

Modelling the PEM fuel cell cathode

K. BROKA, P. EKDUNGE

Department of Chemical Engineering and Technology, Applied Electrochemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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Two models of the cathode of the proton exchange membrane fuel cell, a pseudohomogeneous film model and an agglomerate model, have been compared. The influence of different parameters on the shape of the polarization curves has been shown. Curves simulated by use of the two models and different values of oxygen permeability, effective conductivity and thickness of the active layer as well as thickness of the Nafion[®] film surrounding agglomerates have been presented and compared with the experimental results. On the basis of the simulations and the SEM study of the structure of the active catalyst layer it has been concluded that the agglomerate model is a better representation of the active catalyst layer than the pseudohomogeneous film model.

1. Introduction

Environmental concern has led to a renewed interest in the electric vehicle, however, its short driving range and long recharging time have prohibited its commercialization. An attractive solution of these problems is the use of fuel cells instead of batteries as a power source. The most suitable fuel cells for transport applications are ones with a solid polymer electrolyte due to their high power density, simple and safe construction and fast start-up even at low temperatures. For the commercial introduction of the proton exchange membrane (PEM) fuel cell as a power source for traction application, it is essential to improve its performance and to reduce its cost. Also, the specific power density of the fuel cell should be increased to reduce the size of the cell for it to fit within the restricted space available in a passenger car. The price of the fuel cell has to be competitive with the price of the internal combustion engine.

Low cost and high performance fuel cells require high performance three-dimensional electrodes that combine large active surface area with optimized utilization of the platinum catalyst. Recently, new methods for production of electrodes with low platinum loading and high performance have been presented [1–4]. This has been accomplished by the extension of the reaction zone by means of the penetration of the electrolyte phase into the porous electrode which increases the active surface area and the utilization of the catalyst. This can be achieved by impregnating the porous electrode with a solution of the electrolyte [1, 2] or by casting the catalyst layer from suspended Pt/C catalyst and Nafion[®] solution [3, 4]. By means of these methods, a three-dimensional active catalyst layer consisting of the electrolyte and the porous electrode is obtained. The

performance of the fuel cell largely depends on the structure of this active layer which should possess several important properties, such as high proton conductivity, high oxygen permeability and high electrochemical activity.

Mathematical models are a useful tool for analysis and optimization of the performance of the fuel cell and, particularly, of the cathode. Several models of different degree of complexity have been presented for the PEM fuel cell [5–13]. These models have been developed to study different aspects of the PEM fuel cell, such as transport properties of the membrane [5, 6], transport properties of the electrodes [7–10], or heat and water management [11–13]. The most detailed models of the cathode have been presented in [8–10]. In these models, the active layer has been treated as a pseudohomogenous film. In a recent work of Springer *et al.* [10], the influence of different parameters on the performance of the cathode has been shown. In other models, where the active layer has not been the main point of interest, it has been described as an ultrathin film of negligible thickness. Usually the structure of the active layer is, however, regarded to consist of areas containing Pt/C catalyst and ionomer, and gas pores [10, 14].

An agglomerate structure model has been presented by Ridge *et al.* [15] for the PEM fuel cell under electrolyte supported conditions (i.e., the membrane was saturated with an electrolyte, sulfuric acid, which penetrates into the membrane and fills some pores of the catalytic layer forming agglomerates). Agglomerate structure models have also been developed for alkaline fuel cells [16] and phosphoric acid fuel cells [17].

The aim of this work was to investigate the structure of the active catalytic layer, its influence on the performance of the fuel cell and to compare the structure models with experimental data.

2. Experimental details

2.1. Preparation of membrane–electrode assemblies, construction of the fuel cell system, experimental procedure of electrochemical measurements

The membrane–electrode assembly was prepared according to the procedure described in [1]. 5% Nafion[®] solution was brushed onto catalysed gas diffusion electrodes from E-TEK Inc. with a Pt content of 0.35 mg cm⁻² followed by evaporation of the solvent from the Nafion[®] solution. The impregnated electrodes were hot-pressed to both sides of a purified Nafion[®] membrane at 50 atm pressure and 125 °C for 1 min. A small piece of the electrode was pressed on the anode side of the membrane for use as a reference electrode. The amount of the impregnated Nafion[®] was about 1 mg cm⁻². Nafion[®] 117 membrane was pretreated as follows [1]. It was boiled in 3% H₂O₂ solution for 1 h, and repeatedly rinsed in boiling deionized water. This was followed by boiling in 0.5 M H₂SO₄ for 1 h and rinsing several times in boiling water. The membrane was then stored in deionized water.

The membrane–electrode assembly was incorporated in a single test cell from Globe Technologies. The fuel cell test station (Fig. 1) was equipped with a temperature-controlled humidification system of the reactant gases and temperature control of the cell. Flow rates of oxygen and hydrogen were controlled by means of flowmeters from Brooks Instrument B.V. Atmospheric pressure and flow rate of gases of about 150 ml min⁻¹ was used. Polarization curves were recorded in a galvanostatic manner by means of equipment consisting of a power supply 8701 D Oltronix, model 800 iR measurement system, The Electrosynthesis Company and several multimeters 3468 B, Hewlet Packard for measurement of the potential at the cathode, the anode and also the cell voltage. To minimize the influence of mass transport in the electrode backing, pure oxygen was used in the experiments.

