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Platinum catalysed membranes for proton exchange membrane fuel cells – higher performance

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Abstract

Platinum loading on the Nafion membrane by impregnation/reduction method was optimized for higher performance in the proton exchange membrane fuel cell (PEMFC) electrode development and the performance was correlated to their coating condition in terms of Platinum salt concentration, reaction time and the surface roughness. Surface roughening was used to increase the mass transport of chloroplatinate and tetraborohydrate ions, through the membrane, for the simultaneous deposition and reduction of platinum on the membranes. The current density obtained at 0.7 and 0.6 V was 500 and 1000 mA/cm^2, respectively for a membrane catalysed with a platinum loading of 0.38 mg/cm^2 and the electrochemical utilization of the platinum was found to be 55%.

1. Introduction

There has been an increasing interest in the potential use of proton exchange membrane fuel cells (PEMFC) as zero emission power sources for various applications, because of their major advantages like quick start up, acceptable oxygen reduction kinetics, small diffusional polarization, etc. [1–4]. The solid electrolytes are fluoro carbon ion exchange membranes coated or laminated to an electrocatalyst layer, which is an essential component in many electrochemical devices and are used in fuel cell. They possess excellent chemical and mechanical stability allied to a high ionic conductivity and produce highly acidic environments as a consequence of the sulfonic acid groups within the micelle structure [5,6]. One of the key parameters for a PEM fuel cell electrode is its electrochemically active catalyst area. Since the polymer membrane used for electrolyte is a solid phase, it does not penetrate deeply into the electrode as does a liquid one, therefore the reaction area is limited to the contact surface between the electrode and membrane [7–10].

Increase in the utilisation of catalyst in the interface between the gas diffusion layer and the solid polymer electrolyte, is always a significant factor to lower material costs for PEMFC without sacrificing performance and reliability. Catalyst surface utilisation describes the proportion of metal surface atoms involved in the electrochemical reactions. A common method employed to increase Pt utilization is to add a proton conducting polymer, such as Nafion, into the catalyst layer. Impregnation of the catalyst layers of gas diffusion electrodes with solubilized ionomer increased the utilization by more than 20%. However, due to the morphology, low gas permeability, and poor electronic conductivity of Nafion, there is a limit to the quantity that can be added, before adversely affecting cell performance. Hence, alternative methods of preparing the catalyst layer with a high electrochemical surface area are of interest.

In order to achieve higher utilization, an alternative fabrication method for the membrane electrode assembly was proposed in which the catalyst ink was directly applied on to the membrane apart from the gas diffusion layer [11]. During such lamination, it is important to maximize the active metal surface area to achieve a high metal dispersion on the membrane to promote the desired reactions. During operation, mechanical stresses arise on the membrane due to dimensional changes in the membrane during hydration, dehydration and gas evolution. In order to reduce the ohmic losses and to support high mechanical stresses, good adhesion of the electrocatalyst to the membrane is also necessary. Apart from that, swelling of a Nafion film also makes it very difficult to deposit thin catalyst layers on a membrane electrolyte. Another method to improve the fuel cell perfor-

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mance is to coat the catalysts on the membrane, which are generally carried out by electrochemical deposition, chemical deposition, and by mechanical pressing [10]. Since a mechanically stable electrode with a high surface area can be easily obtained by a chemical reduction process, it has aroused great interest recently. In the chemical reduction route, platinum was deposited on one side of the membrane either by cycling the membrane between the reducing agent and Pt salt solution or by dipping it in the reducing agent after Pt ions are equilibrated in it. The concentration of the reactant, reducing agent and the reaction time play a major role in forming a platinized surface on the membrane. The mass of platinum deposited and the platinum surface area were also affected by the flux of diffusing reagents, the deposition time and the temperature.

Cha et al. [12] studied the performance of PEMFC by direct deposition of Pt on the membrane surface and Hsu et al. [13] reported an innovative process for PEMFC electrodes using the expansion of Nafion film. There were many reports on localisation of platinum in low catalyst loading electrodes to attain high power densities in PEM fuel cells, oxygen reduction reaction kinetics and mechanism on platinum nanoparticles inside Nafion, effect of catalytic ink preparation method on the performance of PEMFC, and effects of gas diffusion layer characteristics on the performance of PEMFC [14–17]. The characteristics of Pt/Nafion electrodes prepared by a Takenata–Torikai method in sensing hydrogen was studied by Hwang et al. [18]. However, the effects of spatial distribution and compactness of the metal onto the Nafion film on the fuel cell for high performance has not been studied in detail.

