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# An analysis of the influence of mass transfer on porous electrode performance

Yan-Ping Sun[a], Keith Scott[b,*]

[a] *Chemical Engineering Department, Taiyuan University of Technology, Shanxi 030024, China*
[b] *School of Chemical Engineering and Advanced Materials, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK*

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**Abstract**

A model for a porous or particulate bed electrode reactor is presented. The model consists of nonlinear second-order ordinary differential equations, a one-dimensional Poisson equation, describing the effect of the electric field on this system, and a one-dimensional diffusion-reaction equation describing the concentration variation associated with diffusion. The model accounts for mass transport and heterogeneous electrochemical reaction. The solution of this model is by the approximate Adomian polynomial method and is used to determine lateral distributions of concentration, overpotential and current density, overall cell polarisation and effectiveness factors, and to simulate the effects of important system and operating parameters, i.e. local diffusion rates and mass transport coefficients.

*Keywords:* Three-dimensional electrode; Mathematical model; Mass transport; Electrochemical porous reactor

## 1. Introduction

There have been several treatments and models of three-dimensional, porous or particulate bed reactors developed over the years [1–8]. Three-dimensional electrodes are generally considered for reactions with low operating current densities in order to increase overall current per unit cell volume. Three-dimensional electrode structures are used in several applications, where high current densities are required at relatively low electrode and cell polarisation, e.g. water electrolysis and fuel cells. There have been several models of the current distribution in porous fuel cell electrodes particularly polymer electrolyte fuel cells which have employed phenomenological transport equations [9–15].

In general applications of porous electrodes it is advantageous that all of the available electrode area is fully utilised when 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. In addition the reaction rate distribution may also be non-uniform due to the influence of diffusion and convective mass transfer [2]. The maximum current density at any position in the electrode structure will be limited by the prevailing conditions of mass transfer, i.e. a limiting current can arise that can effect on the electrode performance and particularly the potential distribution.

The models of mass transfer reaction in porous electrodes, which describe the potential distribution or concentration distribution, are nonlinear differential equation(s), that are usually solved by linearisation and 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. This paper is based on a previous nonlinear analysis of a packed bed electrode model in which the bulk electrolyte reactant concentration was assumed constant, i.e. low reactant concentration [5]. In this paper we extend the model to the situation where there is a simultaneous variation in concentration as well as potential in the porous electrode.

In trying to interpret the non-uniformity of reaction rate and the utilisation of the electrode area a convenient and simple concept of effectiveness, *E*, can be used [2]. This allows the predicted maximum current density to be corrected to give the actual rate. The model solution is obtained using the Adomian's "inverse operator method" (IOM) or "decomposition method" [16]. This is an active field in nonlinear science that is particularly useful in studying nonlinear problems and can solve strong nonlinear differential equations without hypotheses such as linearity, perturbation, etc. [16–18]. In an earlier paper [2] we described the use of

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* Corresponding author. Tel.: +44-191-222-8771;
fax: +44-191-222-5292.
*E-mail address:* k.scott@ncl.ac.uk (K. Scott).

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**Nomenclature**

| | |
|---|---|
| $a$ | specific area of packed bed electrode ($\mathrm{m}^{-1}$) |
| $A_m$ | finite term approximate of Adomian polynomials |
| $A_n$ | Adomian polynomials |
| $c_{\mathrm{O}}$ | concentration of oxidised species in bulk ($\mathrm{mol\,m^{-3}}$) |
| $c_{\mathrm{Os}}$ | surface concentration of oxidised species ($\mathrm{mol\,m^{-3}}$) |
| $c_{\mathrm{R}}$ | concentration of reduced species in bulk ($\mathrm{mol\,m^{-3}}$) |
| $c_{\mathrm{Rs}}$ | surface concentration of reduced species ($\mathrm{mol\,m^{-3}}$) |
| $c_{\mathrm{O}}^0$ | reference concentration of oxidised species in bulk ($\mathrm{mol\,m^{-3}}$) |
| $c_{\mathrm{R}}^0$ | reference concentration of reduced species in bulk ($\mathrm{mol\,m^{-3}}$) |
| $C$ | dimensionless concentration $= c_{\mathrm{Rs}}/c_{\mathrm{R}}$ |
| $C_m$ | components of finite term approximate of dimensionless $C$ |
| $C_{\mathrm{s}}$ | dimensionless surface concentration |
| $D_i$ | diffusivity of species $i$ ($\mathrm{m^2\,s^{-1}}$) |
| $E$ | Effectiveness (dimensionless) |
| $F$ | Faraday constant ($\mathrm{C\,mol^{-1}}$) |
| $\vec{i}$ | current density ($\mathrm{A\,m^{-2}}$) |
| $i_{\mathrm{c}}$ | cathodic current density ($\mathrm{A\,m^{-2}}$) |
| $i_{\mathrm{in}}$ | intrinsic current density ($\mathrm{A\,m^{-2}}$) |
| $i_{\mathrm{l}}$ | limiting current density ($\mathrm{A\,m^{-2}}$) |
| $i_{\mathrm{T}}$ | total current density ($\mathrm{A\,m^{-2}}$) |
| $i_0$ | exchange current density ($\mathrm{A\,m^{-2}}$) |
| $I$ | dimensionless current density $= i_{\mathrm{T}}/ai_0L$ |
| $I_{\mathrm{loc}}$ | local dimensionless current density |
| $I_n$ | approximate of dimensionless current density |
| $L$ | bed length in the direction of current flow (m) |
| $\mathrm{L}^{-1}$ | inverse operator |
| $n$ | number of electrons involved in reaction |
| $N_i$ | flux of species $i$ ($\mathrm{mol\,m^{-2}\,s^{-1}}$) |
| $R$ | universal gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$) |
| $s$ | dimensionless parameter $= ai_0L^2/nFDc_{\mathrm{R}}$ |
| $T$ | temperature (K) |
| $x$ | distance in the direction of current flow (m) |
| $X$ | dimensionless distance in the direction of current flow $= x/L$ |
| *Greek letters* | |
| $\alpha$ | dimensionless parameter $= \alpha_{\mathrm{a}}\phi_1$ |
| $\alpha_{\mathrm{a}}$ | anodic charger transfer coefficient (dimensionless) |
| $\alpha_{\mathrm{c}}$ | catholic charger transfer coefficient (dimensionless) |
| $\beta$ | $nF/\mathrm{RT}$ ($\mathrm{V^{-1}}$) |
| $\gamma = i_{\mathrm{l}}/i_0$ | a dimensionless current density ratio |
| $\eta$ | overpotential $= \phi^1 - \phi^2 - \phi^0$ (V) |
| $\Theta_n$ | approximate of $n$ terms for dimensionless variable $\Phi$ |
| $\kappa$ | effective conductivity of electrolyte phase ($\Omega^{-1}\,\mathrm{m^{-1}}$) |
| $\mu$ | dimensionless parameter $= -\nu^2/\phi_1$ |
| $\nu^2$ | dimensionless parameter $= ai_0L^2\beta/\kappa$ |
| $\phi$ | dimensionless potential $= \beta\eta$ |
| $\phi_m$ | components of finite term approximate of dimensionless potential |
| $\phi_n$ | components of approximate of dimensionless potential |
| $\phi_0$ | dimensionless unknown constant |
| $\phi_1$ | dimensionless potential at membrane ($X = 1$) |
| $\phi^0$ | potential of open circuit (V) |
| $\phi^1$ | potential in conductive solid phase (V) |
| $\phi^2$ | potential in solution phase (V) |
| $\Phi$ | dimensionless potential variable $= \phi/\phi_1$ |
| $\Phi_m$ | components of finite term approximate of dimensionless $\Phi$ |
| $\Omega_n$ | approximate of $n$ terms for dimensionless variable $C$ |