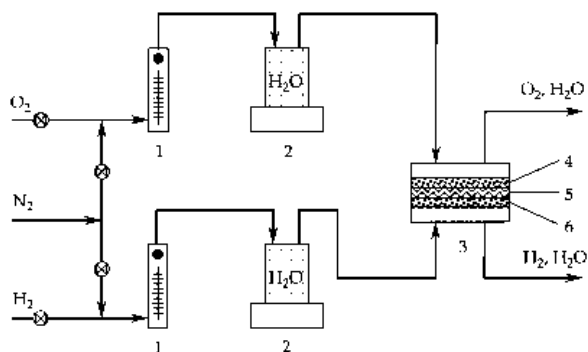


Fig. 1. Fuel cell test station: (1) flowmeters, (2) gas humidifiers, (3) fuel cell, (4) cathode, (5) membrane, (6) anode.

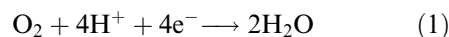
2.2. SEM studies

SEM studies were performed on the membrane–electrode assembly that was obtained as described above. Samples of the membrane–electrode assembly were prepared either by freeze-fracturing or freezing followed by cutting with a glass knife. The microscope used was a Jeol JSM-5400 scanning electron microscope.

3. Model

A mathematical model for the cathode of the PEM fuel cell, based on the assumption that the active layer can be described by a pseudohomogenous film, has been developed and compared with a model, where the active layer of the cathode is described by an agglomerate structure.

Both models are steady-state, one dimensional isothermal models of the kinetics and transport of reactants in the active layer of the cathode of the PEM fuel cell. The active layer is assumed to consist of carbon black supported platinum catalyst, where the electrochemical reaction:



takes place and the pores between the carbon particles contain recast Nafion[®].

Basic assumptions in both models are that: (i) the ionomer phase is an ion-conductive medium with effective proton conductivity κ_{eff} ; (ii) the transport of the reactants to active sites occurs by diffusion through the gas pores and/or through the ionomer in dissolved form; (iii) the catalyst is uniformly dispersed in the active layer; (iv) there is no potential gradient in the electrode phase, since the conductivity of the carbon structure is much higher than that of the ionomer phase; and (v) any excess water in the cathode exists in liquid form.

3.1. Pseudohomogeneous film model

In this model it is assumed that the catalytic layer can be described as a macropseudohomogeneous film, consisting of four superimposed media: a diffusion medium where the transport of the reaction reactants and products takes place, an ionic conduction medium which transports protons, an electrical conduction medium which conducts electrons and a catalytic medium where the electrochemical reaction takes place. A similar model has been presented by Springer *et al.* [10].

The oxygen concentration gradient changes with the local current density in the active layer as:

$$\frac{\partial C}{\partial x} = \frac{I - i}{C_{\text{O}_2}^* D_{\text{eff}} n F} \quad (2)$$

where $C_{\text{O}_2}^*$ is the saturation concentration of oxygen in Nafion[®], C is the dimensionless oxygen concentration in the Nafion[®], $C_{\text{O}_2}/C_{\text{O}_2}^*$, I is the total geometric current density, i is the geometric current

density in the ionomer phase, and D_{eff} is the effective diffusion coefficient of oxygen in the active layer.

The kinetic expression for the oxygen reduction rate per unit volume can be described by a simplified Butler–Volmer expression:

$$\frac{\partial i}{\partial x} = j = j_0 A C \exp\left(-\eta \frac{\beta F}{RT}\right) \quad (3)$$

where j_0 is the exchange current density, and A is the specific active surface area.

Since the matrix phase can be regarded as equipotential, changes in overvoltage in the electrolyte phase follow Ohm's law:

$$\frac{\partial \eta}{\partial x} = \frac{i}{\kappa_{\text{eff}}} \quad (4)$$

where κ_{eff} is the effective conductivity of the active layer.

Equations 2, 3 and 4 describe the catalytic layer according to the pseudo-homogeneous film model.

3.2. Agglomerate model

In the agglomerate model, the active layer is assumed to contain small agglomerates consisting of carbon, platinum and Nafion[®] mixture, which are separated by gas pores. These pores facilitate the transport of oxygen over the whole depth of the active layer. As in the pseudohomogeneous film model, the potential gradient in the active layer can be described by Ohm's law (Equation 4) for the ion transport in the agglomerates. In the agglomerate model, the concentration gradient for oxygen is perpendicular to the potential gradient in the agglomerate, since the oxygen is diffusing from the gas pores into the agglomerate. The effect of the material transport limitation due to the oxygen diffusion in the agglomerates can simply be characterized by an effectiveness factor, in the same way as for porous catalyst particles in heterogeneous catalysis [18]. For a first order irreversible reaction the efficiency factor is given by:

$$E = \frac{\tanh(mL)}{mL} \quad (5a)$$

where mL is Thiele's modulus:

$$mL = L \sqrt{\frac{k}{C_{\text{O}_2}^* D_{\text{eff}}}} \quad (5b)$$

L is the characteristic length of the agglomerate. For a sphere, $L = R/3$ and for a cylinder it is $L = R/2$, for other geometries L can be approximated by V/S where V is the volume and S is the exterior surface of the agglomerate.

The reaction rate constant can be calculated from the simplified Butler–Volmer equation (Equation 3), which gives

$$k = \frac{A j_0}{nF} \exp\left(-\eta \frac{\beta F}{RT}\right) \quad (6)$$

If the agglomerate is covered by a layer of Nafion[®], through which oxygen diffuses into the agglomerate, the current density is given by

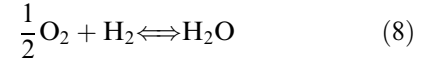
$$\frac{\partial i}{\partial x} = nF \left[\frac{1}{\frac{\delta}{a C_{\text{O}_2}^* D_{\text{eff}}} + \frac{1}{kE}} \right] \quad (7)$$

where a is the specific external surface area of the agglomerates and δ is the thickness of the Nafion[®] film surrounding the agglomerates. Differential Equations 4 and 7 describe the cathode according to the agglomerate model.

