

A current distribution model of a porous fuel cell electrode

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Abstract

A one-dimensional model of the current and potential distribution in a porous electrode, which accounts for internal limitations of mass transport is presented. The electrode kinetics of the reaction are described by the Tafel approximation and the mass transport limitations are described by a mass transfer coefficient. The model is solved analytically to give a convenient algebraic equation to predict the influence of electrode parameters, such as conductivity, thickness and specific surface area on electrode polarisation. The model can also predict the influence of reactant concentration and internal mass transport on the electrode polarisation behaviour. The predicted electrode polarization is in agreement with that observed for a porous platinum based anode. © 2004 Elsevier B.V. All rights reserved.

Keywords: Model; Porous electrode; Current and potential distribution; Fuel cell; Mass transport

1. Introduction

Three-dimensional porous electrodes are generally considered for reactions with low operating current densities in order to increase localised mass transfer rates and/or increase overall current per unit cell volume. Three dimensional electrode structures are also used in several applications, where high current densities are required at relatively low electrode and cell polarisation, e.g., water electrolysis and fuel cells. In these applications it is advantageous that all of the available electrode area is fully utilised in supporting high current densities at low polarisation. However conductivity limitations of three-dimensional electrodes generally cause current and overpotential to be non-uniform in the structure. There have been several treatments and models of three-dimensional and packed bed reactors developed over the years [1–4] and the field is still active due to the many applications of such systems.

In addition, as well as current distributions arising because of conductivity limitations, the reaction rate distribution may also be non-uniform due to the influence of mass transfer [1]. The maximum current

density at any position in the electrode structure is limited by the prevailing conditions of mass transfer. The limiting current thus can also have an effect on the reactor performance and particularly the potential distribution. The models of mass transfer-reaction in porous electrodes, which describe the potential distribution or concentration distribution, are non-linear differential equation(s), that are usually solved by linearization or numerical methods. In this paper we describe a model of the porous electrode in which internal mass transport limitations arise and are described by a simple mass transport coefficient. The objective of the model is to describe the current and potential distribution in the electrode by an analytical solution, which requires the solution of a non-linear algebraic equation.

2. Mathematical model of current distribution

2.1. Model system definition

Fig. 1 shows the model of the porous electrode under consideration. The model is for a one dimensional distribution of current and potential in a catalyst region in which the electrocatalyst is in both ionic and electronic contact.

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Nomenclature

a	specific area of electrode (m^{-1})	J^*	electrochemical reaction rate at the membrane
$\bar{a}$	constant defined in Eq. (35)	K	effective conductivity of electrode phase ($\Omega^{-1} \text{m}^{-1}$)
b	constant defined in Eq. (35)	l	electrode length in the direction of current flow (m)
c	constant defined in Eq. (35)	n	number of electrons involved in reaction
d	constant defined in Eq. (35)	p	constant defined in Eq. (22)
C	concentration in porous structure	q	constant defined in Eq. (22)
C_s	concentration of species at surface (mol m^{-3})	R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
C_{ref}	reference concentration (mol m^{-3})	T	temperature (K)
e	constant defined in Eq. (17)	U	constant defined in Eq. (22)
f	F/RT	x	distance in the direction of current flow (m)
F	Faraday constant (C mol^{-1})	z	dimensionless distance in the direction of current flow
j	proton current density (A m^{-2})	α	anodic charger transfer coefficient (dimensionless)
j_o	exchange current density (A m^{-2})	σ	conductivity in the electrolyte phase ($\Omega^{-1} \text{m}^{-1}$)
j_s	electronic current density (A m^{-2})	η	overpotential (V)
j_l	total current density (A m^{-2})		
j^*	dimensionless current density		
j_o^*	dimensionless variable defined in Eq. (23)		
j_L^*	dimensionless current density defined in Eq. (32)		

The region from $x = 0$ to $x = l$ is the catalyst region in which the concentration of reactant is assumed constant. This situation applies to a system with negligible mass transport resistance in the pores or when an approximate well mixed condition applies.

Applying Ohm's Law to proton and electron motion in the carbon/catalyst region and ionomer region covering the catalyst gives

$$-\sigma \frac{d\phi_m}{dx} = j, \quad (1)$$

$$-K \frac{d\phi_s}{dx} = j_s, \quad (2)$$

where j and j_s denote proton and electronic current density, respectively, ϕ_m and ϕ_s denote electrical potential in the ionomer and carbon phase and σ and K the corresponding effective conductivities.