an approximate Adomian method to solve the problem of a packed bed reactor. In this paper the method described is an improved Adomian decomposition which provides greater accuracy in solution.

## 2. Porous electrode analysis

The three-dimensional or packed bed electrode has a thickness $L$, bounded on one side by a current feeder ($x = 0$) and on the other side by a membrane or free solution ($x = L$) as shown in Fig. 1. Both electrolyte and electrode phases are assumed to be continuous media with uniform effective conductivities and in which the electrical potential obeys Ohm's law. Mass transport of reactant, in the porous electrode, is dominated by dispersion or diffusion, with negligible convective flow of fluid. Locally within the electrode there is a mass transport resistance between the electrode surface and the solution. This situation may, for example, arise when the surface of the electrode is covered by a thin layer of polymer electrolyte or in a fuel cell electrode in which the electrocatalyst is covered by a thin water layer. Thus within the porous structure there is a mass transport limitation between the bulk concentration in the pores and that at the surface of the catalyst particles in the porous electrode matrix. That is the kinetics of the

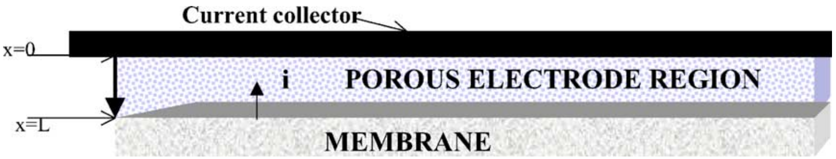

Fig. 1. Schematic diagram of porous electrode system.

electrochemical reaction are influenced by an internal mass transport resistance.

Additional assumptions adopted in this analysis are:

1. Isothermal and steady state conditions apply.
2. Ionic migration of the reacting species is neglected.
3. The electrode is characterised by a uniform specific area, $a$.
4. The mass transfer conditions between the fluid phase and fixed phase are also assumed to be uniform as defined by a single mass transport coefficient.

The model of the electrode is developed as follows [1]:

According to Ohm's law

$$\vec{i} = -\kappa \nabla \phi_2 \tag{1}$$

where $\vec{i}$ is the vector of local current density. $\nabla\phi_2$ is the gradient of potential of electrolyte and $\kappa$ is the effective conductivity of the electrolyte. The divergence of $\vec{i}$ is

$$\nabla \cdot \vec{i} = -\kappa \nabla \cdot \nabla \phi_2 = -\kappa \nabla^2 \phi_2 \tag{2}$$

and

$$\nabla \cdot \vec{i} = a i_0 \left[ \frac{c_{\mathrm{Rs}}}{c_{\mathrm{R}}^0} \exp\left(\frac{\alpha_{\mathrm{a}} nF\eta}{RT}\right) - \frac{c_{\mathrm{Os}}}{c_{\mathrm{O}}^0} \exp\left(-\frac{\alpha_{\mathrm{c}} nF\eta}{RT}\right) \right] \tag{3}$$

where $\nabla{\cdot}i$ is the transfer current per unit volume of the electrode and has the direction of an anodic current, and $\eta$ is the local overpotential, $\eta = \phi^1 - \phi^2 - \phi^0$.

$\phi^1$, the potential of electrode phase, is considered as a constant. $\phi^0$, the open-circuit value of $\phi^1 - \phi^2$ when the concentrations of the reduced and oxidised species are the initial $c_{\mathrm{R}}^0$ and $c_{\mathrm{O}}^0$, can be assumed to be zero [4].

Then the model for potential distribution in one dimension can be written as

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} = \frac{a i_0}{\kappa} \left[ \frac{c_{\mathrm{Rs}}}{c_{\mathrm{R}}^0} \exp\left(\frac{\alpha_{\mathrm{a}} nF\eta}{RT}\right) - \frac{c_{\mathrm{Os}}}{c_{\mathrm{O}}^0} \exp\left(-\frac{\alpha_{\mathrm{c}} nF\eta}{RT}\right) \right] \tag{4}$$

where $c_{\mathrm{R}}$ and $c_{\mathrm{O}}$ are concentrations of reduced and oxidised species (mol m$^{-3}$) and subscript 's' refers to surface concentrations and subscript 'O' the bulk reference concentrations.