For both models the set of nonlinear differential Equations with appropriate boundary conditions was solved by a Runge–Kutta procedure.

3.3. Model parameters

The thermodynamic open-circuit potential for the reaction



was estimated from the relation [9]

$$U_{\text{Th}} = 1.23 - 0.9 \times 10^{-3}(T - 289) + \frac{RT}{4F} \log(P_{\text{H}_2}^2 P_{\text{O}_2}) \quad (9)$$

The kinetic parameters of the oxygen reduction on the platinum–Nafion[®] interface have been investigated as a function of temperature by Parthasarathy *et al.* [19]. They found a change in Tafel slope from low to high at the voltage of 0.75–0.8 V. We used the highest Tafel slope in the simulations since almost the whole of our experimental polarization curve was in the voltage region below 0.8 V.

The exchange current density was determined by Parthasarathy *et al.* [19] for oxygen with 100% relative humidity at a pressure of 5 atm. The value of exchange current used in the simulations was recalculated for oxygen of 1 atm pressure and 100% relative humidity assuming that Henry's law was valid.

The specific active surface area was estimated by dividing the platinum surface area for the electrode [20] by the thickness of the active catalyst layer. In reality, the active surface area is smaller than the total platinum surface area owing to poor utilization of the catalyst. The high value of the parameter A_{j_0} was, nevertheless, used in the simulations, since lower values gave a poorer agreement with the experimental polarization curve.

The oxygen permeability for recast Nafion[®] film [21] and the proton conductivity for Nafion[®] [22] as a function of temperature and relative humidity has been recently investigated in our laboratory under conditions close to those in the fuel cell. Since water is produced in the cathode reaction, the permeability and conductivity of the Nafion[®] phase were assumed to be the same as for Nafion[®] in equilibrium with gas of 100% relative humidity at the actual temperature.

Table 1. Base case parameter values

Parameter	Value	Source
Open circuit potential, U_{Th}	1.16 V	Calculated
Specific exchange current density, A_0	$5 \times 10^4 \text{ A m}^{-3}$	Calculated
Tafel slope, b	$113 \text{ mV decade}^{-1}$	[19]
Oxygen permeability in the Nafion [®] phase, $D \times C^*$	$1 \times 10^{-11} \text{ mol cm}^{-1} \text{ s}^{-1}$	[20]
Ion conductivity of the Nafion [®] phase, κ	0.07 S cm^{-1}	[21]
Thickness of the active layer, l	$15 \text{ }\mu\text{m}$	SEM study
Characteristic length of the agglomerate, L	$3 \text{ }\mu\text{m}$	SEM study
Temperature of the fuel cell	343 K	

The thickness of the active layer and the size of the agglomerate was estimated from the SEM micrographs.

The parameter values used in the base-case simulation are summarized in Table 1.

The effective conductivity and diffusivity were calculated from the Bruggmann relation:

$$D_{\text{eff}} = D\varepsilon^{1.5} \quad (10)$$

$$\kappa_{\text{eff}} = \kappa\varepsilon^{1.5} \quad (11)$$

with an assumed porosity of 0.5 in the active layer.

4. Results and discussion

4.1. SEM observation

The structure of the active catalyst layer was studied by means of a scanning electron microscope. This study was carried out on the membrane–electrode assembly that was obtained by impregnating the electrode with Nafion[®] solution and hot-pressing to the Nafion[®] membrane.

Figures 2–5 present SEM micrographs of samples obtained by two different methods: freeze-fracturing and cutting by a glass knife. It can be observed that the method of sample preparation influenced the appearance of the structure. By analysis and comparison of the micrographs of the samples obtained by these two methods, a good understanding of the structure of the active layer can be achieved.

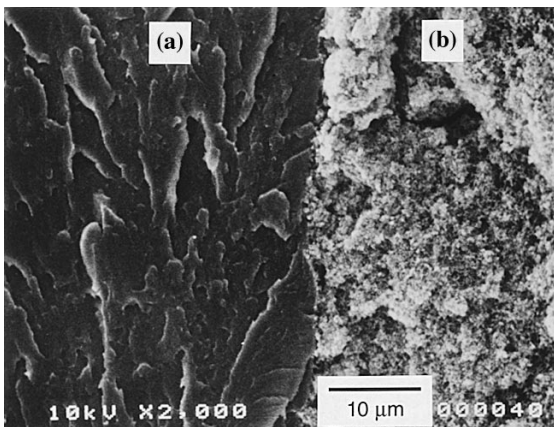


Fig. 2. Freeze-fractured cross section of the membrane–electrode assembly: (a) Nafion[®] 117 membrane, (b) gas diffusion electrode with the impregnated active catalyst layer.

