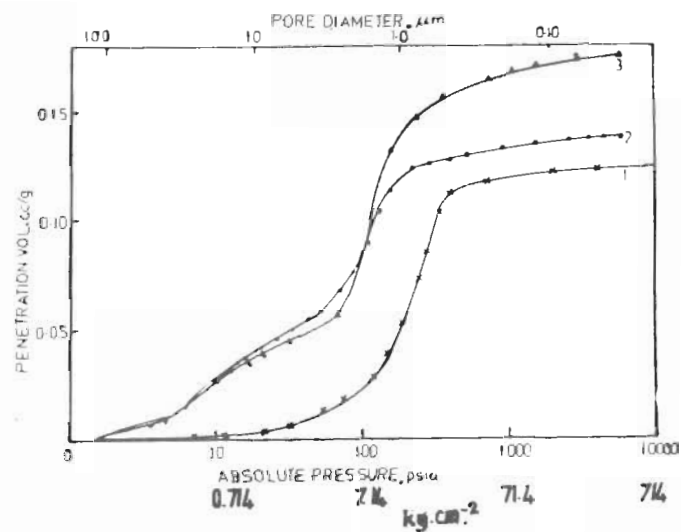


Fig. 2(a): Pore volume mercury penetration curve for hydrogen gas diffusion electrode 1: Electrode No. 11, 2: Electrode No. 4, 3: Electrode No. 1

Figs. 2 (a) and 2(b) show the pore size distribution curves for the electrodes obtained by mercury penetration porosimeter. The general shape and characteristics of the curves in Fig. 2 (a) can be easily explained [8]. The peaks in Fig. 2 (b) correspond to dia of pores formed in different layers. The general characteristics and the values are tabulated in Table II. It is inferred that pores of greater dia (10 to 15 μm) are formed mainly in gas distribution

layer and to some extent in the catalyst layer. Similarly the percentage of pore dia below 1 μm is less in the catalyst layer than in the protective layer. The pores in the diameter range 2 to 6 μm correspond to the interconnected pores formed in the catalyst layer.

TABLE-II: Data from porosimeter

Sl. No.	System	Description	Total true pore vol. (ml. g ⁻¹)	Pore dia range (μm)	Pores in the range (%)	Pore area (m ² .g ⁻¹)	Total pore area (m ² .g ⁻¹)
1.	Nickel type 255	Powder	1.220	5-7 0.6 - 4	5 40	0.15 0.53	1.34
2.	Nickel 255 compacted	Supporting layer	0.06	0.05 -1.5	70	0.23	0.48
3.	Nickel + filter	Gas diffusion layer	0.153	>10 2-4 < 2	53 18 25	- 0.016 -	0.32
4.	Activated charcoal	Catalyst powder	5.950	4-6 0.1-2.0	13 30	0.087 3.70	10.80
5.	Nickel & activated charcoal catalyst	Two layer electrode	0.125	>10 2-4 < 2	28 11 55	0.03 0.063 0.60	0.84
6.	Nickel & skeletal nickel catalyst	Catalyst layer	0.125	>10 2-4 < 2	13 52 25	- 0.08 -	0.18
7.	Nickel-skeletal nickel catalyst	Three layer electrode	0.116	>10 2-4 < 2	20 15 60	- 0.05 0.19	0.4