For an anodic current only, Eq. (4) can be written with dimensionless variables as

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}X^2} = \nu^2 C_{\mathrm{s}} \exp(\alpha_{\mathrm{a}}\phi) \tag{5}$$

where

$$\phi = \beta\eta, \quad \beta = \frac{nF}{RT}, \qquad X = \frac{x}{L},$$

$$\nu^2 = \frac{a i_0 L^2 \beta}{\kappa}, \qquad C_{\mathrm{s}} = \frac{c_{\mathrm{Rs}}}{c_{\mathrm{R}}^0}$$

Assuming that diffusion in the porous electrode can be described by Fick's law, we have

$$\vec{N}_i = -D_i \nabla c_i \tag{6}$$

where $\vec{N}_i$ is the vector of local flux of reactant $i$, $\nabla c_i$ is the gradient of concentration of reactant $i$ and $D_i$ is the diffusion coefficient of $i$.

For the mass transfer only in the form of diffusion, the divergence of $\vec{N}_i$ should be

$$\nabla \cdot \vec{N}_i = -D_i \nabla \cdot \nabla c_i = -D_i \nabla^2 c_i \tag{7}$$

and a material balance for the key component in a volume element [1,4]

$$\nabla \cdot \vec{N} = R = \frac{a i_0}{nF} \left[ \frac{c_{\mathrm{Rs}}}{c_{\mathrm{R}}^0} \exp\left(\frac{\alpha_{\mathrm{a}} nF\eta}{RT}\right) - \frac{c_{\mathrm{Os}}}{c_{\mathrm{O}}^0} \exp\left(-\frac{\alpha_{\mathrm{c}} nF\eta}{RT}\right) \right] \tag{8}$$

where $R$ is the reaction term.

The concentration distribution in one dimension can be written as

$$\frac{\mathrm{d}^2 c_{\mathrm{R}}}{\mathrm{d}x^2} = \frac{a i_0}{nFD_{\mathrm{R}}} \left[ \frac{c_{\mathrm{Rs}}}{c_{\mathrm{R}}^0} \exp\left(\frac{\alpha_{\mathrm{a}} nF\eta}{RT}\right) \right] \tag{9}$$

$$\frac{\mathrm{d}^2 c_{\mathrm{O}}}{\mathrm{d}x^2} = \frac{-a i_0}{nFD_{\mathrm{O}}} \left[ \frac{c_{\mathrm{Os}}}{c_{\mathrm{O}}^0} \exp\left(\frac{\alpha_{\mathrm{c}} nF\eta}{RT}\right) \right] \tag{10}$$

For an anodic current, the Eq. (9) can be written with dimensionless variables as

$$\frac{\mathrm{d}^2 C}{\mathrm{d}X^2} = s C_{\mathrm{s}} \exp(\alpha_{\mathrm{a}}\phi) \tag{11}$$

where

$$C = \frac{c_{\mathrm{R}}}{c_{\mathrm{R}}^0}, \qquad s = \frac{a i_0 L^2}{nFD_{\mathrm{R}} c_{\mathrm{R}}^0}$$

Introducing the mass transfer parameter, for a Tafel-type reaction, assuming migration is negligible, the local flux will be

$$N_{\mathrm{loc}} = k_{\mathrm{avg}}(c_{\mathrm{R}} - c_{\mathrm{Rs}}) = \frac{i_{\mathrm{a}}}{nF} = i_0 \frac{c_{\mathrm{Rs}}}{c_{\mathrm{R}}^0} \exp(\alpha_{\mathrm{a}}\phi) \tag{12}$$

where $k_{\mathrm{avg}}$ is the average mass transfer coefficient in the electrode.

Then we can obtain

$$C_{\mathrm{s}} = \frac{C}{(i_0/nFk_{\mathrm{avg}}c_{\mathrm{R}}^0)\exp(\alpha_{\mathrm{a}}\phi)+1} \tag{13}$$

Thus the current density becomes

$$i_{\mathrm{a}} = \frac{C}{(1/i_0\exp(\alpha_{\mathrm{a}}\phi)) + (1/i_{\mathrm{l}})} \tag{14}$$

where the limiting current density $i_{\mathrm{l}} = nFk_{\mathrm{avg}}c_{\mathrm{R}}^0$.

Substituting Eq. (13) or (14) into Eqs. (5) and (11), the model equation can be rewritten as

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}X^2} = \nu^2\frac{C}{(1/\exp(\alpha_{\mathrm{a}}\phi)) + (1/\gamma)} \tag{15}$$

$$\frac{\mathrm{d}^2C}{\mathrm{d}X^2} = s\frac{C}{(1/\exp(\alpha_{\mathrm{a}}\phi)) + (1/\gamma)} \tag{16}$$

where $\gamma = i_{\mathrm{l}}/i_0$.

For convenience, let $\Phi = \phi/\phi_1$, $\mu = \nu^2/\phi_1$ and $\alpha = \alpha_{\mathrm{a}}\phi_1$. Hence a set of ordinary different equations with boundary conditions, which describes the potential and concentration distributions, can be obtained as

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}X^2} = \mu\frac{C}{(1/\exp(\alpha\Phi)) + (1/\gamma)} \tag{17}$$

$$\frac{\mathrm{d}^2C}{\mathrm{d}X^2} = s\frac{C}{(1/\exp(\alpha\Phi)) + (1/\gamma)} \tag{18}$$

$$X = 0, \qquad \frac{\mathrm{d}\Phi}{\mathrm{d}X} = 0, \qquad \frac{\mathrm{d}C}{\mathrm{d}X} = 0 \tag{19}$$

$$X = 1, \qquad \Phi = 1, \qquad C = 1 \quad \text{or} \quad \frac{\mathrm{d}\Phi}{\mathrm{d}X} = \mu I, \qquad \frac{\mathrm{d}C}{\mathrm{d}X} = sI \tag{20}$$

The dimensionless total current density, $I = i_{\mathrm{T}}/ai_0L$, where $i_{\mathrm{T}}$ is the total current density based on the cross-sectional area of the electrode.