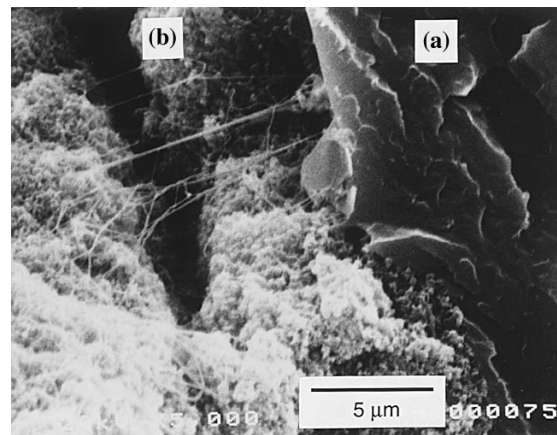


Fig. 3. Freeze-fractured cross section of the membrane–electrode assembly: (a) Nafion[®] 117 membrane, (b) impregnated active catalyst layer.

Figures 2–5 show parts of the membrane–electrode assembly where the membrane is hot-pressed to the impregnated electrode. The SEM micrographs show a very good attachment between the electrode and the membrane. The impregnated Nafion[®] layer is more clearly distinguished in the SEM micrograph of the sample that was prepared by cutting with the glass knife. In this case, Nafion[®] in the form of thin ‘fibres’ was stretched along the cut surface. The impregnated layer exhibits pores and voids, which is particularly apparent in the samples prepared by knife-cutting (Figs 4 and 5). The microstructure of the active layer

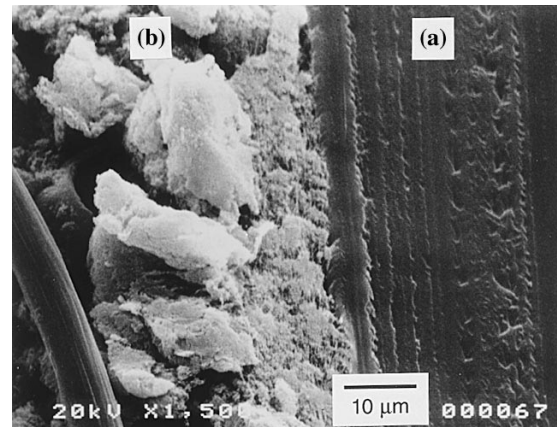


Fig. 4. Cross section of the membrane–electrode assembly (cut by a glass knife): (a) Nafion[®] 117 membrane, (b) electrode with the impregnated active catalyst layer.

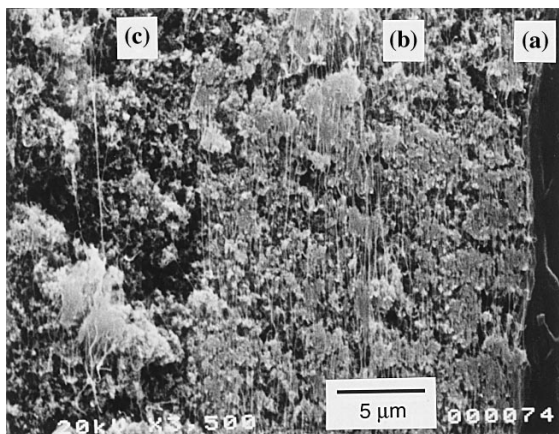


Fig. 5. Cross section of the membrane-electrode assembly (cut by a glass knife): (a) Nafion® 117 membrane, (b) impregnated active catalyst layer, (c) electrode.

of the membrane-electrode assemblies supports the idea stated on the basis of permeability measurements [21] that the catalyst layer is porous with channels for gas transport and therefore the agglomerate model of the catalyst layer gives a better representation of the reaction zone than the pseudohomogeneous film model. The agglomerate size is about 1–5 μm which can be seen in Figs 4 and 5. The thickness of the active layer was estimated to be 10–20 μm.

4.2. Simulations

Current and concentration profiles over the active layer as well as polarization curves have been calculated and compared for the two models.

If the same values are used for effective permeability and the same thickness of the active layer is assumed for both models, the agglomerate model gives the lowest overvoltage, see Fig. 6. The relatively high overvoltage for the curve obtained by the pseudohomogeneous film model is due to the fact that at high current densities, oxygen does not pe-

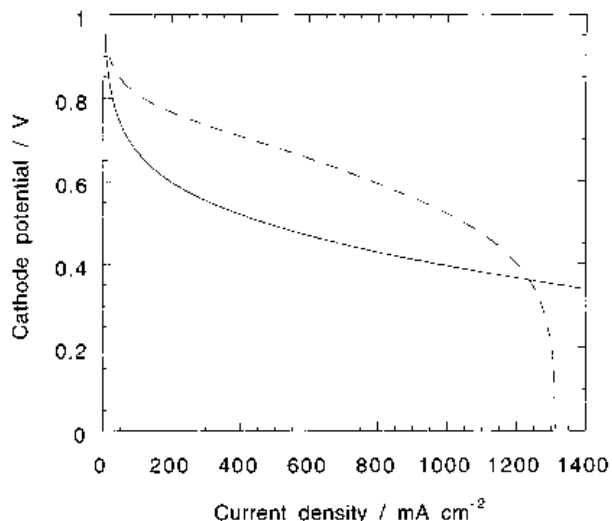


Fig. 6. Polarization curves for the cathode calculated by use of agglomerate (---) and pseudohomogeneous (—) film models (base-case parameter values).