The proton and electron current densities are related to the respective molar fluxes according to

$$dj/dx = -dj_s/dx. \quad (3)$$

Integrating over the catalyst layer gives

$$j + j_s = j_l, \quad (4)$$

where j_l is the current density loading for the cell, noting that at $x = 0$, the membrane is electronically insulating, i.e.,

$$j|_{x=0} = 0$$

and thus

$$j_l = j|_{x=l}.$$

In the catalyst region the overpotential, η , driving reaction is defined as

$$\eta = -(\phi_s - \phi_m). \quad (5)$$

The change in overpotential, from Eqs. (1) and (5), is

$$\frac{d\eta}{dx} = -\left(\frac{j}{\sigma} - \frac{j_s}{K}\right). \quad (6)$$

Substituting Eq. (4) into (6) gives

$$\frac{d\eta}{dx} = -j \left[\frac{1}{K} + \frac{1}{\sigma} \right] + \frac{j_l}{K}. \quad (7)$$

In many cases, e.g., for carbon supports, the electrical conductivity in the membrane is much less than that in the carbon layer and the terms $1/K$ can be ignored in Eq. (7), except at low current densities. However other lower conductivity supports are being considered in certain fuel cells (e.g., conducting polymers) and thus we do not adopt this assumption. In this way we can explore the influence of the relative conductivities of catalyst support and ionomer on fuel cell performance.

In the fuel cell, we adopt the following Butler–Volmer expression for electrochemical kinetics

$$j = j_{\text{oref}} \frac{C_s^\gamma}{C_{\text{ref}}^\gamma} \exp\left(\frac{\alpha_c F \eta}{RT}\right) \left[1 - \exp\left(-(\alpha_c + \alpha_a) \frac{F \eta}{RT}\right) \right], \quad (8)$$

where j_{oref} is the exchange current density at a reference concentration, C_{ref} , C_s is the reactant concentration in the pores, (at the catalyst surface) γ is the reaction order, α_c and α_a are transfer coefficients.

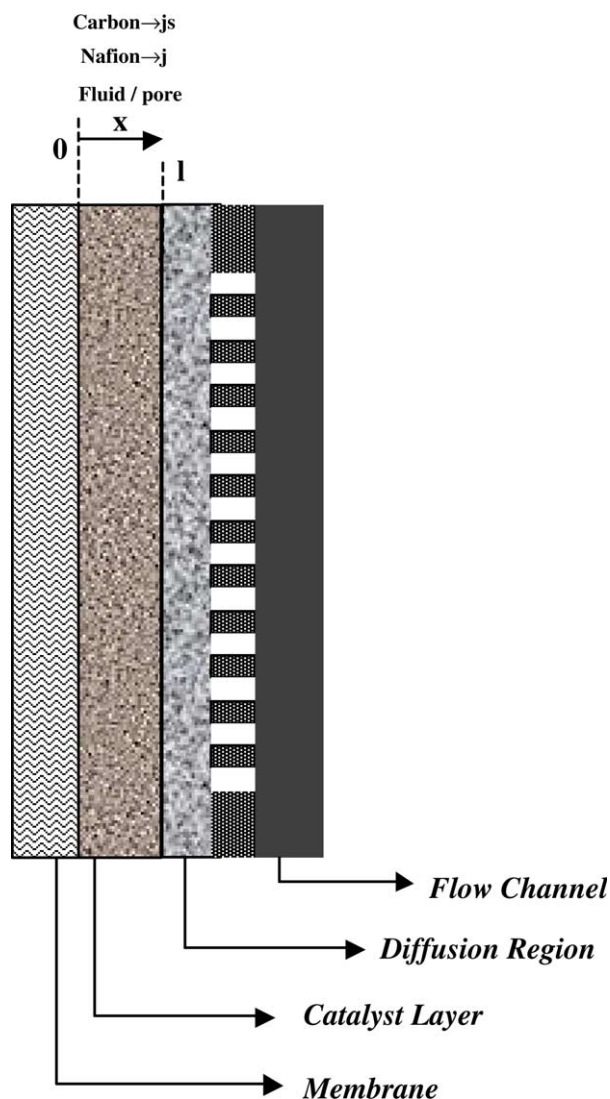


Fig. 1. Schematic diagram of the electrode model.