The measurable or total current density, $i_{\mathrm{T}}$, based on the cross-sectional area of the electrode is given by

$$i_{\mathrm{T}} = \kappa\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)_{x=L} \tag{21}$$

or

$$i_{\mathrm{T}} = nFD\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_{x=L} \tag{22}$$

and

$$i_{\mathrm{T}} = ai_0LI = \frac{ai_0L}{\mu}\left(\frac{\mathrm{d}\Phi}{\mathrm{d}X}\right)_{X=1} = \frac{\phi_1\kappa}{L\beta}\left(\frac{\mathrm{d}\Phi}{\mathrm{d}X}\right)_{X=1} \tag{23}$$

or

$$i_{\mathrm{T}} = ai_0LI = \frac{ai_0L}{s}\left(\frac{\mathrm{d}C}{\mathrm{d}X}\right)_{X=1} = \frac{nFDc_{\mathrm{R}}^0}{L}\left(\frac{\mathrm{d}C}{\mathrm{d}X}\right)_{X=1} \tag{24}$$

where the dimensionless total current density, $I = i_{\mathrm{T}}/ai_0L$.

To assist in the solution of these difference equations we can obtain a relationship between $\Phi$ and $C$ combining Eqs. (17) and (18) to give

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}X^2} = \frac{\mu}{s}\frac{\mathrm{d}^2C}{\mathrm{d}X^2} \tag{25}$$

which on integration results in

$$\Phi - 1 = \frac{\mu}{s}(C-1) \tag{26}$$

Hence the potential and concentration drops across the electrode structure are related by the four parameters $\alpha$, $\gamma$, $\mu$ and $s$.

Combining Eqs. (17), (18) and (26) gives two independent different equations:

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}X^2} = \mu\frac{[1+(s/\mu)(\Phi-1)]}{(1/\exp(\alpha\Phi)) + (1/\gamma)} \tag{27}$$

$$X = 0, \qquad \frac{\mathrm{d}\Phi}{\mathrm{d}X} = 0$$

$$X = 1, \qquad \Phi = 1 \quad \text{or} \quad \frac{\mathrm{d}\Phi}{\mathrm{d}X} = \mu I$$

and

$$\frac{\mathrm{d}^2C}{\mathrm{d}X^2} = s\frac{C}{(1/\exp\{\alpha[1+(\mu/s)(C-1)]\}) + (1/\gamma)} \tag{28}$$

$$X = 0, \qquad \frac{\mathrm{d}C}{\mathrm{d}X} = 0$$

$$X = 1, \qquad C = 1 \quad \text{or} \quad \frac{\mathrm{d}C}{\mathrm{d}X} = sI$$

The effectiveness factor $E$ is given by

$$E = \frac{I}{\exp(\alpha_{\mathrm{a}}\phi_1)} = \frac{(\mathrm{d}\Phi/\mathrm{d}X)_{X=1}}{\mu\exp(\alpha)} \tag{29}$$

or

$$E = \frac{I}{\exp(\alpha_{\mathrm{a}}\phi_1)} = \frac{(\mathrm{d}C/\mathrm{d}X)_{X=1}}{\mu\exp(\alpha)} \tag{30}$$

## 3. Solution by Adomian's decomposition method

Wazwaz recently reviewed the Adomian decomposition method [19]. For a differential equation, Adomian's decomposition method suggests that the solution $u(x)$ be decomposed by an infinite series of components

$$u(x) = \sum_{n=0}^{\infty} u_{n(x)} \tag{31}$$

and the nonlinear function $f(x, u(x))$ by an infinite series of polynomials

$$f(x, u(x)) = \sum_{n=0}^{\infty} A_n \tag{32}$$

where $A_n$ are the so-called Adomain polynomials that can be generated for all types of nonlinearity according to algorithms set by Adomian [16].

In an operator form, Eqs. (27) and (28) can be written as

$$\mathrm{L}\Phi = \mu f_1(s, X, \Phi(X)) \tag{33}$$

$$\mathrm{L}C = s f_2(\mu, X, C(X)) \tag{34}$$

where $\mathrm{L} = \mathrm{d}^2/\mathrm{d}X^2$, and the inverse operator $\mathrm{L}^{-1}$ is a two-fold integral operator given by

$$\mathrm{L}^{-1}(\cdot) = \int_0^1 \left( \int_0^1 (\cdot)\,\mathrm{d}X \right) \mathrm{d}X \tag{35}$$

Applying $\mathrm{L}^{-1}$ to both sides of Eq. (10) yields

$$\Phi(X) = \mu \mathrm{L}^{-1}(f(X, \Phi(X)) \tag{36}$$

$$C(X) = s\mathrm{L}^{-1}(f(X, C(X)) \tag{37}$$

The decomposition series for $\Phi(X)$ and $C(X)$ can be given as

$$\sum_{n=0}^{\infty} \Phi_n(X) = \mu \mathrm{L}^{-1} \left( \sum_{n=0}^{\infty} A_n \right) \tag{38}$$

$$\sum_{n=0}^{\infty} C_n(X) = s \mathrm{L}^{-1} \left( \sum_{n=0}^{\infty} A_n \right) \tag{39}$$

where the Adomian polynomials $A_n$ are not the same in Eqs. (38) and (39).