The object of the present study is to optimise the membrane coating using a chemical reduction cycling method to catalyse the Nafion membranes with varying degree of coating, in order to increase the reaction sites in the catalyst layer ie. the catalyst utilization in fuel cells for better performance. Initially, the electrode parameters were optimized in terms of hydrophobic and hydrophilic contents and the catalyst loading on the membrane was optimized by varying the concentration of the platinum salt solution for high performance. The results of real fuel cell experiments carried out with the help of catalysed membranes are presented. The electrochemically active catalyst area, is determined by cyclic voltammetry, as shown by electrochemical hydrogen adsorption/desorption has also been discussed in detail.

2. Experimental

2.1. Membrane catalysation

Nafion 1035 membrane of 89 μm thickness from Dupont de Nomours was pretreated by boiling in deionosed water containing 5 wt.% hydrogen peroxide for about 1 h at about 70–80 °C to remove organic impurities and then the process was repeated with high purity water three or four times to remove H_2O_2 and traces of soluble organic impurities. The metallic impurities were also removed by similar heat pretreatment in 0.5 M H_2SO_4 and several times with high purity water to remove the sulfuric acid. A square piece of membrane of 4 cm × 4 cm was mounted horizontally between two acrylic flanges. The acrylic flanges had a dip of 2.2 cm × 2.2 cm at the center to accommodate the platinum salt solution on one flange and reducing agent on the other flange. The different concentrations of salt solutions of platinum varying from 0.5 to 5%, were prepared using chloroplatinic acid in aqueous medium. Similarly reducing solution was prepared containing 0.1 M of $NaBH_4$ and 1 M of NaOH. Prior to coating, the surface to be coated by platinum was roughened by abrasion with 1200 grade silicon carbide paper, in order to increase the penetration rate of platinum and reducing agent. One membrane face was exposed to the solution of H_2PtCl_6 for half an hour and without disturbing the assembly, reducing solution was injected slowly in to the centre dip of the other flange. Large amounts of hydrogen generated need to be removed, during the deposition process, it was achieved by manually shaking the membrane or by slow agitation at regular intervals. After 3 h, the Pt-coated Nafion membranes were left in concentrated H_2SO_4 for about 12 h at 30 °C, in order to leave the membrane in hydrated acid form. The membrane was washed thoroughly in deionised water prior to electrochemical studies.

2.2. Electrochemical studies

For the electrochemical characterization of the electrocatalysts towards oxygen reduction in solid polymer electrolyte membrane fuel cells, the membrane electrode assemblies (MEA) were obtained by sandwiching the Pt-coated Nafion 1035 membrane between the anode and cathode. Both the anode and cathode layer consists of backing layer, diffusion layer and catalyst layer. To prepare the catalyst layer, the required amount of the catalyst was divided in to two parts. One part was mixed with 5% Teflon suspension. The other part was suspended in water and ultrasonicated by adding 5 wt.% Nafion solution. The paste thus obtained was brushed on to the teflonised carbon paper GDL-10 10-H, SGL carbon group technologies, Sigracet, and pressed at 130 °C at 1000 psi for 2 min. The anode contained a Pt loading of 0.25 mg/cm^2, and cathode 0.25 mg/cm^2, which was kept identical in all the MEAs. The catalysed surface of the membrane was used for the cathode side. The operating conditions were kept constant to facilitate comparative evaluation of various MEA. The anode and cathode were contacted on their rear with gas flow field plates machined from high density graphite blocks from Electrochem, USA, in which channels are machined to achieve minimum mass polarisation in the PEMFC. Humidified gases are passed to the electrodes from a Novatech Test station. Adjacent to both the graphite blocks, gold coated current collectors are used, which are connected to the Won A-Tech (HPCS 1) DC load box with a suitable software for various cycles of current loading and for activating the electrode. Galvanostatic-polarization data were obtained at various temperatures. The geometric area of the electrode was 5 cm^2.

