

# An analytical approach on effect of diffusion layer on ORR for PEMFCs

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## Abstract

The effect of an immobilized diffusion layer on the catalyst layer and the oxygen reduction reaction in polymer electrolyte fuel cells (PEMFCs) have been studied. Since, the oxygen reduction reaction is an inhibitive reaction, much effort has been devoted to the improvement of this reaction in PEMFCs. In this work, the effect of an immobilised hydrophobe carbon layer as the diffusion layer in the gas diffusion electrode has been evaluated. The study of various electrochemical methods in this research, as well as the evaluation of cell polarisation curves showed that the efficiency of electrodes with the diffusion layer in the high current density regions is higher than the electrodes with no diffusion layer. While in the lower current density region the electrodes without the diffusion layer are more efficient than the other type. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Gas diffusion layer; Analytical approach; Oxygen reduction reaction; Polymer electrolyte fuel cell

## 1. Introduction

The membrane electrode assembly (MEA) is the key component of proton exchange membrane fuel cells (PEMFC) [1]. The effective parameters on MEA performance are also effective on cell performance. Much research has been carried out about the effect of structural parameters [2,3], performance conditions [4–6] and MEA fabrication methods [7–10]. As well as the experimental methods, mathematical modelling methods have been used in these studies [11,12].

One of the effective structural parameters on the PEMFC performance is the diffusion layer in the MEA [13]. This layer can be used as an immobilised layer or as a distinct layer on the catalyst layer. This layer provides a physical micro porous base for the catalyst layer. Within its channels the reactions are introduced onto the catalyst layer. Enormous research has been reported concerning the morphological and structural characteristics of this layer and its effect on cell performance [14–20].

In this research, we have studied the role of a diffusion layer in the cell performance and in the electrodes with/without this layer. A three-electrode system and complete cell experiments have been used in this work. Among the electrodic reactions, the hydrogen oxidation reaction (HOR) has a low oxidation overpotential due to the ease of

hydrogen oxidation and the high kinetic rate of this reaction, while the low reaction rate of the oxygen reduction reaction (ORR) leads to a high reduction overpotential in the performance condition of PEMFC [21–25]. In this work, the cathodic reaction has been considered as the main target for improvement of PEMFC performance. The experiments have been carried out in two distinct parts: (1) evaluation of constructed electrodes for the ORR by using a three-electrode system and electroanalytical methods; (2) the use of results obtained from part one for the preparation of MEAs and test of them on a single cell. In the three-electrode tests, various electrochemical techniques such as voltammetry, chronoamperometry and AC impedance spectroscopy have been used. Besides analysis of the diffusion layer, the innovation of fast, easy, efficient and low cost methods in the characterisation and evaluation of the electrodes and MEAs are the important subjects of this paper.

## 2. Experimental

An AutoLab potentiostat–galvanostat model PGSTAT 30 has been used for the electrochemical experiments. The electrochemical cell consisted of an Ag/AgCl reference electrode (Azar Electrode), a Teflon body for handling of working electrode and a glassy jacket. A flowmeter with 0–100 ml min<sup>-1</sup> range (OMEGA) and a regulator (PAKKENS) are used for the control of reactants flow rate in the successive experiments. The reactant gases enter into a glass humidifier

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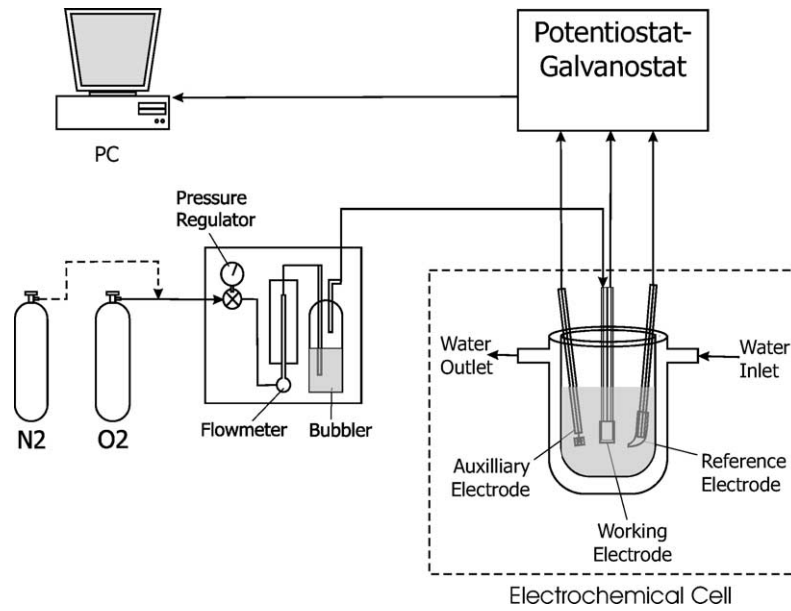