For example, the first few Adomian polynomials $A_n$ for the equation of potential distribution are defined [3–5] by

$$\begin{gathered}
A_0 = f(\Phi_0) = \frac{1 + (s/\mu)(\Phi_0 - 1)}{(1/\exp(\alpha\Phi)) + (1/\gamma)} \\
A_1 = f^{(1)}(\Phi_0)\Phi_1 \\
A_2 = f^{(1)}(\Phi_0)\Phi_2 + \tfrac{1}{2} f^{(2)}(\Phi_0)\Phi_1^2 \\
A_3 = f^{(1)}(\Phi_0)\Phi_3 + f^{(2)}(\Phi_0)\Phi_1\Phi_2 + \frac{1}{3!} f^{(3)}(\Phi_0)\Phi_1^3 \\
\vdots \\
A_n \\
\vdots
\end{gathered} \tag{40}$$

The derivatives of the $n$th degree for the nonlinear term can be calculated as follows:

$$\text{Let}\, u = 1 + \frac{s}{\mu}(\Phi - 1) \quad \text{and} \quad v = \frac{1}{(1/\exp(\alpha\Phi_0)) + (1/\gamma)}$$

The first derivative of $u$ will be

$$u^{(1)} = \frac{s}{\mu} \tag{41}$$

The $n$th degree derivative of $v$ will be

$$v^n(\Phi_0) = \frac{n![-\alpha \exp(\alpha\Phi_0)^n]}{[\exp(-\alpha\Phi_0) + (1/\gamma)]^{n+1}} \tag{42}$$

Hence the derivative of the $n$th degree for the nonlinear term will be

$$\begin{aligned}
f^{(1)}(\Phi_0) &= uv^{(1)} + \frac{s}{\mu} v \\
f^{(2)}(\Phi_0) &= uv^{(2)} + 2\frac{s}{\mu} v^{(1)} \\
f^{(3)}(\Phi_0) &= uv^{(3)} + 3\frac{s}{\mu} v^{(2)} \\
f^{(4)}(\Phi_0) &= uv^{(4)} + 4\frac{s}{\mu} v^{(3)} \\
&\vdots \\
f^{(n)}(\Phi_0) &= uv^{(n)} + n\frac{s}{\mu} v^{(n-1)} \\
&\vdots
\end{aligned} \tag{43}$$

According to Eq. (38), the components of solution can be written as

$$\Phi(X) = \sum_{n=0}^{\infty} \Phi_n(X) \tag{44}$$

in which

$$\begin{gathered}
\Phi_0 = \text{unknown constant} \\
\Phi_1 = \mu \mathrm{L}^{-1}(A_0) = \mu f(\Phi_0) \frac{X^2}{2!} \\
\Phi_2 = \mu \mathrm{L}^{-1}(A_1) = \mu [f'(\Phi_0)\Phi_1] \frac{X^2}{3 \times 4} \\
\Phi_3 = \mu \mathrm{L}^{-1}(A_2) = \mu [f'(\Phi_0)\Phi_2 + \tfrac{1}{2} f''(\Phi_0)\Phi_1^2] \frac{X^2}{5 \times 6} \\
\Phi_4 = \mu \mathrm{L}^{-1}(A_3) = \mu \left[ f'(\Phi_0)\Phi_3 + f''(\Phi_0)\Phi_1\Phi_2 + \frac{1}{3!} f'''(\Phi_0)\Phi_1^3 \right] \frac{X^2}{7 \times 8} \\
\vdots \\
\Phi_n \\
\vdots
\end{gathered} \tag{45}$$

For easier calculation, we suggest rearranging the solution into an even power series form

$$\Phi(X) = \mu \left( b_0 + \sum_{n=1}^{\infty} b_n \frac{X^{2n}}{(2n)!} \right) \tag{46}$$

where the constant coefficients will be

$$\begin{aligned} b_0 &= \frac{\Phi_0}{\mu} \\ b_1 &= f(\Phi_0) \\ b_2 &= f^{(1)}(\Phi_0)b_1 \\ b_3 &= f^{(1)}(\Phi_0)b_2 + 3f^{(2)}(\Phi_0)b_1^2 \\ b_4 &= f^{(1)}(\Phi_0)b_3 + 15f^{(2)}(\Phi_0)b_1b_2 + 15f^{(3)}(\Phi_0)b_1^3 \\ &\vdots \end{aligned} \tag{47}$$

The derivative of the solution can be obtained directly

$$\frac{\mathrm{d}\Phi(X)}{\mathrm{d}X} = \mu\sum_{n=1}^{\infty} b_n \frac{X^{2n-1}}{(2n-1)!} \tag{48}$$

The solution and its derivative are in series form, in which the constant $\phi_0$, the value of the potential at $X = 0$, is undetermined, as yet.

The $n$-term approximates are

$$\Theta_n = \sum_{m=0}^{n} \Phi_m \tag{49}$$

$$\frac{\mathrm{d}\Theta_n}{\mathrm{d}X} = \sum_{m=0}^{n} \left(\frac{\mathrm{d}\Phi_m}{\mathrm{d}X}\right) \tag{50}$$

or

$$\Omega_n = \sum_{m=0}^{n} C_m \tag{51}$$

$$\frac{\mathrm{d}\Omega_n}{\mathrm{d}X} = \sum_{m=0}^{n} \left(\frac{\mathrm{d}C_m}{\mathrm{d}X}\right) \tag{52}$$

and serve as the approximate solution and its derivatives, and should satisfy the boundary conditions.

To determine the unknown constant $\Phi_0$, we impose the boundary condition $\Phi = 1$ or $C = 1$ at $X = 1$, or $\mathrm{d}\Phi/\mathrm{d}X = \mu I$ or $\mathrm{d}C/\mathrm{d}X = sI$ at $X = 1$ on the approximants. This will lead to an algebraic equation for each approximation with different terms. Having determined the constant $\phi_0$, the solution in a series form follows immediately.