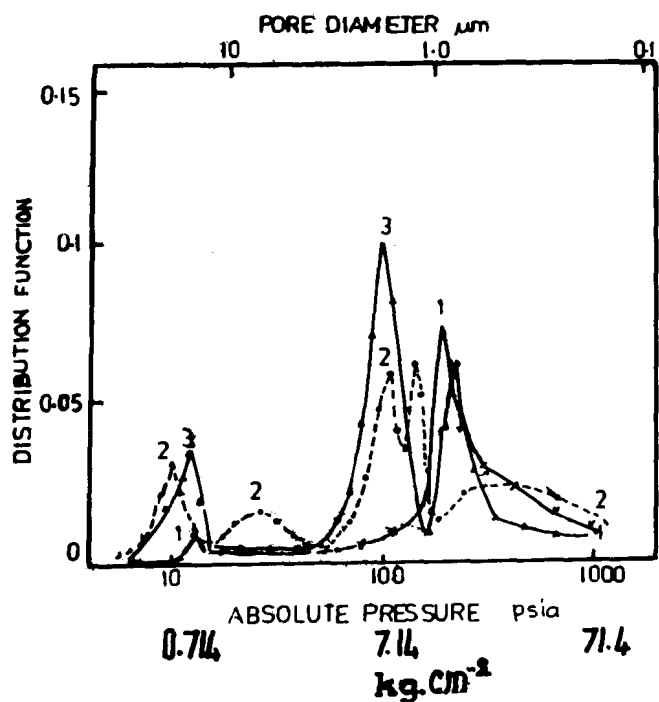


Fig.2(b): Pore size distribution curves for the electrodes as in Fig.2(a)

The steady state galvanostatic polarisation curves for electrodes (Table I B) are shown in Figs. 3(a) and 3(b). It can be seen

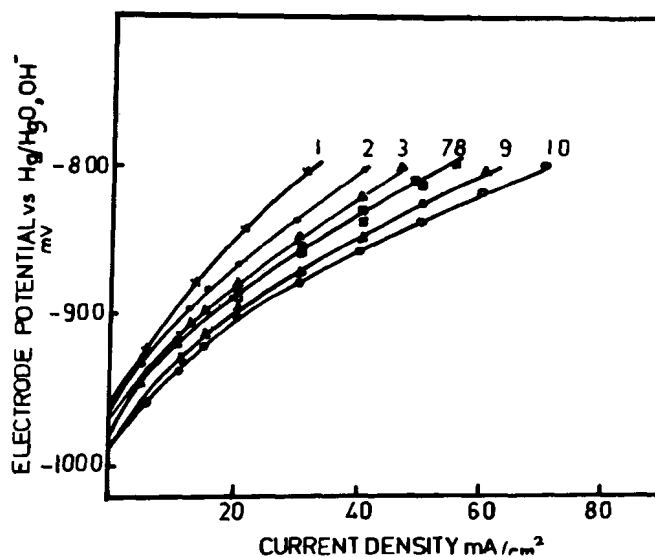


Fig.3(a): Steady state galvanostatic polarisation curves in 6.0 M KOH at 333K ($p_{H_2} = 1.0 \text{ kg. cm}^{-2}$) (Curve numbers correspond to electrodes Table 1B.)

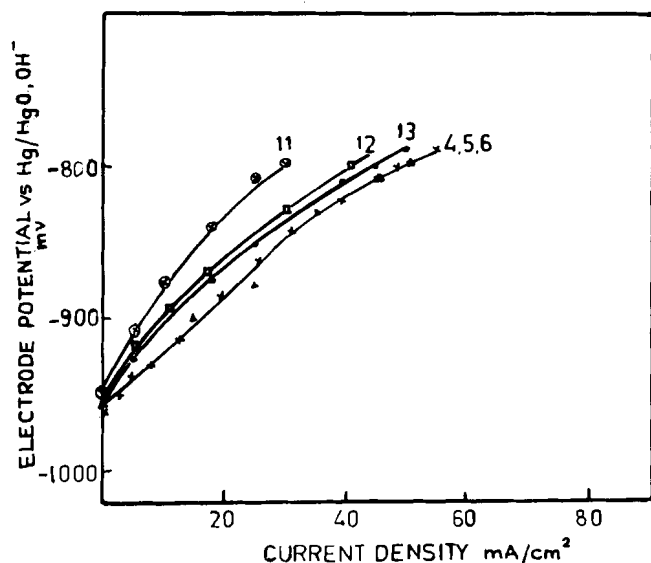


Fig.3(b): Steady state galvanostatic polarisation curves in 6.0 M KOH at 333K ($p_{H_2} = 1.0 \text{ kg. cm}^{-2}$) (Curve numbers correspond to electrodes Table 1B.)

that the electrodes containing skeletal nickel catalyst can be loaded up to 30 mA.cm^{-2} (curve 1) while the electrodes containing Pt as promoters can withstand current densities upto 50 mA. cm^{-2} at a potential of -800 mV . The high activity obtained for electrodes 9 and 10 indicates that incorporation of Pd has an additional effect similar to the effect of bimetallic catalysts on carbon supports for fuel cell electrode reaction [13,14]. Increase of noble metal content in the catalyst layer increases the performance.