In certain cases, we can assume symmetry of the forward and reverse electrochemical reactions, i.e., $\alpha_c = \alpha_a = \alpha$

$$j = j_{\text{oref}} \frac{C_s^\gamma}{C_{\text{ref}}^\gamma} \exp(\alpha f \eta) (1 - \exp(-f \eta)), \quad (9)$$

where $f = F/RT$

With a Tafel approximation applied to high overpotentials we have from (9)

$$j = j_o C_s^\gamma \exp(\alpha f \eta), \quad (10)$$

where

$$j_o = j_{\text{osref}} / C_{\text{ref}}^\gamma.$$

It is known that, in fuel cells at high overall current density loads, mass transport limitations can arise. These mass transport limitations are due to several phenomena, which include fluid diffusion in gas diffusion regions, and reactant diffusion through ionomer

regions (also covered with water) in the electrocatalyst. We thus in the catalyst region define an effective mass transport coefficient, k_L , in the catalyst region such that

$$j = n F k_L (C - C_s) = k_L^* (C - C_s), \quad (11)$$

where C is the concentration of reactant in the pore.

2.1.1. Model solution

In the first instance we seek a solution to the current distribution problem assuming Tafel kinetics for the reaction. From this we will establish the overall electrode potential current density relationship for the electrode.

In the catalyst region, the change in ionic current density, i.e., due to proton conductivity is given by

$$\frac{dj}{dx} = -aj, \quad (12)$$

where a is a specific reaction surface area (m^{-1}).

Combining this with the Tafel Eq. (10).

$$\frac{dj}{dx} = -a C_s^\gamma j_o \exp(\alpha f \eta). \quad (13)$$

Differentiating Eq. (13) gives

$$\frac{d^2 j}{dx^2} = -a C_s^\gamma j_o \alpha f \exp(\alpha f \eta) \frac{d\eta}{dx}. \quad (14)$$

Eliminating $d\eta/dx$ using Eq. (7) gives

$$\frac{d^2 j}{dx^2} = a j \alpha f \left(j \left[\frac{1}{K} + \frac{1}{\sigma} \right] - \frac{j_l}{K} \right). \quad (15)$$

Noting Eq. (12) we obtain

$$\frac{d^2 j}{dx^2} = -\frac{dj}{dx} \alpha f \left[j \left(\frac{1}{K} + \frac{1}{\sigma} \right) - j_l / K \right] \quad (16)$$

and introducing the following dimensionless variables

$$z = x/l, \quad j^* = \alpha f l \left(\frac{1}{K} + \frac{1}{\sigma} \right) j,$$

$$\frac{d^2 j^*}{dz^2} + j^* \frac{dj^*}{dz} - e \frac{dj^*}{dz} = 0, \quad (17)$$

where

$$e = \alpha (f l / K) j_l.$$

Noting that $j^* dj^* = \frac{1}{2} d(j^*)^2$, Eq. (17) gives

$$\frac{d^2 j^*}{dz^2} + \frac{1}{2} \frac{d(j^*)^2}{dz} - e \frac{dj^*}{dz} = 0. \quad (18)$$

Integrating Eq. (18) gives

$$\frac{dj^*}{dz} + \frac{1}{2} j^{*2} - e j^* = \frac{dj^*}{dz} \Big|_0 + \left(\frac{j_o^*}{2} - e \right) j_o^*. \quad (19)$$

The term $-dj^*/dz|_0$ is the electrochemical reaction rate, J^* at the membrane, catalyst interface and is given by

$$\begin{aligned} -J^* &= \frac{dj^*}{dz} \Big|_0 = -\alpha l j_1 \\ &= -\alpha f l^2 \left(\frac{1}{K} + \frac{1}{\sigma} \right) j_0 C_s \exp(\alpha f \eta_0), \end{aligned} \quad (20)$$

where η_0 is the overpotential for the electrocatalyst region.

The term j_o^* in Eq. (19) is the dimensionless proton current density for the electrode. Integration of Eq. (19) over the electrode will give the polarization current density characteristics of the electrode from

$$\int_{j^*=j_o^*}^{j^*=0} \frac{dj^*}{[-J^* + ((j_o^*/2) - e)j_o^*] + ej^* - j^{*2}/2} = \int_z^1 dz. \quad (21)$$

Integration¹ gives

$$\begin{aligned} j_o^* &= e + \sqrt{q} \tan \left[\left(\sqrt{q} \frac{(1-z)}{2} \right) - U \right] \iff j_o^* \\ &= e + \sqrt{q} \frac{\left(\tan \left(\sqrt{q} \frac{(1-z)}{2} \right) - \tan U \right)}{1 + \left(\tan \left(\sqrt{q} \frac{(1-z)}{2} \right) \tan U \right)}, \end{aligned} \quad (22)$$

where

$$q = -e^2 - 2p,$$

$$p = -J_o^* + j_o^{*2}/2 - j_o^* e \quad (q > 0),$$

$$U = \tan^{-1} \left[\frac{e}{\sqrt{q}} \right] \iff \tan U = \left[\frac{e}{\sqrt{q}} \right].$$