Consequently, the local and total dimensionless currents $I_\mathrm{l}$ and $I$, respectively, and the effectiveness factor, $E$, can be calculated according to Eqs. (20), (29) and (30):

$$I_{\mathrm{l},n} = \frac{1}{\mu}\left(\frac{\mathrm{d}\Theta_n}{\mathrm{d}X}\right) = \frac{1}{s}\left(\frac{\mathrm{d}\Omega_n}{\mathrm{d}x}\right) \tag{53}$$

$$I_n = \frac{1}{\mu}\left(\frac{\mathrm{d}\Theta_n}{\mathrm{d}X}\right)_{X=1} = \frac{1}{s}\left(\frac{\mathrm{d}\Omega_n}{\mathrm{d}X}\right)_{X=1} \tag{54}$$

$$E_n = \frac{I_n}{\exp(\alpha_\mathrm{a}\phi_1)} = \frac{(\mathrm{d}\Theta_n/\mathrm{d}X)_{X=1}}{\mu\exp(\alpha_\mathrm{a}\phi_1)} = \frac{(\mathrm{d}\Omega_n/\mathrm{d}X)_{X=1}}{s\exp(\alpha_\mathrm{a}\phi_1)} \tag{55}$$

## 4. Discussion

The following describes the results of the model and the influence of the dimensionless parameters on potential and current distribution and effectiveness factors. All data were calculated by the decomposition method which was compared against a finite difference method using the BAND program [7]. In general the Adomian method gave faster convergence than that of the finite difference method, for the model over a wide range of parameters. The solutions obtained with 3, 4, 5 and 6 terms of Adomian polynomials have been compared and solution with four-term approximates of the Adomian polynomial achieved three-decimal point convergence for all data.

Fig. 2 shows the typical variation in local current density with distance in the electrode for different values of dimensionless potential. Increasing the potential has the expected effect of increasing the local current density and thereby increasing the overall variation in current density throughout the electrode. The term $\nu$ represents the relative influence of electrode kinetics to ionic conductance. An increase in the term $\nu$ (equivalent to higher surface area or thicker electrode) has the effect of decreasing the variation in dimensionless current density. In absolute terms an increase in $\nu$ will increase the current density (both $\nu$ and $I$ contain the term "$ai_0L$"). An increase in conductivity, which decreases the value of $\nu$, will increase the dimensionless current density through a more uniform potential distribution and a greater utilisation of the available electrode area. In general the relative effect of an increase in $\nu$ is more significant for the case of a lower value of $\gamma$, i.e. lower ratio of limiting current density to exchange current density, as this limits the current density that can be achieved due to mass transport constraints.

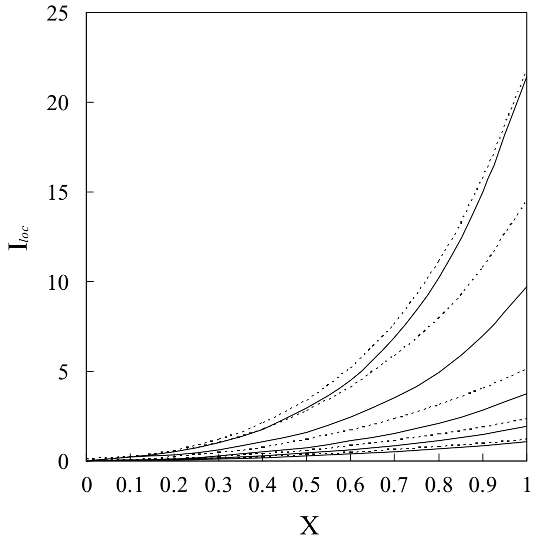

Fig. 2. Dimensionless current $I_\mathrm{loc}$ distributions with dimensionless distance $X$: $\alpha = 0.5$, $\gamma = 50$, $s = 0.1$; $\phi_1 = 0.5$, 1.0, 2.0, 4.0, 16.0 (from down to up). Solid line: $\nu^2 = 1.0$; dashed line: $\nu^2 = 0.1$.

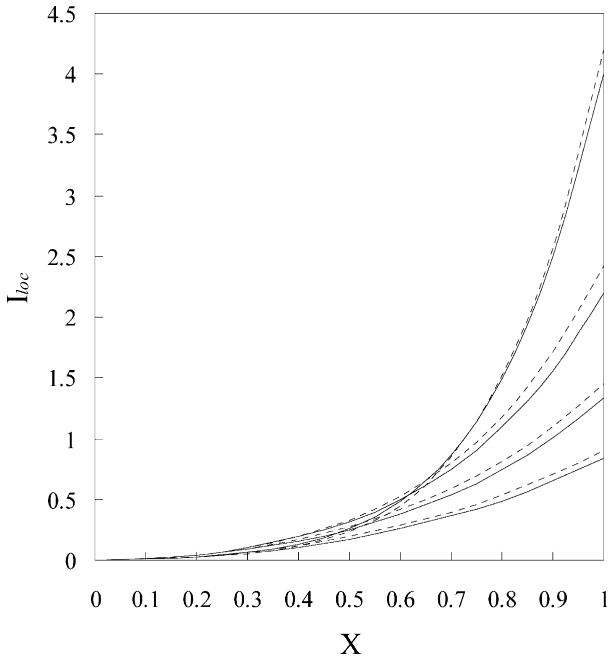

Fig. 3. Distribution of local dimensionless current densities $I_{\mathrm{loc}}$ with dimensionless distance $X$: $\alpha = 0.5, \gamma = 50, s = 1.0$; $\phi_1 = 0.5$, 1.0, 2.0, 8.0 (from up to down). Solid line: $\nu^2 = 1.0$; dashed line: $\nu^2 = 0.1$.