Fig. 1. A schematic diagram of experimental half cell set-up.

with 100 ml volume before the entrance into the cell. The Fig. 1 shows the set-up of half cell experiments. In all research based on the application of half electrodes, reproducibility is a very important topic [4,5,25–27]. In the present work a custom made punch was used for cutting the electrodes with  $0.5 \text{ cm}^2$  surface area. All the parts of the cell

set-up and controlling system (Fig. 2) were designed and integrated by experts of fuel cell vehicle project in R&D Center of the Iran Khodro Company. The procedure of [8] was used for the preparation of MEAs. For the preparation of half cells, at first a small sheet of carbon paper was cut by means of the punch. Then the diffusion layer with 20% PTFE and

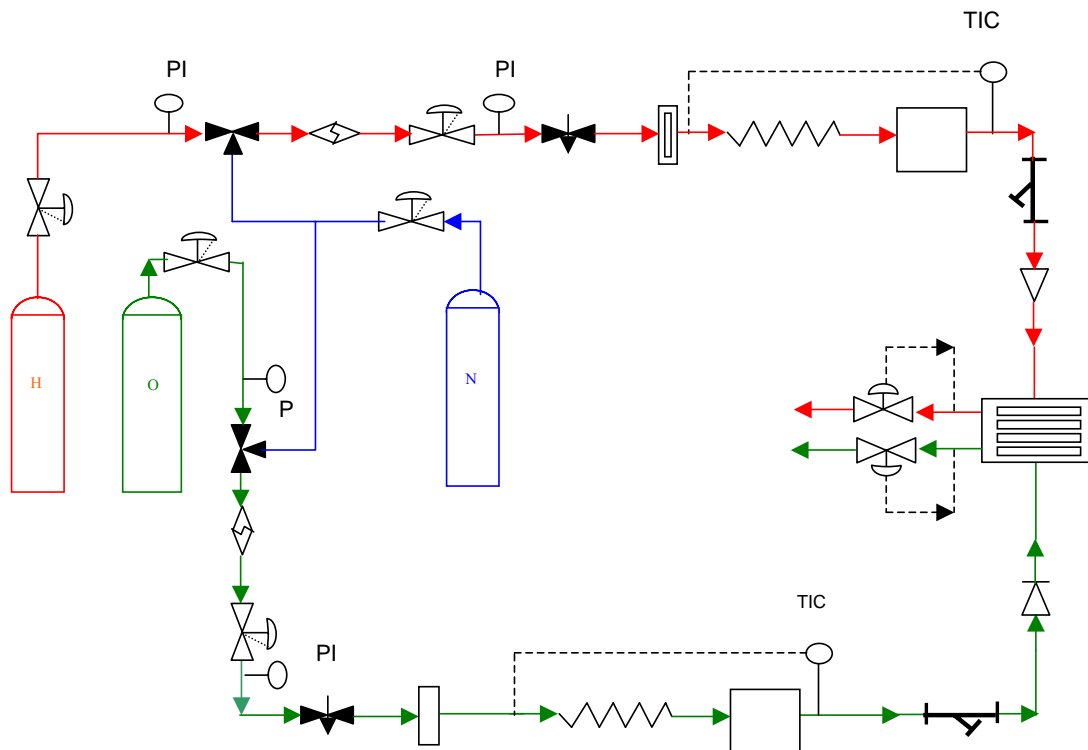


Fig. 2. Schematic flow diagram of experimental set-up.