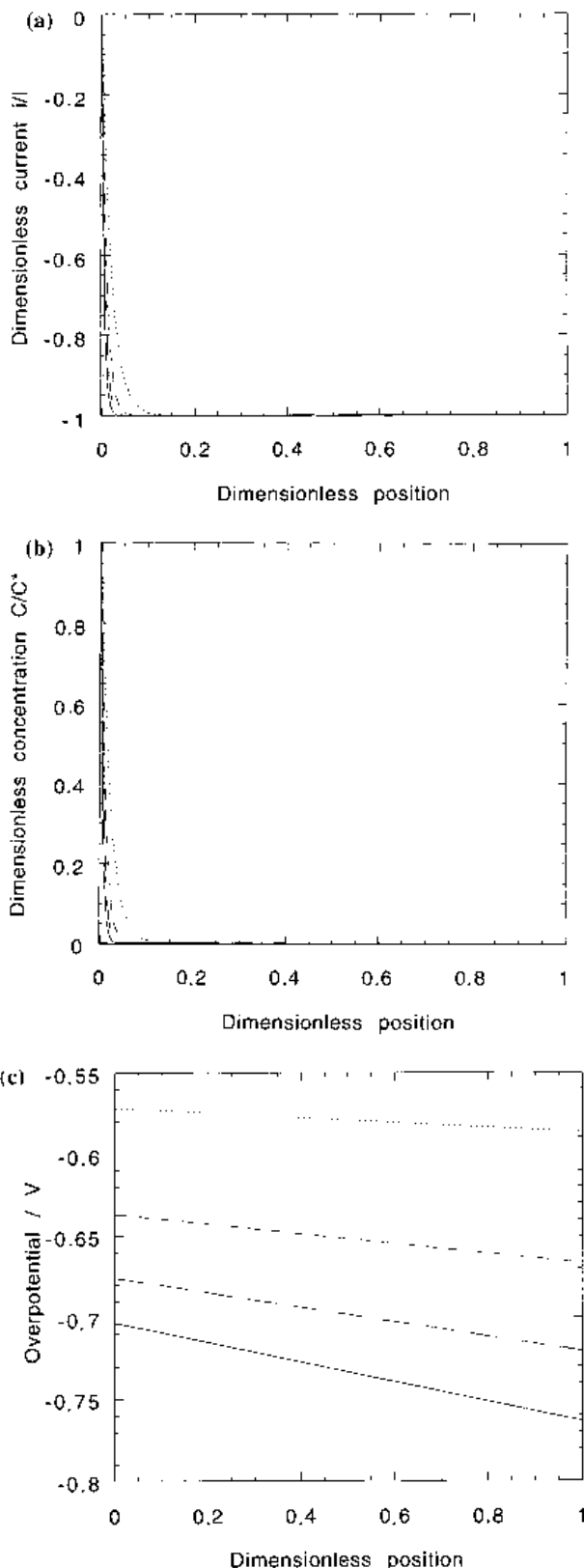


Fig. 7. Current (a), concentration (b) and overvoltage (c) distribution in the active catalyst layer for the film model at different current densities (base-case parameter values):(· · ·) 250, (- - -) 500, (- - -) 750 and (—) 1000 mA cm⁻².

netrate into the inner part of the active layer, which results in a very uneven current distribution. At 1000 mA cm⁻² the entire electrochemical reaction is concentrated within the outermost 1/20 of the active layer (see Fig. 7).

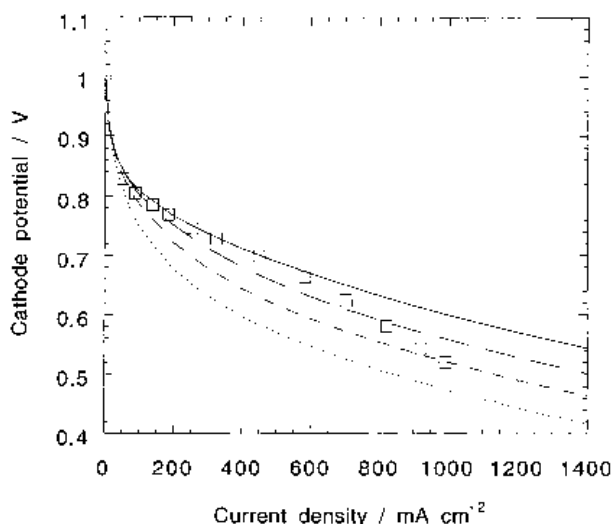


Fig. 8. Polarization curves for the cathode calculated by use of the film model for different values of oxygen permeability: (—) 1×10^{-9} , (— — —) 5×10^{-10} , (- - -) 2.5×10^{-10} and (· · ·) 1×10^{-10} mol $\text{cm}^{-1} \text{s}^{-1}$; (□) experimental values.

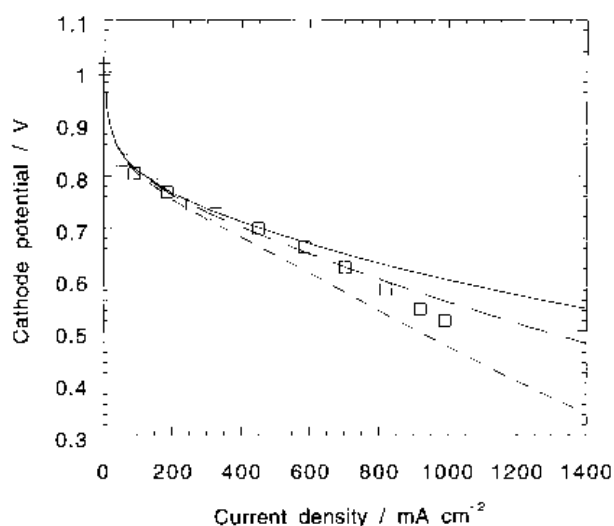


Fig. 9. Polarization curves for the cathode calculated by use of the film model for different values of effective conductivity: (—) 0.07, (— — —) 0.035 and (- - -) 0.0175 S cm^{-1} ; (□) experimental values.