Cyclic voltammetry (CV) technique was used to measure the electrochemical surface area (ESA) of fuel cell electrodes, in order to get the localization of platinum near their front surfaces, using the EG&G M270 electrochemical system. By passing the argon for the test electrode and hydrogen through the counter electrode chamber, the potential was swept between 0 and 1.2 V versus RHE at a scan rate of 15 mV/s. Because of the negligible overpotential at the counter electrode for the hydrogen oxidation or evolution reaction, it served as hydrogen reference electrode. From the CV, the charge equivalent to the area under the hydrogen desorption region was evaluated and electrochemical surface area was calculated assuming that the charge required for the adsorption/desorption of a monolayer of atomic hydrogen on the surfaces is 210 μC/cm^2.

3. Results and discussion

3.1. Membrane catalysation

In the cycling method, the two components namely, BH_4^- and metal ions, Pt^{2+}, separated by a membrane react simultaneously when they diffuse through the membrane and form reduced Pt in the membrane surface according to the following redox reactions [19].

$$PtCl_6{}^{2-} + 4e^- \rightarrow Pt + 6Cl^- \quad (1)$$

$$BH_4{}^- + 3H_2O + 4e^- \rightarrow BO_3{}^{3-} + 2H_2 + 6H^+ \quad (2)$$

The overall reaction can be written as

$$PtCl_6{}^{2-} + BH_4{}^- + 3H_2O \rightarrow Pt + BO_3{}^{3-} + 6Cl^- + 2H_2 + 6H^+ \quad (3)$$

The catalysation of the membrane leaves a thin film of black coating on the membrane surface, over an area of 2.2 cm × 2.2 cm for PEMFC studies. During the reaction, initially there was a thin non uniform black colouration in the membrane which increases with time. Since the membrane gets converted into sodium form, there was lot of hydrogen evolution, which was removed by manual shaking. This process improves the uniformity of the catalysation also, since the pores of the membrane gets simultaneously filled by the Pt salt and gets reduced in situ by the borohydride ion. The thickness of the platinum film depends on the concentration of the solution. It was found that the low concentration salt solution of 0.5% gave a thin non uniform coating while 5% solution gave a thick uniform coating. It was also observed that platinum just forms a thin film on the membrane surface, which gets easily washed off. However, abrasion of the membrane surface by fine 1200 grade silicon carbide paper increases the flux of the reactant and reducing agents through the membrane. Fig. 1 shows the effect of H_2PtCl_6 concentration on the mass of platinum deposited. The platinum loading on the Nafion membranes were evaluated from the concentration of the salt solution, assuming that complete reduction has taken place. The platinum loading in the membrane vary from 0.38 to 3.8 mg/cm^2 in the concentration region of the platinum salt solution studied. The concentration of the reducing agent was optimized for complete reduction of the platinum salt. In order to ensure the complete reduction of chloroplatinate ions by the borohydride ions through the membrane, a qualitative experiment was carried out by taking the remaining droplets of solution on the membrane, and was allowed to react with reducing agent in a petridish and found that there was no black colouration, as in the case of membrane.

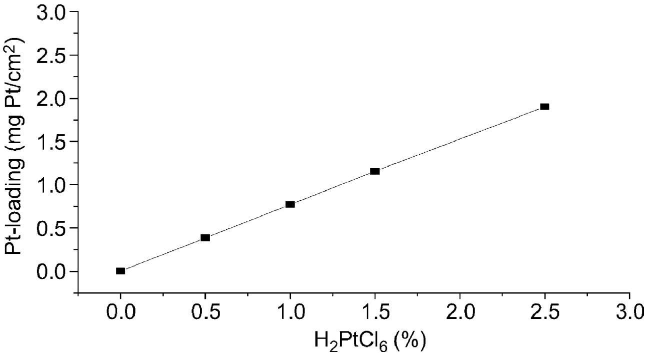

Fig. 1. Variation of platinum concentration in the membrane with respect to the chloroplatinic acid salt solution concentration.