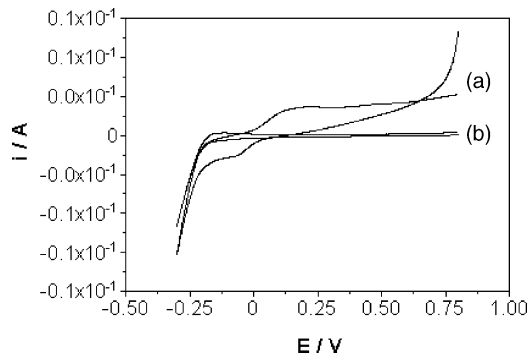


Fig. 3. Cyclic voltamograms of half cells without DL (a) and with DL (b) in the presence of  $N_2$  and in  $0.5\text{ M H}_2\text{SO}_4$ ,  $v = 10\text{ mV s}^{-1}$ .

$2.5\text{ mg cm}^{-2}$  carbon loading was sprayed on the carbon paper. After that the electrode was coated by spraying of the catalyst layer with  $0.2\text{ mg cm}^{-2}$  Pt loading and 15% PTFE. Finally the prepared electrodes were hot pressed on a  $1\text{ cm}^2$  Nafion 117 sheet at the  $130^\circ\text{C}$  and  $120\text{ kg cm}^{-2}$  pressure for 60 s. The same procedure was used for the preparation of half and complete cells without diffusion layers by eliminating the diffusion layer spraying step. All of the half cell experiments were performed in a  $0.5\text{ M H}_2\text{SO}_4$  solution and at room temperature ( $25^\circ\text{C}$ ).

### 3. Results and discussion

#### 3.1. Part 1

##### 3.1.1. Cyclic voltammetry

Fig. 3 shows the cyclic voltamograms (CVs) of electrodes without diffusion layer (DL) (3a) and with DL (3b) in the presence of  $N_2$ . As seen, the electrode with DL shows a higher active surface area than the other electrode. Hence it is expected that, (a) has lower ORR overpotential and higher cathodic current densities. Fig. 4 demonstrates the CVs of the two electrodes in the presence of  $O_2$ . As was expected, the electrode without DL shows a higher activity toward the ORR due to its higher active surface area. On

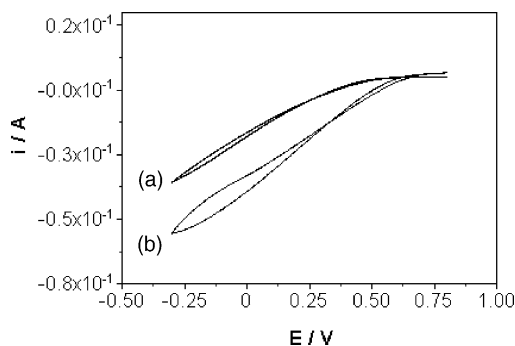


Fig. 4. Cyclic voltamograms of half cells without DL (a) and with DL (b) in the presence of  $O_2$  and in  $0.5\text{ M H}_2\text{SO}_4$ ,  $v = 10\text{ mV s}^{-1}$ .

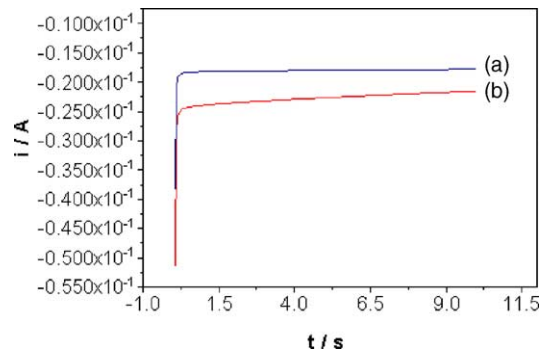


Fig. 5. Chronoamperograms of half cells without DL (a) and with DL (b) in the presence of  $O_2$ ,  $E_{app} = 0.2\text{ V}/(\text{Ag}/\text{AgCl})$ .

the basis of this figure, the reduction of  $O_2$  at (a) initiates at about  $0.65\text{ V}$  versus  $\text{Ag}/\text{AgCl}$ , while at the surface of (b), the initial potential of ORR is about  $0.4\text{ V}$  versus  $\text{Ag}/\text{AgCl}$ . Thus, the half cell without DL shows better performance than the other type.