When $z = 0$, this equation gives the electrode characteristics as

$$\begin{aligned} j_o^* &= e + \sqrt{q} \tan \left[\frac{\sqrt{q}}{2} - U \right] \iff j_o^* \\ &= e + \sqrt{q} \frac{\left(\tan \frac{\sqrt{q}}{2} - \tan U \right)}{1 + \left(\tan \frac{\sqrt{q}}{2} \tan U \right)}, \end{aligned} \quad (23)$$

i.e., in dimensionless variables

$$j_o^* = \alpha f l \left(\frac{1}{K} + \frac{1}{\sigma} \right) j_1,$$

hence

$$e = j_o^* \frac{1}{1 + (K/\sigma)}.$$

The electrode polarization characteristics can be determined through Eq. (10), i.e.,

$$J_o^* = -\frac{dj^*}{dz} \Big|_{z=0} = -\alpha f l \left(\frac{1}{K} + \frac{1}{\sigma} \right) j_0 C_s \exp(\alpha f \eta_0), \quad (24)$$

where η_0 is the overpotential of the electrode.

Thus, we can obtain the relationship between j_o and η_0 at the membrane interface and the polarisation curve for the electrode based on the current density per unit cross-section area.

We note that with the condition $K \gg \sigma$, Eq. (23) simplifies to

$$j_o^* = \sqrt{-2p} \tan \left(\sqrt{\frac{-p}{2}} \right), \quad (25)$$

$$\int_0^{j^*} \frac{(1 + \frac{e}{al}) dj^*}{\bar{J} - j^{*2}/2} = \int_1^z dz \quad (26)$$

gives

$$\left(1 + \frac{e}{al} \right) \left(\sqrt{\frac{2}{-\bar{J}}} \tan^{-1} \left(\sqrt{\frac{-1}{2\bar{J}}} j^* \right) \right) = 1 - z \quad (J < 0), \quad (27)$$

i.e.,

$$j^* = \sqrt{-2\bar{J}} \tan \left[\frac{(1-z)\sqrt{-\bar{J}}}{1 + e/al} \right], \quad (28)$$

where

$$\bar{J} = -J^* + \left(\frac{j_o^*}{2} - e \right) j_o^*.$$

2.2. The effect of mass transport

At high overpotential, we consider the situation where mass transport limitations arise due to diffusion of the reactant in water/ionomer layers covering the electrocatalyst. We consider the case of a first order reaction, i.e., $\gamma = 1.0$. Eqs. (10) and (11) combine to give

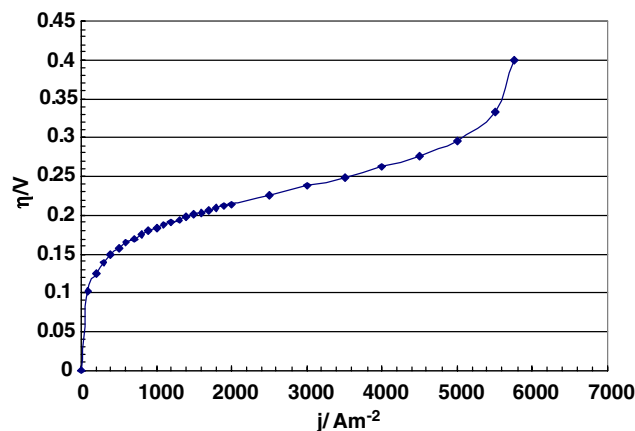


Fig. 2. The effect of mass transport on overpotential characteristics of a pseudo one-dimensional high-surface-area porous electrode. Predicted by Eq. (29) with $j_0 = 0.0046$, $C = 1000 \text{ mol m}^{-3}$, $\alpha = 1$, $k_1^* = 5.79$.

¹ Note that an alternative solution can be obtained via integration of Eq. (19) in the form.

$$j = \frac{C}{\left[\frac{1}{k_L^*} + \frac{1}{j_0 \exp(\alpha f \eta)} \right]} = \frac{C}{\sum R}. \quad (29)$$

Fig. 2 shows typical characteristics predicted by this equation for the case of an anode of a direct methanol fuel cell. The data are representative of a high surface area porous electrode of uniform potential in which mass transport limitations can result in limiting current behaviour. The purpose of this model is to apply the situation of “internal” mass transport limitations to a porous electrode exhibiting a significant current distribution in the direction of current flow through the electrode.