SEM measurements were carried out in a Philips XL series (XL 30S FEG) unit. The Pt/Nafion samples were cooled to 77 K and cold fractured to examine the crossections of the coating, by the adhesion of platinum coated Nafion membrane on the carbon tape without any Au/Pt coating. Fig. 2 shows the SEM picture of the crosssection of the membrane coated with 1% Pt solution and investigation of the morphology of the platinum deposit shows a coating thickness varying from 80 to 150 nm in the concentration region studied. Membranes loaded with higher concentration solutions, especially 5% solution, showed some cracks in the surface, which might have arised during deposition or during cold fracture, because of the increase in the internal tensile stress in the deposit.

3.2. Electrochemical measuremnts

The current voltage characteristics of PEMFCs fabricated by making use of the catalysed membranes are obtained by activating the electrodes, gradually between open circuit potential and increasing the current. The same procedure was followed for all the catalysed membranes, prior to the polarization studies. We observed that this activation cycle was necessary to activate the electrodes for higher performance. Fig. 3a–e shows the current voltage characteristics of the fuel cell electrodes, with various loadings of platinum at the membrane surface at various temperatures and pres-

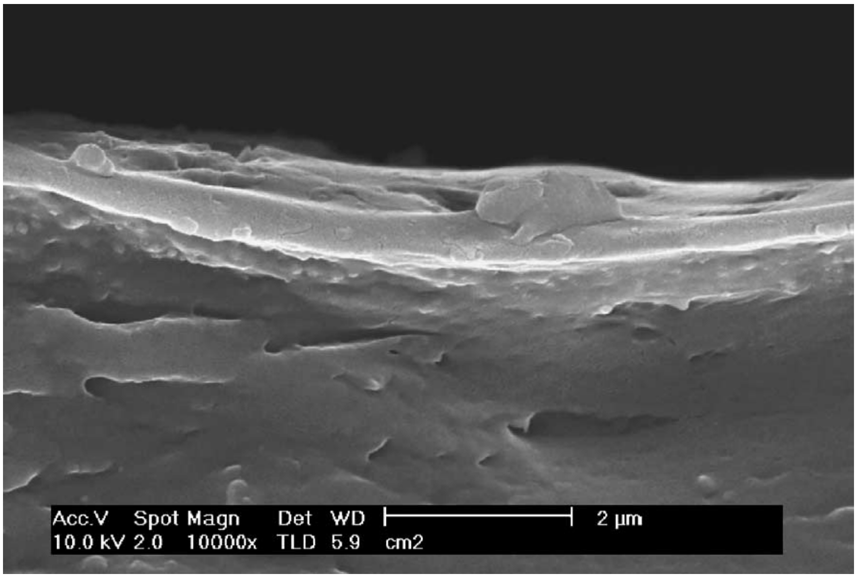

Fig. 2. SEM photograph of the cross section of the platinum coated membrane.

sures. One can clearly see from the figures that all these catalysed membranes gave almost the same performance at 50 °C. However, the membrane catalysed with 1.5% solution gave a very low performance. From the figures one can clearly see that all the catalysed membranes gave a current density of 800 mA/cm^2 at 0.6 V. However, the membrane catalysed with 0.5% solution, gave a higher current density of 1000 mA/cm^2 at 0.6 V. The cell potential E, against current density I is represented as follows [20].

$$E = E_o - b \log(I) - R(I) \tag{4}$$

where E_o, b and R are the open circuit potential, tafel slope and the ohmic resistance respectively. The experimental curves were fitted to the above polynomial equation and the kinetic parameters were evaluated and are summarised in Table 1 along with polarization data at 80 °C with 15 psi.

From Table 1, it is clear that the open circuit potential of 1.5 and 2.5% catalysed membrane is higher by about 70–100 mV, compared to other MEAs. However, the fuel cell performance was not higher compared to other concentrations, and the ohmic resistance was also higher. This could be due to the increased resistance due to interfacial contact between the membrane and the catalyst. In order that the coated platinum particles form an effective surface for the electrochemical reactions of the PEMFC, they should be electrolytically connected to the Nafion membrane and electrically bound to each other. Nafion ionomer plays the role of the electrolytic connector. It was observed that an optimum amount for the Nafion ionomer in the catalyst layer is required for a good bonding to reduce the interfacial resistance. The catalytic site is not fully utilised, if there is not enough ionomer. On the other hand, triple access requirement is difficult to meet, if the ionomer amount is high. When the catalyst coating on the membrane is thick and uniform, without any cracks, there is a less bonding during pressing the MEA, as the electrolyte flow between the membrane to the electrode was prohibited by the uniform catalyst coating. On the other hand, non uniformity in the catalyst coating, and some cracks in the coating lead to a better bonding, which in turn increases the fuel cell performance.