##### 3.1.2. Chronoamperometry

For the quantitative comparison of diffusibility of the two types of electrodes the chronoamperometry method was used. This method is the usual method to determine the diffusion coefficients of electroactive species at the surface of electrodes. Fig. 5 shows the chronoamperograms of the electrodes discussed. The observed limited currents are given by the equation:

$$i = nFA \left( \frac{D}{\pi t} \right)^{1/2} C^*$$

In this equation,  $i$  is the limited current (mA),  $n$  the number of electrons,  $F = 96485\text{ mol}^{-1}$ ,  $A$  the surface of electrode ( $\text{cm}^2$ ),  $D$  the diffusion coefficient ( $\text{cm}^2\text{ s}^{-1}$ ),  $T$  the time (s) and  $C$  the concentration of reactant ( $\text{mM cm}^{-3}$ ).

Drawing of an  $I$  versus  $t^{-1/2}$  gives a line with a slope of  $nFA(D/\pi)^{1/2}C^*$ . The values of  $n$ ,  $F$ ,  $A$ , and  $C^*$  are necessary for the calculation of  $D$ . Considering that the reactant ( $O_2$ ) is used as a humidified gas the value of  $C^*$  is indefinite. Hence  $D^{1/2}C^*$  is considered as a new parameter in order to determine the total diffusibility of the electrode. On the basis of this method,  $D^{1/2}C^*$  is calculated as  $5.43 \times 10^{-9}\text{ mM cm}^{-2}\text{ s}^{-1/2}$ , for the half cell without DL and  $2.12 \times 10^{-9}\text{ mM cm}^{-2}\text{ s}^{-1/2}$  for the DL included half cell with DL. It can be seen that the  $D^{1/2}C^*$  or in the other words the diffusibility of the electrode without DL is almost 2.5 times greater than the other type.

##### 3.1.3. DC amperometry

The above mentioned experiments showed that, the DL included electrode has better characteristics than the electrode without DL for the ORR. One of the important topics in the PEMFCs, is the durability of cell performance. For the evaluation of durability of the two types of electrode, we used the DC amperometry method. Fig. 6, shows the cathodic

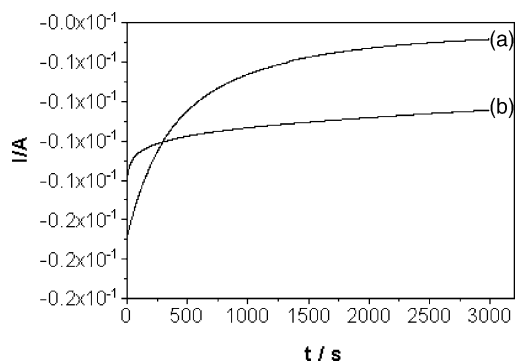


Fig. 6. DC amperograms of half cells without DL (a) and with DL (b) in the presence of O<sub>2</sub> at E<sub>app</sub> = 0.2 V/(Ag/AgCl).

currents of half cells at a fixed potential (0.2 V/(Ag/AgCl) in the presence of O<sub>2</sub> in a 3000 s time window. As can be seen in the figure, the half cell (a) (without DL) shows higher currents than other cell (b). While at the later times (after 300 s) the cathodic current of electrode (a) begins rapidly to decrease and at late times its decrease becomes smooth. In contrast to the electrode (a) the initial reduction of current is very slower at electrode (b). The rate of current decrease at the middle and late times are slow and similar in both of electrodes. This behaviour is seen due to the stabilisation of the moisture layer thickness formed by the accumulation of water molecules. It is seemed that the layer thickness of the electrode with DL is lower due to its higher hydrophobicity. Thus, on the basis of this experiment, the half cell with DL shows a higher durability than the other and is most suitable for the preparation of an MEA at higher current densities.