Substituting Eq. (29) into (12) and differentiating

$$\frac{d^2 j}{dx^2} = \frac{-\alpha f C}{(\sum R)^2} \frac{1}{j_0 \exp(\alpha f \eta)} \frac{d\eta}{dx}. \quad (30)$$

Substituting Eq. (7) gives

$$\frac{d^2 j}{dx^2} = \alpha f \left(\left[j^2 - \frac{j^3}{k_L^* C} \right] \left(\frac{1}{K} + \frac{1}{\sigma} \right) - \left(j - \frac{j^2}{k_L^* C} \right) \frac{j_1}{K} \right). \quad (31)$$

In terms of dimensionless variables, Eq. (31) becomes

$$+ \frac{d^2 j^*}{dz^2} = \frac{1}{3j_L^*} \frac{dj^{*3}}{dz} + e \frac{dj^*}{dz} - \frac{1}{2} \frac{dj^{*2}}{dz} - \frac{1}{2} \frac{e}{j_L^*} \frac{dj^{*2}}{dz}, \quad (32)$$

where

$$j_L^* = k_L^* C \alpha f l \left(\frac{1}{K} + \frac{1}{\sigma} \right).$$

Integration of Eq. (32) gives

$$\begin{aligned} \frac{dj^*}{dz} - \frac{j^{*3}}{3j_L^*} - ej^* + \frac{j^{*2}}{2} \left(1 + \frac{e}{j_L^*} \right) \\ = -J_0^* - \frac{j_0^{*3}}{3j_L^*} - ej_0^* + \frac{j_0^{*2}}{2} \left(1 + \frac{e}{j_L^*} \right) = \hat{J}. \end{aligned} \quad (33)$$

Re-arrangement of Eq. (33) enables integration

$$\frac{dj^*}{dz} \left[1 + \frac{e}{al} + \frac{j^{*2}}{3alj_L^*} \right] = \hat{J} - \frac{j^{*2}}{2} \left(1 + \frac{e}{j_L^*} \right) \quad (34)$$

to give

$$\left(\bar{a} - \frac{bc}{d} \right) \frac{1}{\sqrt{cd}} \tan^{-1} \left(j^* \sqrt{\frac{d}{c}} \right) + \frac{b}{d} j^* = (1 - z), \quad (35)$$

$$\bar{a} = 1 + \frac{e}{al}, \quad b = \frac{1}{al3j_L^*}, \quad c = -\hat{J}, \quad \bar{d} = \frac{1}{2} \left(\frac{e}{j_L^*} + 1 \right).$$

The overpotential current density arrangement is obtained when $z = 0$ as

$$\left(\bar{a} + \frac{b\hat{J}}{d} \right) \frac{1}{\sqrt{-\hat{J}d}} \tan^{-1} \left(j_0^* \sqrt{-\frac{d}{\hat{J}}} \right) + \frac{b}{d} j_0^* = 1.0. \quad (36)$$

For $z = 0$ Eq. (36) becomes

$$j_0^* = \frac{1}{\sqrt{\frac{d}{-\hat{J}}}} \tan \left[\frac{-\frac{b}{d} j_0^* + 1}{\frac{1}{\sqrt{-\hat{J}d}} \left(\bar{a} + \frac{b\hat{J}}{d} \right)} \right].$$

In this equation, a major parameter affecting mass transport is “ b ”. If this is small then no effect of mass transport would be seen.

In the absence of mass transport limitations $b \rightarrow 0$ and the solution becomes

$$\left(1 + \frac{e}{al} \right) \frac{1}{\sqrt{-\hat{J}/2}} \tan^{-1} \left(\frac{j^*}{\sqrt{-2\hat{J}}} \right) = (1 - z), \quad (37)$$

$$j^* = \sqrt{-2\hat{J}} \tan \left[\frac{(1 - z)\sqrt{-\hat{J}/2}}{1 + e/al} \right]. \quad (38)$$

When $e \rightarrow 0$ ($K \gg \sigma$) Eq. (36) gives the polarization behaviour as

$$\left(1 + 2b\hat{J} \right) \frac{1}{\sqrt{-\hat{J}/2}} \tan^{-1} \left(j_0^* \sqrt{-\frac{1}{2\hat{J}}} \right) + 2bj_0^* = 1.0, \quad (39)$$

$$j_0^* = \frac{\tan \left(\frac{\sqrt{-\hat{J}/2}}{(1 + 2b\hat{J})} (1 - 2bj_0^*) \right)}{\sqrt{-\frac{1}{2\hat{J}}}}.$$

3. Model results

3.1. Current distribution and electrode polarisation

Fig. 3 shows the variation of dimensionless current density with dimensionless overpotential. The variables are defined by Eqs. (23) and (24), respectively. The behaviour shows the expected increase of overpotential with current density. For the situation when the con-