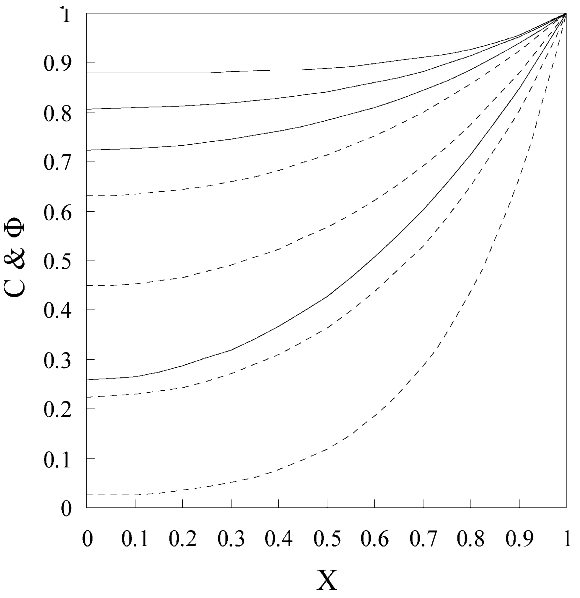

Fig. 5. The distributions of relative dimensionless potential $\Phi$ and dimensionless concentration $C$ with values of $\phi_1$ at membrane: $\alpha = 0.5$, $\nu^2 = 1.0$, $\gamma = 50.0$, $s = 1.0$; $\phi_1 = 0.5$, 2.0, 4.0, 8.0 (from up to down for $C$, from up to down for $\Phi$). Solid line: relative dimensionless potentials $\Phi$; dashed line: dimensionless concentration $C$.

The term $s$ represents a ratio of the kinetic rate to the diffusion rate in the electrode. Fig. 3 shows the effect of increasing the value of $s$, i.e. decreasing the diffusion rate relative to the kinetic rate, on the current distribution. It is evident in Fig. 3 that local current densities have been significantly reduced and that more of the electrochemical activity of the electrode is focused closer to the membrane. This is a consequence of the reduced concentration of reactant away from the membrane due to for example a slower diffusion rate (lower diffusion coefficient).

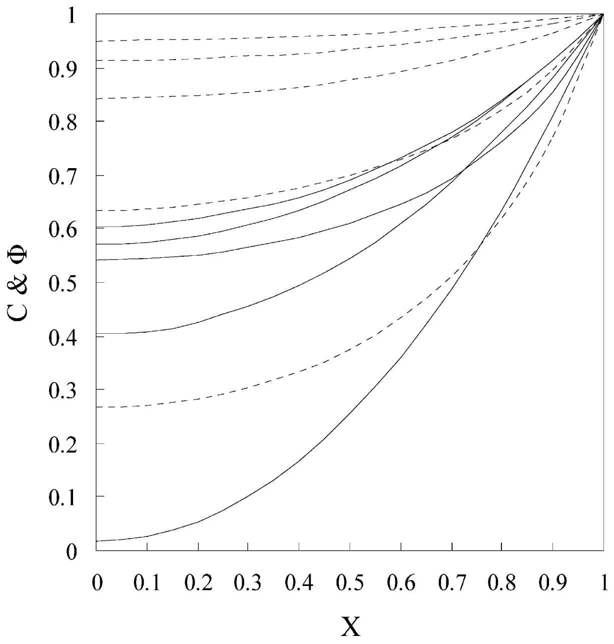

Fig. 4. The distributions of relative dimensionless potential $\Phi$ and dimensionless concentration $C$ with values of $\phi_1$ at membrane: $\alpha = 0.5, \nu^2 = 1.0, \gamma = 50.0, s = 0.1$. Dashed line—dimensionless concentration $C$: $\phi_1 = 0.5$, 2.0, 4.0, 8.0, 16.0 (from up to down); solid line—relative dimensionless potentials $\Phi$: $\phi_1 = 0.5$, 2.0, 4.0, 8.0, 16.0 (from up to down).

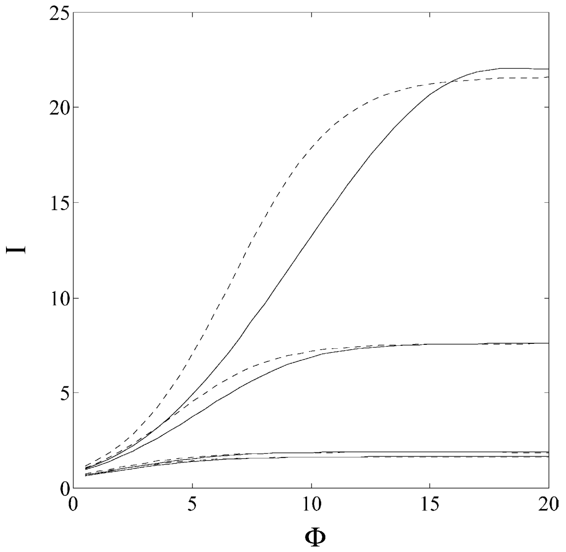

Fig. 6. The dependence of dimensionless total current density $I$ with dimensionless potential $\phi_1$ at membrane: $\alpha = 0.5$ for all data. Dashed line: $\nu^2 = 0.1$ for all data; $\gamma = 50$, $s = 0.1$; $\gamma = 50$, $s = 1.0$; $\gamma = 10$, $s = 0.1$; $\gamma = 10$, $s = 1.0$ (from up to down). Solid line: $\nu^2 = 1.0$ for all data; $\gamma = 50$, $s = 0.1$; $\gamma = 50$, $s = 1.0$; $\gamma = 10$, $s = 0.1$; $\gamma = 10$, $s = 1.0$ (from up to down). The data of third and fourth sets almost overlapped for both sets above.

Fig. 4 shows the variation in dimensionless concentration and overpotential in the electrode under conditions equivalent to those of Fig. 3. As expected the concentration and relative overpotential decrease further away from the membrane due to the combined effect of diffusion mass transport and the poor penetration of current into the electrode due to ionic conductivity limitations.