The chemical reduction of Pt-salts with NaBH_4 produces Pt black agglomerates, the distribution of which is rather nonuniform by the post catalysation technique. However, the particle size of the Pt-crystallites has an influence in the reaction rate [15] and the use of small catalyst particle size less than $10 \mu\text{m}$ for effective utilisation has been reported [14]. The etching nature of NaBH_4 on nickel surface, which produces high internal surface area, also contributes to the increased reaction rate. But the working difficulties like retaining the platinum inside the matrix itself without getting lost during washing of the electrode and distribution of the catalyst uniformly, make this method of little value.

In order to achieve the effective distribution of the promoter element, precatalysation technique was employed to deposit platinum on nickel, skeletal nickel and activated charcoal by the well known colloidal dispersion method [9]. The performance of these electrodes containing the catalysts is shown in Fig. 3(b). By comparing the two sets of curves 11, 12 and 13 with 4,5 and 6 it can be inferred that platinum dispersion on skeletal nickel gives better performance characteristics than on activated charcoal, though the latter has been frequently employed in the development of fuel cell electrodes. From

the pore size distribution curves of these electrodes, it is seen that the pore dia. of majority of pores in the catalyst layer is below $2 \mu\text{m}$. The catalyst layer will be flooded with electrolyte at 1.0 kg.cm^{-2} , and more gas pressure ($>1.7 \text{ kg.cm}^{-2}$) will be required to generate high current. This explains their poor performance.

CONCLUSION

The post catalysation technique is a convenient process in applying the promoter platinum element to the electrode surface. The resulting increase in the performance is expected to be improved for long life studies and for development of commercial prototype alkaline fuel cell. The precatalysation technique is advantageous in spreading the catalyst clusters uniformly but the amount is to be increased from the present 1:1000 to 1:100 or 1:10 so that thin electrodes could be fabricated and more catalyst is effectively utilised.

REFERENCES

1. K V Kordesch, (a) *Fuel Cell Symposium*, ACS Meeting Atlanta N J Sep (1965) 17 (b) *J Electrochem Soc*, **125** (1978) 77; 271C
2. P Stonhart, *Int J Hydrogen Energy*, **9** (1984) 921
3. E W Justi and A W Winsel, *Kalte Verbrennung Wiesbaden*, Franz Steiner (1962) p 397
4. K Mund, G Richter and F V Sturm, *J Electrochem Soc*, **124** (1977) 1
5. M Jung and von Dohren, *5th Proc Int Symp Power Sources*, Brighton (1966) p 497
6. R Pattabiraman, T R Jayaraman and V K Venkatesan, *Proc 3rd Nat Conf Power Sources*, SAEST India (1979) p 149
7. I Arulraj, R Pattabiraman, R Chandrasekaran, S Deenadayalan and V K Venkatesan, *Trans SAEST*, **18** (1983) 207
8. R Pattabiraman, R Chandrasekaran and V K Venkatesan, *Proc Adv Electrochem Energy Storage and Conversion*, Karaikudi, India (1983) No 3.2
9. V M Jalan and C L Bushnell, U S Pat 4, 137 373 (1979); U S Pat 4, 136 059 (1979)
10. S Birlasekaran and R Kaçidoss, *B Electrochem*, **1** (1985) p 195
11. R Chandrasekaran, R Pattabiraman, T R Jayaraman and V K Venkatesan, *Proc 2nd Nat Conf Power Sources*, SAEST India (1979) p 149
12. (a) K Tomantschger, *Electrochem Soc Spring Meeting*, Extended Abs. No. 646 May (1985) p 904 (b) R Manoharan, A K Shukla *J Power Sources*, **10** (1983) 333
13. K V Ramesh and A K Shukla, *ibid*, **19** (1987) 279
14. K Tomantschger, F Mcclusky, L Operto, A Reid and K Kordesth, *ibid*, **18** (1986) 317
15. P Stonhart and K Kinoshita, *Electrochim Acta*, **20** (1975) 101