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*Highlights (for review)

- The time independent nonlinear reaction-diffusion equations have been formulated and solved analytically for the first time
- Applied the new approach of Homotopy perturbation method
- Analytical solutions are compared with zero order analytical solutions.

A New Mathematical Modelling Using Homotopy Perturbation Method to Solve Nonlinear Equations in Enzymatic Glucose Fuel Cells

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Abstract

For the first time a mathematical modelling of the enzymatic glucose membraneless fuel cell with direct electron transfer has been reported. The niche of this mathematical modelling is the description of the new Homotopy perturbation method to solve the nonlinear differential equations that describes glucose concentration and hydrogen ions respectively. The analytical results of an enzymatic fuel cell should be used, while developing fuel cell, to estimate its various kinetic parameters to attain the highest power value. Our analytical results are compared with limiting case results and satisfactory agreement is noted. The influence of parameters on the concentrations are discussed.

Keywords: Mathematical modelling; Nonlinear differential equation; Enzyme; Biofuel cell; New Homotopy perturbation method.

1. Introduction

Glucose cells are energy devices that convert chemical energy from glucose fuel to electricity [1-2]. Theoretically, glucose can be completely oxidized to carbon dioxide and water, releasing 24 electrons per glucose molecule [3]. An enzymatic glucose biofuel cell uses glucose as fuel and

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4 enzymes as biocatalyst, to transform biochemical energy into electrical energy [4]. Enzymatic
5 fuel cells convert the chemical energy of biofuels into electrical energy. Unlike traditional fuel
6 cell types, which are mainly based on metal catalysts, the enzymatic fuel cells employ enzymes
7 as catalysts [5].
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11 Enzymatic fuel cells (EFCs) have been proposed that can catalyse oxidation of fuels at anodes
12 and/or reduction of oxidants at cathodes to provide electrical power. Electron transfer as opposed
13 to hydrogen transfer was demonstrated in the oxidation-reduction of the flavour protein enzyme
14 system [6]. Recent research into enzymatic fuel cells has focused on the use of glucose as a fuel
15 [7].
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19 Modeling biofuel cells play an important role in understanding and developing new energy
20 devices. The enzymatic fuel cells mathematical models are based on a system of non-linear
21 equations, including reaction and transport kinetics [8, 9], statistical analysis [10] and metabolic
22 control analysis [11]. Theoretical, numerical and experimental methods for estimating the biofuel
23 cell performance was discussed by various authors [12 - 15]. Ivan Ivanov presented the major
24 research activities concerned with the enzymatic biofuel cells by highlighting the current
25 problems [5]. Osman *et al.* [15] developed a two-dimensional steady-state and dynamic models
26 for an enzymatic fuel cell. Baronas *et al.* [16], discussed a mathematical model of a chemically
27 modified amperometric biosensor. Nonlinear reaction-diffusion equations in this model are
28 solved using the finite difference technique. Saravanakumar *et al.* [17] analyzed the current-
29 potential response of the enzyme-catalyzed as well as the redox polymer mediated kinetic
30 scheme pertaining to biofuel cells. Saravanakumar *et al.* [18] discussed theoretical treatment of a
31 reaction and diffusion processes in a biofuel cell electrode, for the steady and non-steady state
32 condition. Rasi *et al.* [19] solved the one-dimensional nonlinear reaction-diffusion equation in an
33 enzyme-catalyzed oxygen reduction reaction in biofuel cells. Malini Devi *et al.* [20] analyzed the
34 theoretical behavior of biofuel cell/biosensor.
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38 Rubin developed an analytical model for enzymatic glucose membraneless fuel cell with direct
39 electron transfer [1]. Though there are several models and expressions available in the literature
40 that corresponds to various phenomena and processes at biofuel cells, to the best of our
41 knowledge, there are not rigorous analytical expressions for the steady state current for
42 enzymatic glucose biofuel cells. In this paper we have derived the analytical expression for the
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concentration of glucose and hydrogen ions in the enzyme layer and outside the enzyme layer, corresponding current density and electrical power in the enzymatic fuel cells.