### 3.1.4. AC impedance

Much research has been carried out using impedance measurements in PEMFCs [25–27]. In order to make a quantitative evaluation of resistance against the ORR, the AC impedance method has been used. Fig. 7 shows the Nyquist plots for oxygen reduction on the electrodes with and without DL in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The results obtained from this experiment have been shown in Table 1. As seen, there is a small difference in linear resistance (R<sub>s</sub>) between the two types a electrode. The linear resistance due to DL addition on the electrode is not valuable, but leads to a small increasing polarisation resistance, (R<sub>p</sub>). Thus the electrode without DL shows a slightly better performance toward the ORR than the electrode with DL. Further information about the diffusion layer effect can be achieved by using this method,

Table 1  
The values of R<sub>s</sub> and R<sub>p</sub> for half cells constructed with/without DL in ORR

	R	
	R <sub>s</sub> (Ω)	R <sub>p</sub> (Ω)
Half cell with DL	3.84	3.25
Half cell without DL	3.60	2.65

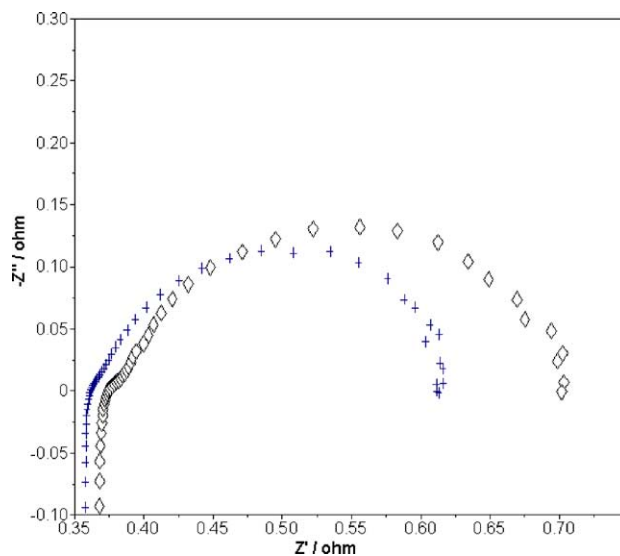


Fig. 7. Nyquist plots for ORR at 0.2 V/(Ag/AgCl) on half cell without DL (+) and with DL (◇).

e.g. it is possible to evaluate the DL effect on the reaction by time scanning or successive operation of the experiment.

### 3.2. Part 2

#### 3.2.1. Complete cell experiments

In this part, the performance of the complete cell has been evaluated. Cell potential–current density curves for cells of varying MEAs are shown in Fig. 8. This plot is recorded under the optimum cell operating conditions. These conditions are shown in Table 2. H<sub>2</sub> and O<sub>2</sub> have been used as pure

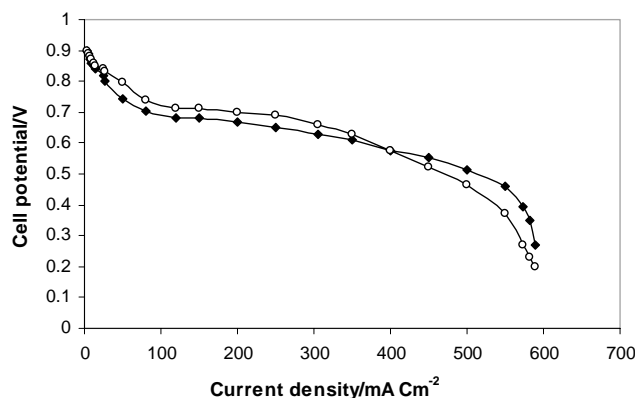


Fig. 8. Potential–current curves for cells with DL (○) and without DL (◆).

Table 2  
Optimum cell operating conditions

Humidifier temperature (°C)		Gas flow rate (sccm)		Cell temperature (°C)
O <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	
75	85	45	25	80

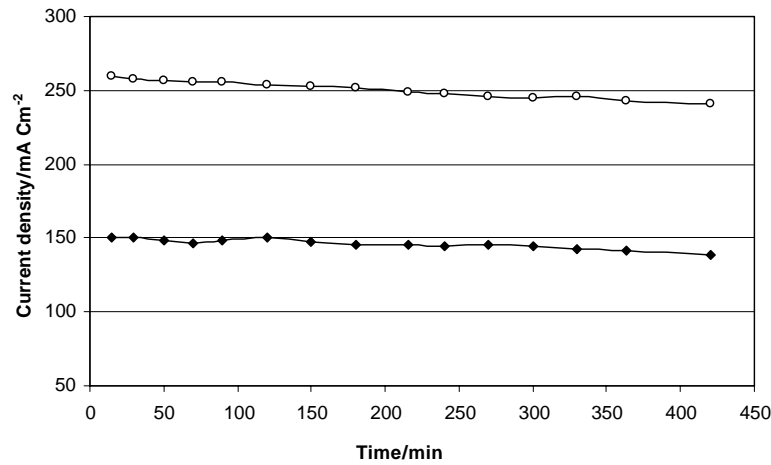


Fig. 9. Current–time curves for cells with DL (○) without DL (◆) at  $V_{\text{cell}} = 0.7$ .