From the comparison of the simulated curves with the experimental polarization curve, it can be seen that the film model predicts considerably higher overvoltages. By increasing the value of the effective permeability, a lower overvoltage can be obtained for the film model curves. Figure 8 shows the influence of the effective permeability on the performance of the electrode. With a value of effective permeability that is 100 times higher than the measured one [21] a good agreement between the experimental and simulated polarization curve is obtained up to about 600 mA cm^{-2} . This high value of the oxygen permeability was also used by Springer *et al.* [5, 10] in the simulation of the active layer of the cathode in the PEM fuel cell. They justified the usage of this high permeability value by considering the diffusion of oxygen into micro pores of the carbon particles within the active layer [5].

The experimental polarization curve exhibit a change of shape at about 600 mA cm^{-2} . It has been shown that by decreasing the effective conductivity similar changes in polarization curve shape can be obtained with the pseudohomogeneous film model [10]. The influence of the effective conductivity on the polarization curves is shown in Fig. 9. A decrease of the effective conductivity by a factor of four gives a form of the polarization curve similar to that of the experimental curve, but at a lower potential.

The oxygen concentration profile, and hence current density, is more evenly distributed over the active layer in the film model with 100 times higher oxygen permeability than in the model where the measured permeability value was used. The current and overvoltage distribution in the active layer for the two models are compared in Figs 10 and 11. These figures illustrate a great influence of oxygen diffusion in the active catalytic layer on the performance of the electrode in the film model. Even with the highest value of oxygen permeability, the limited oxygen transport in the active layer results in a very uneven current distribution which is more pronounced at high current densities. The agglomerate model gives a more uniformly distributed current over the whole depth of the active layer, since the oxygen is evenly distributed in the active layer. In contrast to the film model, the highest values of the current density are obtained in the inner part of the electrode, where the values of overvoltage are highest (see Fig. 11).

In the agglomerate model, the oxygen concentration is constant over the whole depth of the active layer. The decreased utilization of the catalyst due to the restricted oxygen diffusion manifests itself in a decreased effectiveness factor, which is illustrated in Fig. 12. The utilization of the inner parts of the agglomerates decreases with increasing current density, but alteration of the value of the effectiveness factor over the depth of the active layer is rather small even at high current densities.

The agglomerate model predicts a limiting current at about 1300 A cm^{-2} for the base-case conditions. The limiting current is dependent on the mass transport restriction in the film surrounding the agglomerates, and hence proportional to the factor δ/a . The influence of the factor δ/a on the polarization curves is shown in Fig. 13. In the base-case, the value of the factor δ/a was chosen in such a way that the best fit with the experimental curve was obtained.

The two models predict a different influence of the thickness of the active layer. The film model gives an increased overvoltage with increasing thickness at high current densities, due to an increased barrier of mass transport and limited proton conductivity (see Fig. 14). For the agglomerate model, this limiting current is proportional to the total external surface of the agglomerates. An increase in the thickness therefore gives an increase in the limiting current density if the specific external surface of the agglomerates is constant (see Fig. 15).