2. Mathematical formulation of the problem

The change of hydrogen ions concentration and glucose is associated with the diffusion and the enzymatic reaction. The kinetics and mass transport in the enzyme layer ($0 < x < L$) can be represented by the following non-linear differential equations for steady state condition.

$$D_{H^+} \frac{d^2 c_{H^+}}{dx^2} + \frac{2k_{cat}[E_T][G]}{K_M + [G]} = 0 \quad (1)$$

$$D_G \frac{d^2 [G]}{dx^2} - \frac{2k_{cat}[E_T][G]}{K_M + [G]} = 0 \quad (2)$$

where D_G, D_{H^+} are the diffusion coefficients of glucose and hydrogen ions respectively, c_{H^+} is the concentration of hydrogen ions and $[G]$ is the concentration of glucose .

Outside of the enzyme layer ($L < x < d$), the hydrogen ions diffusion can be expressed by the following equation: [1].

$$D_{bH^+} \frac{d^2 c_{H^+}}{dx^2} = 0 \quad (3)$$

Boundary conditions

Let $x=0$ represents the anode surface, while $x=L$ is the boundary between the anode and the buffer solution. The concentration of hydrogen ions and glucose at the anode surface ($x=0$) are represented by the following equations: [1].

$$c_{H^+} \Big|_{x=0} = c_0 \quad (4)$$

$$[G] \Big|_{x=0} = [G_0] \quad (5)$$

where c_0 is the hydrogen ions concentration between the glucose reservoir and an anode and $[G_0]$ is the glucose concentration in the glucose reservoir. Since the amount of charge is proportional to the amount of material passed through the interface, another boundary condition is represented by the following equation:

$$\frac{d[G]}{dx} \Big|_{x=0} = \frac{-g_{1s}}{zD_G} \quad (6)$$

where $g_{1s} = \frac{k_{cat}[E_s][G]}{K_M + [G]}$ is the surface reaction rate and z is the number of elementary ionic charges. In the bulk solution the hydrogen ions concentration remain constant [1].

$$c_{H^+} \Big|_{x=d} = c_d \quad (7)$$

On the boundary between two regions having different diffusivities, the matching conditions are defined by the Eq. (8) and Eq. (9) [1].

$$D_{H^+} \frac{dc_{H^+}}{dx} (\text{flux of the hydrogen ions inside the enzyme layer}) \Big|_{x=L} = D_{bH^+} \frac{dc_{H^+}}{dx} (\text{flux of the hydrogen ions outside the enzyme layer}) \Big|_{x=L} \quad (8)$$

$$c_{H^+} (\text{concentration of hydrogen ions inside the enzyme layer}) \Big|_{x=L} = c_{H^+} (\text{concentration of hydrogen ions outside the enzyme layer}) \Big|_{x=L} \quad (9)$$

These conditions mean that the equal species fluxes through the same surface and conditions of a continuity for concentrations. Eq. (8) and Eq. (9) describe the boundary conditions between the anode and the bulk where $x=L$ for hydrogen ions. Boundary conditions employed in the enzymatic glucose fuel cell for the glucose and hydrogen ions are also represented in Figure 1. Current density j occurring at the electrode surface due to reduction or oxidation of c_{H^+} is given by Eq. (10):

$$j = zFD_{H^+} \left(\frac{dc_{H^+}}{dx} \right)_{x=0} \quad (10)$$

3. Dimensionless form

We make the nonlinear PDE (Eqs. (1) – (3)) dimensionless by defining the following parameters which are depicted in Eq. (11):

$$\bar{c}_{H^+} = \frac{c_{H^+}}{c_0}, \quad [\bar{G}] = \frac{[G]}{[G_0]}, \quad \bar{X} = \frac{x}{d}, \quad \alpha = \frac{2d^2 k_{cat}[E_T]}{D_G K_M}, \quad \beta = \frac{[G_0]}{K_M}, \quad \xi_1 = \frac{D_G}{D_{H^+}}, \quad \xi_2 = \frac{D_{H^+}}{D_{bH^+}} \quad \text{and} \quad c_i = \frac{[G_0]}{c_0} \quad (11)$$

where \bar{c}_{H^+} , $[\bar{G}]$, \bar{X} , α , β , ξ_1 , ξ_2 and c_i represent dimensionless concentration of hydrogen ions for glucose, distance, reaction diffusion parameter, saturation parameter, ratio between diffusion coefficients and ratio between initial concentration of glucose and hydrogen ions respectively.