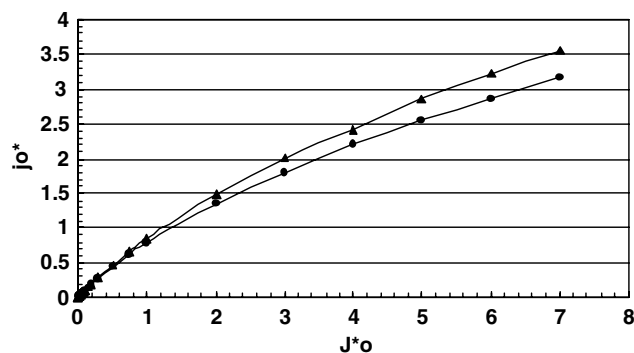


Fig. 3. Variation of dimensionless current density with dimensionless overpotential. $l = 10^{-5}$ m, $a = 118317$ m $^{-1}$, $\alpha = 1$, $j_0 C_s = 6 \times 10^4$ A m $^{-2}$, ▲: $K = 40$ Ω $^{-1}$ m $^{-1}$; ●: $K = 4000$ Ω $^{-1}$ m $^{-1}$, $\sigma = 3.4$ Ω $^{-1}$ m $^{-1}$.

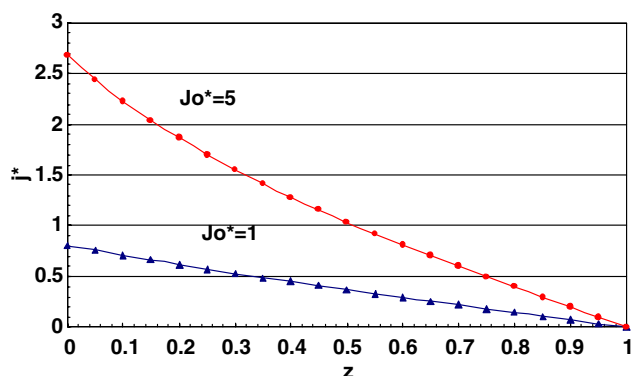


Fig. 4. Typical variation in current distribution in the absence of mass transport limitations. Parameters as in Fig. 3.

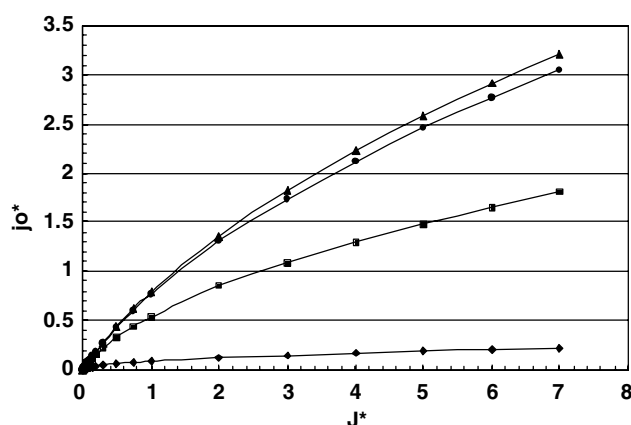


Fig. 5. The effect of the dimensionless electrode surface area on the dimensionless current distribution $K = 40 \Omega^{-1} \text{ m}^{-1}$, $\sigma = 3.4 \Omega^{-1} \text{ m}^{-1}$, a value varies as follows: $\blacktriangle$: 118000; $\bullet$: 59160; $\blacksquare$: 5916; $\blacklozenge$: 59.

ductivity of the electrode support is greater than that of the ionomer conductivity, a higher electrode (catalyst support) conductivity produces a higher current density at the same level of overpotential. This behaviour is a consequence of a greater depth of penetration of current into the electrode which improves the utilisation of the catalyst area.

Fig. 4 shows typical variation in current distribution in the absence of mass transport limitations. The current density, as expected, decreases from its maximum value at the membrane|catalyst electrode interface and decreases to zero at the point of current collection from the electrode. As expected a greater distribution in current density is seen with higher electrode polarization.

Fig. 5 shows the effect of the dimensionless electrode surface area on the dimensionless cell polarization behaviour. As would be expected, a higher surface area increases the overall current density at a given level of polarisation potential.