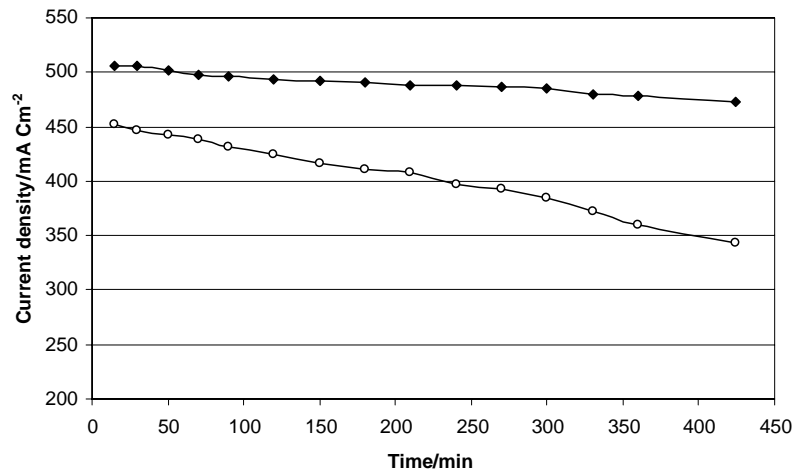


Fig. 10. Current–time curves for cells with DL (○) without DL (◆) at  $V_{\text{cell}} = 0.48$ .

gases and the cell operation pressure was atmospheric. As can be seen in the Fig. 8, both types of MEAs show similar activity in the activation region of the polarization curve. It is clear that the application of the DL is not effective on the kinetic rates of reactions occurring at the catalytic sites of the MEAs.

The DL included MEA shows higher current densities in the ohmic region of the  $i$ – $v$  plot. This is observed due to the lower diffusion limitation and lower ohmic drop of potential at the MEA without the DL. On the contrary, in the mass drop region of the  $i$ – $v$  plot the MEA with DL shows higher current densities and current overload is observed at higher current densities than for other type. The two curves cross each other at about 400 mA. This indicates that the existence of the DL has no utilization in cell performance before this point. But after this point the application of the DL cause an improvement in cell performance. For more elucidation of this fact we have performed experiments at low and high current densities. Fig. 9 shows current density–time plot for cells of the two types at a fixed cell potential 0.7 V. These

curves are recorded along a 6-h period. It is seen that the cell without the DL shows current densities 100 mA higher than the other cell. The durability of the two cells is almost identical. Fig. 10 shows the same plot at  $V_{\text{cell}} = 0.48$  V. As can be seen in Fig. 10, the cell with the DL shows a better performance at higher current densities. Besides achieving higher current densities, the DL included MEA shows more durability than other type. The influence of diffusion layer characteristics has been discussed by Passalacqua et al. [23] and Forsyth and co-workers [22].

#### 4. Conclusions

The effect of the diffusion layer on gas diffusion electrodes and cell performance was studied. A three–electrode system, as well as a complete cell system, were used for characterisation of MEAs constructed with/without the diffusion layer. The oxygen reduction reaction was considered as the main reaction affecting the evaluation of the electrodes

by using the three-electrode system and various electrochemical methods. The diffusibility of the electrode was determined by the application of chronoamperometry and a new parameter as  $D^{1/2}C^*$  was defined for this purpose. The results obtained from the complete cell experiments were consistent with the results obtained from the three-electrode system. On the basis of these experiments the MEAs including the diffusion layer showed a higher efficiency than the MEAs without the diffusion layer at high current densities. At low current densities the MEAs without the diffusion layer showed better performance than other type.

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