Cyclic voltammograms were recorded after a run time of minimum 1 h. During this first hour, the electrode has been cycled in the potential between 50 and 1200 mV at a sweep rate of 50 mV/s, in order to establish the membrane electrode interface and to gain stable reproducible voltammogram. Depending on the nature of the catalyst in the active layer, and the applied pretreatment of gas diffusion electrodes, cyclic voltammetry reveals varying H-adsorption/desorption characteristics and catalyst surface utilisation properties. Generally, the H$^+$ ions are supposed to adsorb at the Pt/Nafion interface and be reduced to H$_{ad}{}^-$ atoms. Also surface conductivity plays a role in the catalyst utilisation. In the case of

Table 1
Platinum loading, PEMFC performance and kinetic parameters of various catalysts

Pt salt concentration (%)	E_o (V)	b (mV/decade)	R (Ω cm^2)	Voltage (mV) @ 500 mA/cm^2	Voltage (mV) @ 1000 mA/cm^2
0.5	0.932	55.4	0.16	705	604
1.0	1.024	90.9	0.22	677	530
1.5	1.031	106.6	0.21	636	491
2.5	1.024	71.6	0.26	648	474
5.0	0.971	78	0.18	680	535

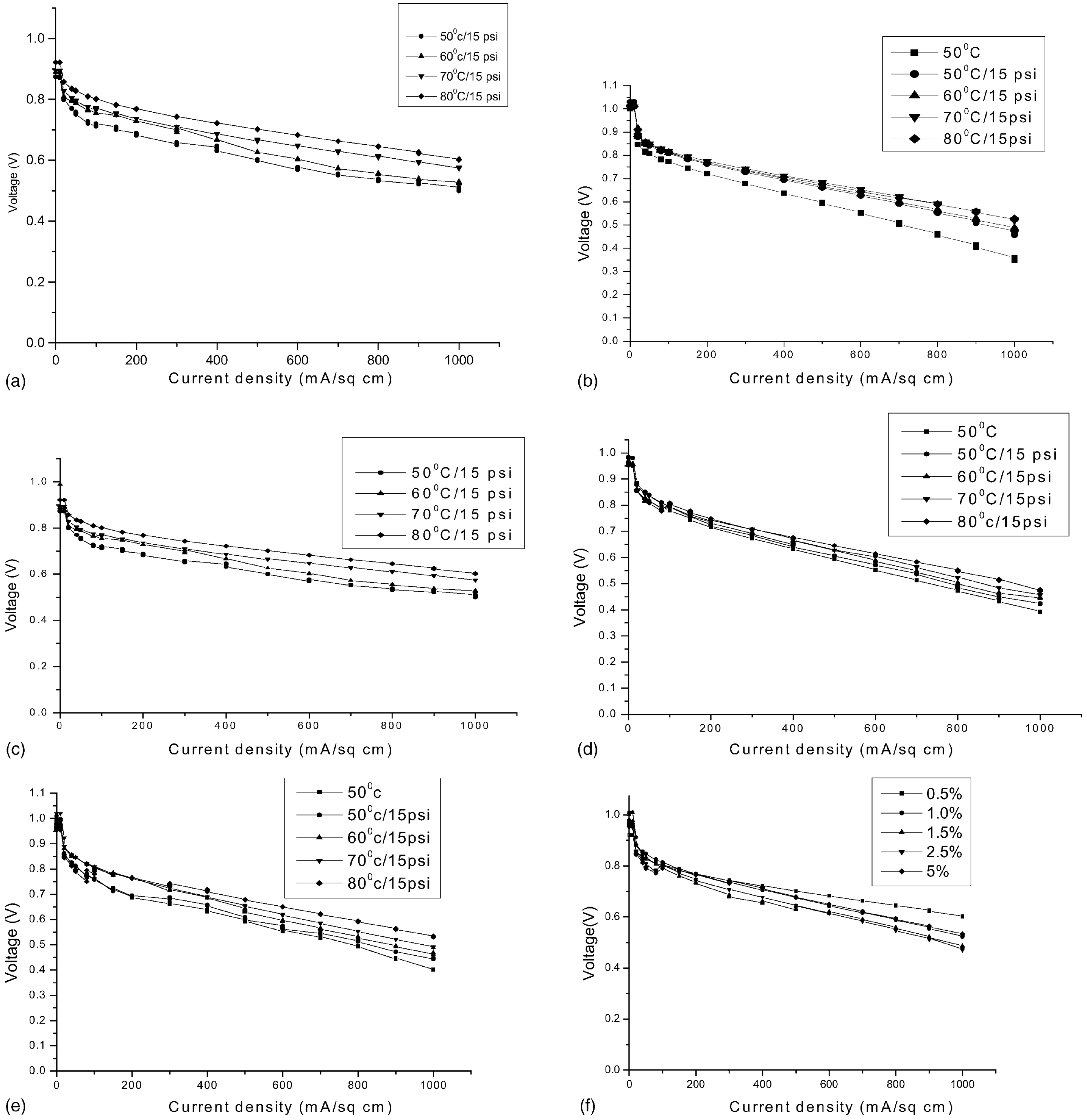

Fig. 3. Polarisation curve of the PEMFC at various temperatures and pressures, using the membrane catalysed with: (a) 0.5% concentration of salt solution; (b) 1.0% concentration of salt solution; (c) 1.5% concentration of salt solution; (d) 2.5% concentration of salt solution; (e) 5% concentration of salt solution; (f) comparison of *I–V* characteristics of all the catalysed membranes at 80 °C/15 psi.

cells purged with humidified argon, a thin liquid conductive film is formed along the walls or even to electrolyte filled channels. This would principally allow the diffusion of H^+ ions within the film and/or absorption and reduction of H^+ ions along the complete catalyst surface.

However, the use of this parameter has a number of limitations, including the fact that it cannot be measured while the fuel cell is actually operating, and the full Pt area that is active for hydrogen adsorption is unlikely to be active for the fuel cell reaction because of insufficient reactant gas access and resistance losses at high current densities. Due to the extended porous structure of the gas diffusion electrodes, it can be assumed that only a part of the platinum with a direct contact to the Nafion membrane is electrochemically active.

Fig. 4 shows the cyclic voltammogram of all the catalysed membranes which gives a measure of the electro-