Overall the behaviour of the electrode predicted by the model is similar to that reported previously in other work on current distribution in porous electrodes [2,3]. We now however consider the case when the current

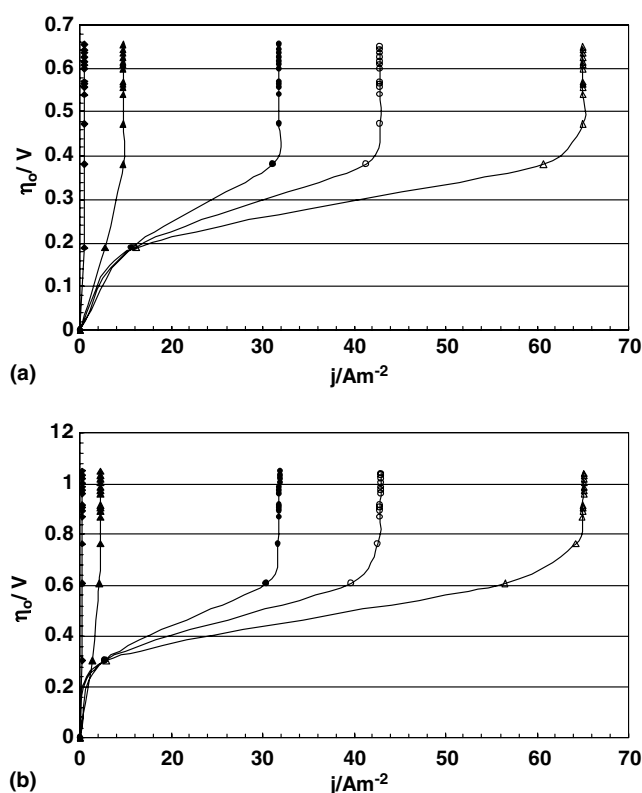


Fig. 6. The effect of surface area on the anode polarisation. (a) $K = 40 \Omega^{-1} \text{ m}^{-1}$, $j_1^* = 0.00413$, $\sigma = 3.4 \Omega^{-1} \text{ m}^{-1}$, a in m^2/m^3 varies as $\blacklozenge$: 1000; $\blacktriangle$: 10000; $\bullet$: 100000; $\circ$: 150000; $\triangle$: 250000, $C = 1000 \text{ mol m}^{-3}$, $k_1^* = 0.58$, $\alpha = 0.8$, $j_0 C_s = 28.9 \text{ A m}^{-2}$. (b) $K = 10 \Omega^{-1} \text{ m}^{-1}$, $j_1^* = 0.00413$, $\sigma = 1 \Omega^{-1} \text{ m}^{-1}$, a in m^2/m^3 varies as $\blacklozenge$: 1000; $\blacktriangle$: 10000; $\bullet$: 100000; $\circ$: 150000; $\triangle$: $C = 1000 \text{ mol m}^{-3}$, $k_1^* = 0.58$, $\alpha = 0.8$, $j_0 C_s = 62.2 \text{ A m}^{-2}$.

densities of operation are constrained by internal mass transport limitations.

3.2. The effect of mass transport

Fig. 6 shows the effect of mass transport on the current distribution in a porous electrocatalytic anode. The data are for a relatively low value of mass transport coefficient of approximately 10^{-6} m s^{-1} . The data show the general anticipated trend of a Tafel characteristic at lower overpotential which develops into a limiting current density situation with increase in overpotential. The data clearly show the advantage of using a higher surface area electrode (greater value of a) in that higher current densities are achieved at the same values of overpotential and that higher limiting current densities occur. Furthermore comparing Figs. 6(a) and (b), it can be seen that the higher exchange current density gives lower values of overpotential at the same current density.

Fig. 7 shows the effect of methanol concentration on anode polarization. As expected higher values of concentration decrease the extent of polarisation at a fixed current density and produce higher values of limiting currents.

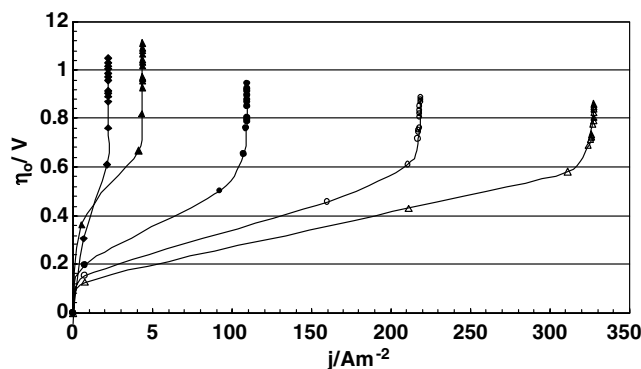


Fig. 7. The effect of reactant concentration on anode polarisation. $K = 10 \Omega^{-1} \text{ m}^{-1}$, $\sigma = 1 \Omega^{-1} \text{ m}^{-1}$, $\alpha = 100\,000 \text{ m}^2/\text{m}^3$, $k_1^* = 0.58$, $\alpha = 0.5$, C in mol m^{-3} varies as $\blacklozenge$: 500; $\blacktriangle$: 1000; $\bullet$: 2500; $\circ$: 5000; $\triangle$: 7500.