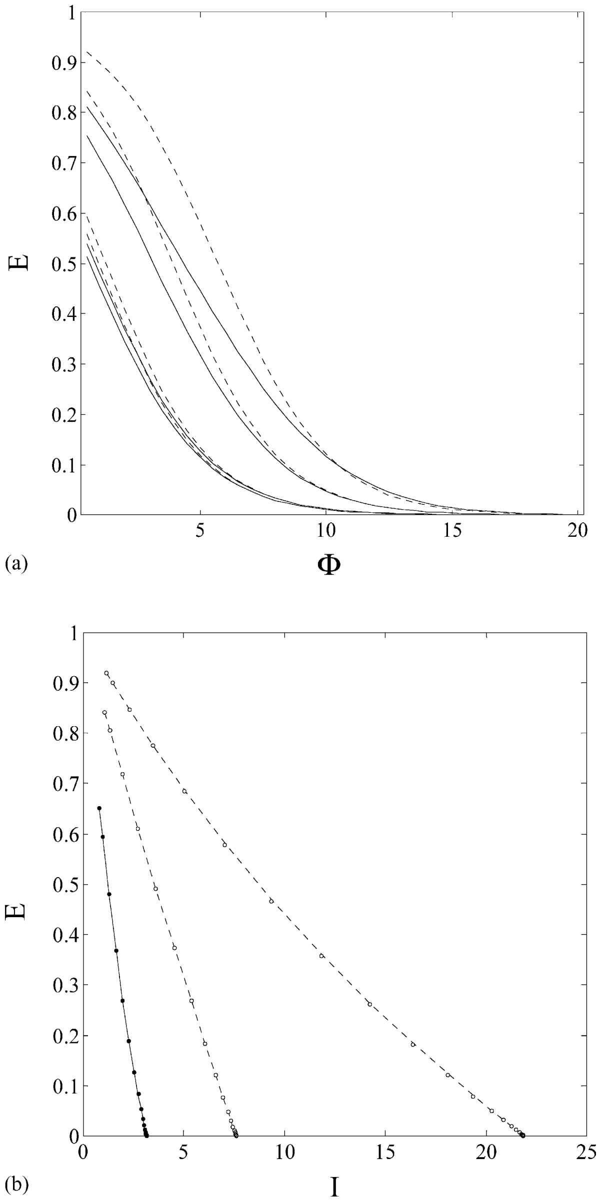

Fig. 7. (a) The dependence of effectiveness factor $E$ and the dimensionless potential $\phi_1$ at membrane for a Tafel reaction influenced by mass transport $\alpha = 0.5$ for all data. Dashed line: $\nu^2 = 0.1$ for all data; $\gamma = 50$, $s = 0.1$; $\gamma = 10$, $s = 0.1$; $\gamma = 50$, $s = 1.0$; $\gamma = 10$, $s = 1.0$ (from up to down). Solid line: $\nu^2 = 1.0$ for all data; $\gamma = 50$, $s = 0.1$; $\gamma = 10$, $s = 0.1$; $\gamma = 50$, $s = 1.0$; $\gamma = 10$, $s = 1.0$ (from up to down). (b) The comparison of decomposition data with numerical data for the dependence of effectiveness factor $E$ and the dimensionless total current $I$ for a Tafel reaction influenced by mass transport: $\alpha_c = 0.5$; $\gamma = 10.0$, $s = 1.0$; $\gamma = 10.0$, $s = 0.1$; $\gamma = 50.0$, $s = 0.1$ (from left to right). Solid line: $\nu^2 = 1.0$, (●) numerical result; dashed line: $\nu^2 = 0.1$, (○) numerical result.

Fig. 5 shows the variation in dimensionless concentration and overpotential in the electrode when the relative rate of kinetics to diffusion has been increased, i.e. an increase in the parameter $s$ (from 0.1 to 1.0). Clearly there is a greater variation in concentration with an increase in the parameter, $s$, at a given overpotential due to a relatively slower diffusion rate.

Fig. 6 shows predictions of the overall electrode polarisation characteristics, i.e. dimensionless overpotential versus current behaviour. As expected as the value of the overpotential at the membrane increases the electrode takes on limiting current density characteristics. As expected as the value of the parameter $\gamma$ decreases (local mass transport coefficient is lower) the electrode approaches a lower mass transport limiting current density state as overpotential rises. The overall dimensionless limiting currents are also higher at lower values of the parameter $\nu$. In addition as the relative rate of internal diffusion decreases ($s$ increases), the values of the overall limiting current densities are lower.

Fig. 7a and b shows the typical variation in effectiveness factor with dimensionless potential and current density respectively as a function of the mass transfer parameter $\gamma$. As expected effectiveness falls as either overpotential or current density increases. The effectiveness is greater as the parameter $\gamma$ increases due to an increase in the relative value of limiting current density. At a fixed value of dimensionless potential, effectiveness is higher at lower values of the parameter $\nu$, due an improved current distribution, for example, due to higher conductivity of electrolyte. Notably with high values of limiting currents high values of effectiveness are achieved at lower overpotentials or very low overall current densities.

Also shown in Fig. 7b are values of the cell polarisation, predicted by solution of the model using the BAND finite difference method. There is generally good agreement between the two solutions and confirms the suitability of the Adomian method for the solution of this type of nonlinear model. An advantage of the decomposition method is that it leads to a faster convergence in solution.

## 5. Conclusions

The solution of the nonlinear problem of the potential distribution in three-dimensional electrodes has been obtained using the Adomian decomposition method. The model is able to predict the influence of key kinetic and operational parameters on current and potential distribution, effectiveness and overall cell polarisation. The solution method gives results which are comparable to those obtained with an efficient finite difference method, although with a faster convergence than that method.

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