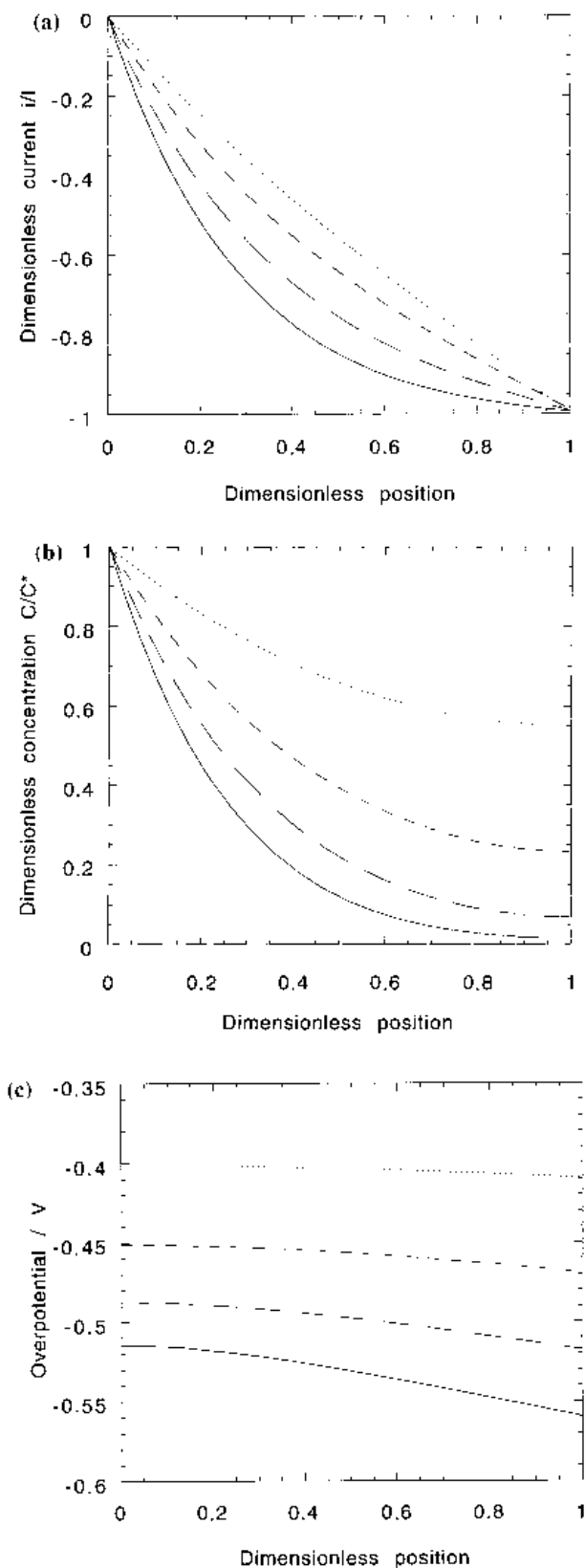


Fig. 10. Current (a), concentration (b) and overvoltage (c) distribution in the active catalyst layer for the film model at different current densities (oxygen permeability 1×10^{-9} mol cm⁻¹ s⁻¹): (···) 250, (- - -) 500, (- · - ·) 750 and (—) 1000 mA cm⁻².

5. Conclusions

The structure of the active layer of the cathode has a great influence on the performance of the PEM fuel

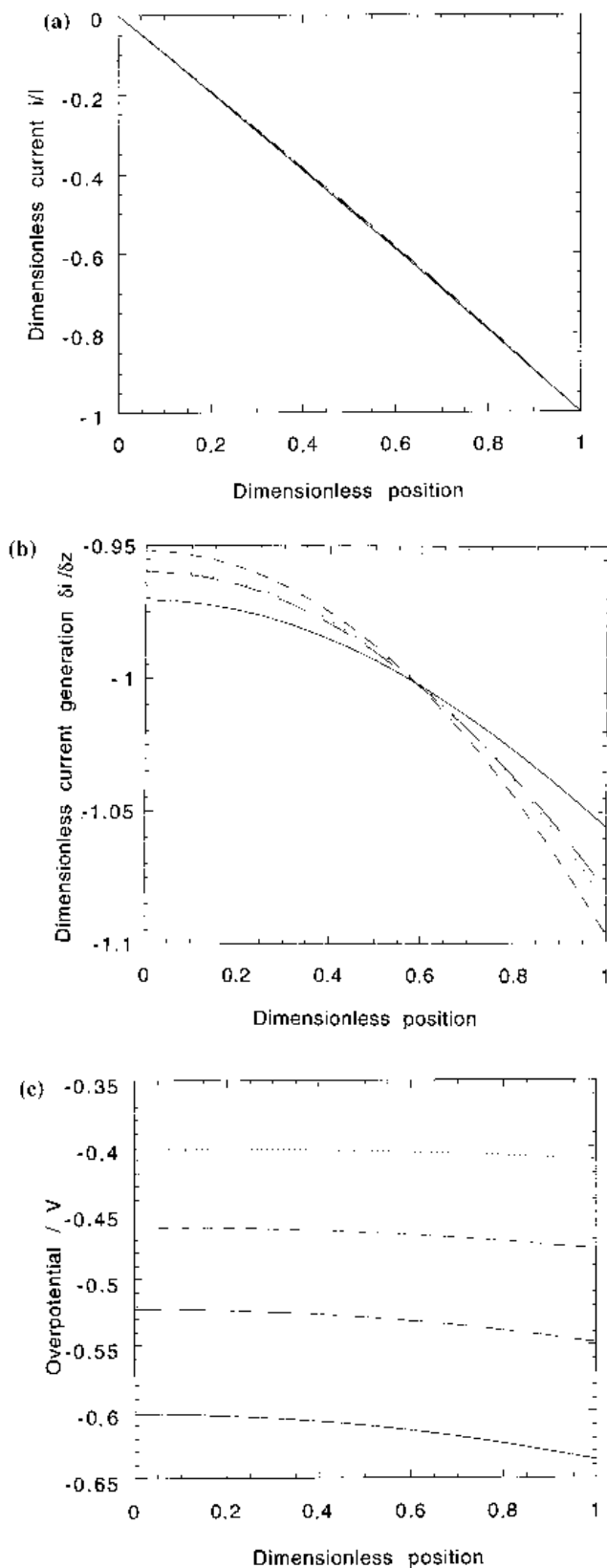


Fig. 11. Current distribution (a), current generation (b) and overvoltage distribution (c) in the active catalyst layer for the agglomerate model at different current densities (base-case parameter values): (···) 250, (- - -) 500, (- · - ·) 750 and (—) 1000 mA cm⁻².

cell. SEM studies show that the active layer produced by impregnating the electrode with Nafion[®] solution exhibits regions of Nafion[®] and electrode material separated by voids and pores.

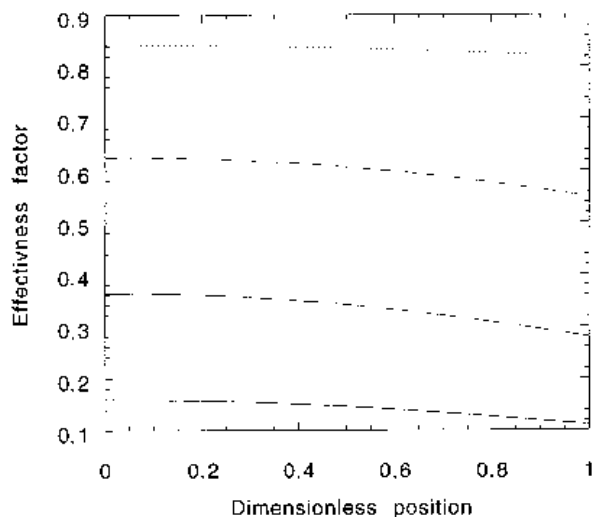


Fig. 12. Effectiveness factor as a function of the position in the active layer for the agglomerate model at different current densities: (···) 250, (- · - ·) 500, (- - -) 750 and (—) 1000 mA cm⁻².