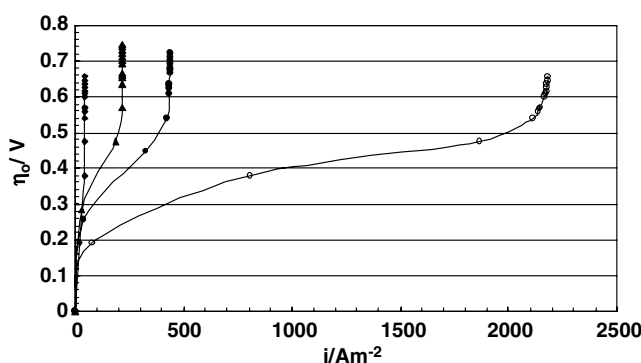


Fig. 8. The effect of pore mass transport coefficient on anode polarisation. $K = 40 \Omega^{-1} \text{ m}^{-1}$, $\sigma = 3.4 \Omega^{-1} \text{ m}^{-1}$, $\alpha = 100\,000 \text{ m}^2/\text{m}^3$, $C = 1000 \text{ mol m}^{-3}$, $\alpha = 0.8 k_1$ in m s^{-1} varies as $\blacklozenge$: 10^{-6} ; $\blacktriangle$: 5×10^{-6} ; $\bullet$: 5×10^{-5} ; $\circ$: 10^{-5} .

Fig. 8 shows the effect of mass transport on anode polarisation behaviour. A high value of mass transport coefficient locally in the electrode would prevent limiting currents of operation being reached internally until high values of overpotential occurred. Thus, as expected, an increase in mass transport coefficient has the effect of increasing the overall limiting current density for the electrode as well as reducing the overpotential at a fixed value of current density, when j is a significant fraction of j_L . Overall, the variation of current density with overpotential is in qualitative agreement with experimental data, shown in Fig. 9, for the oxidation of methanol at a fuel cell anode at a temperature of 60°C [5]. These data were obtained in a direct methanol fuel cell (9 cm^2) cross-sectional area, using a carbon supported Pt–Ru anode (2 mg cm^{-2}) hot pressed onto a Nafion® 117 membrane. A quantitative comparison between experiment and model data requires measurements to be made on methanol oxidation on the supported catalysts to provide appropriate basic kinetic data. In addition physical and electrical data characterizing the electrode are also required, all of which is outside the scope of the paper. However the character-

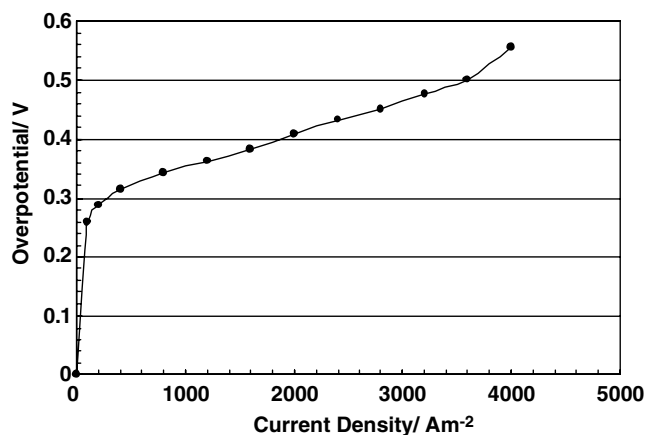


Fig. 9. Experimental data for the oxidation of methanol at a fuel cell anode at a temperature of 60°C [5]. Methanol flow rate $15 \text{ cm}^3 \text{ min}^{-1}$, 1.0 M aqueous methanol feed, air at ambient temperature and pressure.

istics of kinetic, mixed and mass transport control as shown experimentally are predicted by the model.

4. Conclusions

A one-dimensional model of a porous electrode has been developed, which accounts for the internal limitations of mass transport. The mass transport limitations are described by a simple mass transfer coefficient. The model predicts the influence of reactant concentration and internal mass transport on the electrode polarisation behaviour. The electrode polarisation is in agreement with that observed for a porous platinum based anode for the oxidation of methanol in a direct methanol fuel cell. Further experimental data are required to give a suitable validation to the model.

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