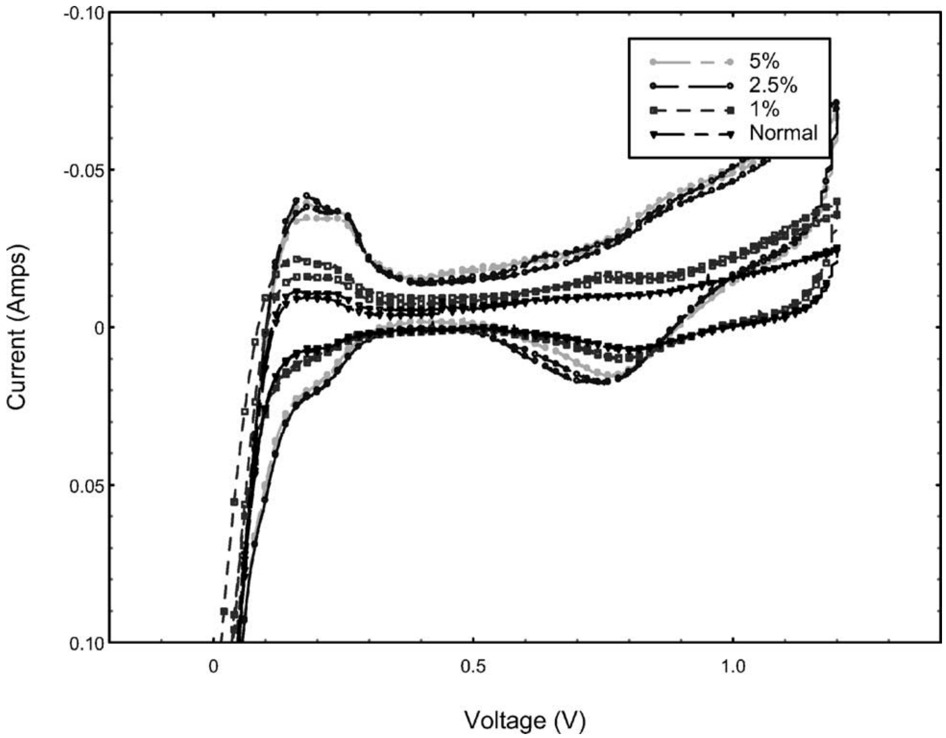

Fig. 4. CV of all the catalysed membranes along with non-catalysed membrane at a scan rate of 15 mV/s.

chemical surface area. Having the high surface area of the active layer of gas diffusion electrodes and a porous structure these data indicate that in the case of electrodes prepared with as received Pt/C, only a small part of the overall amount of Pt, most likely the platinum which is close to the polymer electrolyte, is electrochemically active. In the case of catalysed membranes, however, Pt without direct contact to the Nafion electrolyte membrane obviously takes part in the H adsorption/desorption process. By comparing all these figures it is clear that the general shapes of these curves are similar, except for minor differenecs of relative height of peaks for the hydrogen desorption current, which can be ascribed to the different electrochemical utilisation. The peaks from 0.0 to 0.4 V provide information on the hydrogen adsorption and desorption which occurs on the platinum surface and from 0.4 to 0.5 V is regarded as double layer region. Compared to coated membranes, the hydrogen absorption/desorption peaks are not well resolved in normal electrode. The well resolved peaks observed in other catalysed membranes are independent of the applied sweep rate. One peak observed at 155 mV corresponds to the desorption of weakly adsorbed hydrogen and the other peak at 252 mV corresponds to desorption of a strongly adsorbed hydrogen. The two desorption peaks are merged into single one peak, in some coated membranes, due to different faceting of the particles present in the catalyst layer [21,22]. The platinum electrochemical surface area can be calculated from the current densities of hydrogen absorption and desorption and were integrated separately and referred to a charge of 210 μC/cm^2, which is correlated to a mono-layer of hydrogen adsorption on the platinum surface [23]. Apparently, the MEA without any catalysation has a smaller integrated area compared to catalysed membranes.

The real surface area of a catalyst can be orders of magnitude greater than the geometric area. Since adsorption and catalytic reaction rates are based on real surface area, it is important to be able to measure this value. It is assumed that each surface platinum atom is associated with one chemisorbed hydrogen atom, allowing the charge corresponding to the area under the weak and strong hydrogen absorption peaks. The enhancement of real electrochemical surface area, in comparison with a smooth surface can be described by a roughness factor

$$\mathrm{RF} = \frac{A_{\mathrm{ec}}}{A_{\mathrm{g}}} \tag{5}$$

Where A_{ec}, electrochemical surface area and A_{g} geometric area of the electrode. Using this value, the fraction of platinum surface area that is electrochemically can be active, which are listed in Table 2.

From Table 2, it is clear that the electrochemical utilization of platinum is maximum in the case of membranes coated with 0.5%, compared to membranes, where there was a thick uniform coating. These results are in comparison with fuel cell performance, in which higher electrochemical surface area gives rise to higher fuel cell performance in our case. Sometimes, they do not neces-

Table 2

Pt salt concentration (%)	ESA (μC/cm^2)	RF	Utilisation (%)
Normal	294.6	58.9	23.56
0.5	1388.1	277.6	55.5
1.0	715.2	143.1	28.62
1.5	883.8	176.7	35.3
2.5	925.4	185.1	37.6
5.0	968.1	193.6	38.72

sarily translate to a higher performance as a result of kinetic, ohmic and mass transport losses within the electrode matrix [8].

4. Conclusion

In the present paper, we have optimized the catalysation of Nafion membrane for higher performance in fuel cells by simultaneous impregnation reduction method, by varying the reactant concentration and also evaluated the percentage of utilization of platinum in the fuel cell electrodes. We observed that the high performance of 0.6 V @ 1 A/cm^2 and 0.7 V @ 0.5 A/cm^2 was obtained for a low platinum loading of 0.5% salt solution with platinum utilization of about 55%, compared to membranes with thick and uniform catalyst layer.

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