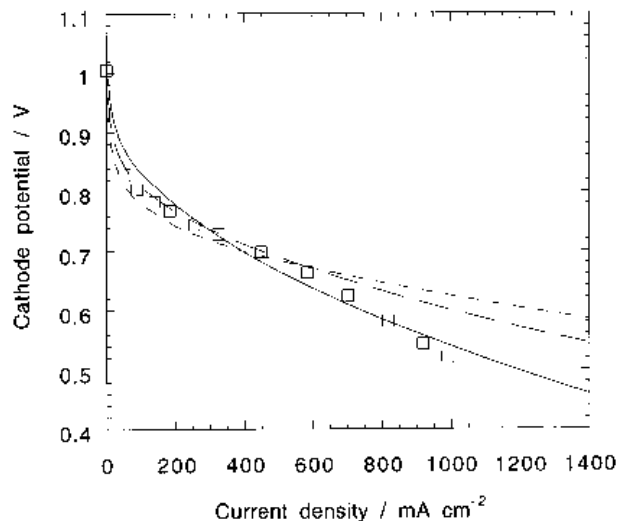


Fig. 14. The influence of the thickness of the active catalyst layer on the curves calculated by use of the film model: (- · - ·) $l = 7.5$, (- - -) $l = 15$ and (—) $l = 30$ μm.

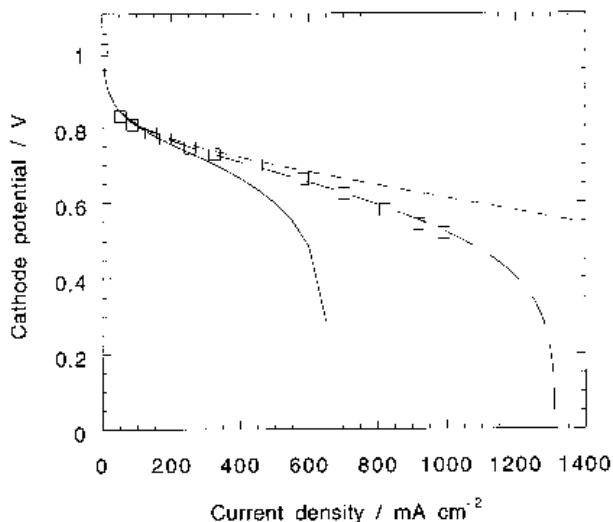


Fig. 13. Polarization curves for the agglomerate model for different values of thickness of the Nafion[®] film surrounding agglomerates: (- · - ·) $\delta = x/2$, (- - -) $\delta = x$, (—) $\delta = 2x$.

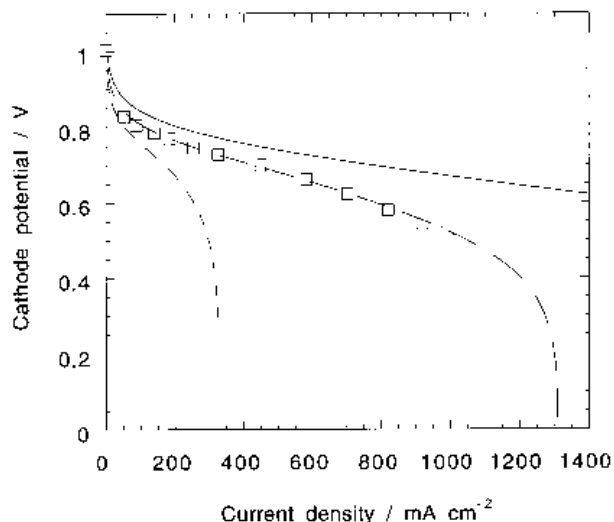


Fig. 15. The influence of the thickness of the active catalyst layer on the curves calculated by use of the agglomerate model: (- · - ·) $l = 7.5$, (- - -) $l = 15$ and (—) $l = 30$ μm.

Polarization curves for cathodes running on pure oxygen exhibit a change in shape at about 600 mA cm⁻² indicating mass transport limitation. These polarization curves cannot be satisfactorily simulated by use of a simple pseudohomogeneous film model. By means of the agglomerate model, a good agreement with the experimental curves can be achieved.

For cathodes running on air, the similar shapes of polarization curve can be explained by mass transport limitation in the electrode backing [10]. For oxygen cathodes, the film model has to be extended by introducing an extra diffusion restriction. This diffusion restriction could be a water film covering the active layer. However, the SEM study and permeability measurements of the electrodes impregnated by Nafion[®] [21] indicate an agglomerate structure.

Both the simulation of the structure of the active layer as well as the SEM observations indicate that

the active layer of the electrodes possess agglomerate structure. The active layer consists of agglomerates with a size of a few micrometres. The high performance of these electrodes is due to the gas pores which enables the utilization of the entire depth of the active layer even at high current densities. In the process of manufacturing of a membrane-electrode assembly, the active layer of the electrode is impregnated with a solution containing about 5% Nafion[®] in alcohols. After drying, the volume of the Nafion[®] phase decreases by about 95%. Taking this into account, it is reasonable to believe that voids in the active layer are produced during the evaporation of the solvent. By changing drying temperature and pressure, it may be possible to control the drying rate and the size of the agglomerates, and hence optimize the structure of the active layer.

Acknowledgements

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