Now in $(0 < \bar{X} < L/d)$, Eq. (1) and Eq. (2) reduces to the following dimensionless forms which are represented by Eqs. (12) and (13):

$$\frac{d^2 \bar{c}_{H^+}}{d\bar{X}^2} + \frac{\alpha \xi_1 c_i [\bar{G}]}{1 + \beta [\bar{G}]} = 0 \quad (12)$$

$$\frac{d^2 [\bar{G}]}{d\bar{X}^2} - \frac{\alpha [\bar{G}]}{1 + \beta [\bar{G}]} = 0 \quad (13)$$

In the bulk $(L/d < \bar{X} < 1)$, the hydrogen ions (Eq. (3)) reduced to

$$\frac{d^2 \bar{c}_{H^+}}{d\bar{X}^2} = 0 \quad (14)$$

The boundary conditions Eqs. (4) - (7) are reduced to [1].

$$\bar{c}_{H^+} = 1 \text{ at } \bar{X} = 0 \text{ when } (0 < \bar{X} < L/d) \quad (15)$$

$$\bar{c}_{H^+} = \frac{c_d}{c_0} \text{ at } \bar{X} = 1 \text{ when } (L/d < \bar{X} < 1) \quad (16)$$

$$[\bar{G}] = 1 \text{ at } \bar{X} = 0 \text{ (} 0 < \bar{X} < L/d \text{)} \quad (17)$$

$$\left. \frac{d[\bar{G}]}{d\bar{X}} \right|_{\bar{X}=0} = \frac{-dg_{1s}}{zG_0 D_G} = \frac{-\alpha L}{2dz(1 + \beta)} \text{ when } (0 < \bar{X} < L/d) \quad (18)$$

The matching boundary conditions (8) and (9) are defined in dimensionless form as follows.

$$\xi_2 \left. \frac{d\bar{c}_{H^+}}{d\bar{X}} \right|_{\bar{X}=L/d} \text{ (flux inside the enzyme layer)} = \left. \frac{d\bar{c}_{H^+}}{d\bar{X}} \right|_{\bar{X}=L/d} \text{ (flux outside the enzyme layer)} \quad (19)$$

$$\bar{c}_{H^+} \Big|_{\bar{X}=L/d} \text{ (concentration inside the enzyme layer)} = \bar{c}_{H^+} \Big|_{\bar{X}=L/d} \text{ (concentration outside the enzyme layer)} \quad (20)$$

The dimensionless current density I becomes

$$I = \frac{jd}{zFD_{H^+} c_0} = \left(\frac{d\bar{c}_{H^+}}{d\bar{X}} \right)_{\bar{X}=0} \quad (21)$$

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4 **4. Analytical expression of substrate and products concentration using new Homotopy**
5 **perturbation method**
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7 By solving the Eqs. (12) and (13) using boundary conditions Eqs. (15) - (20), we can obtain the
8 glucose concentration and hydrogen ions (Appendix A) inside the enzyme layer ($0 < \bar{X} < L/d$)
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$$[\bar{G}](\bar{X}) = \cosh\left(\sqrt{\frac{\alpha}{1+\beta}}\bar{X}\right) - \left(\frac{L}{2dz}\sqrt{\frac{\alpha}{1+\beta}}\right)\left(\sinh\left(\sqrt{\frac{\alpha}{1+\beta}}\bar{X}\right)\right) \quad (22)$$

$$\bar{c}_{H^+}(\bar{X}) = 1 + \frac{1}{\mu_2}\left[\mu_0 + \mu_1\left(1 - \frac{L}{d}\right)\right]\bar{X} + \xi_1 c_i \left[1 - \cosh\left(\sqrt{\frac{\alpha}{1+\beta}}\bar{X}\right) + \sqrt{\frac{\alpha}{1+\beta}}\left(\frac{L}{2dz}\right)\sinh\left(\sqrt{\frac{\alpha}{1+\beta}}\bar{X}\right)\right] \quad (23)$$

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19 By solving the Eq. (14) using boundary conditions (Eqs. (15)- (20)), we can obtain the
20 concentration of hydrogen ions in outside the enzyme layer ($L/d < \bar{X} < 1$) as follows:
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$$\bar{c}_{H^+}(\bar{X}) = \frac{c_d}{c_0} + \frac{1}{\mu_2}\left(\xi_2\mu_0 - \frac{\mu_1 L}{d}\right)(\bar{X} - 1) \quad (24)$$

23
24 The dimensionless current density becomes
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$$I = \frac{jd}{zFD_{H^+}c_0} = \left(\frac{d\bar{c}_{H^+}}{d\bar{X}}\right)_{\bar{X}=0} = \frac{1}{\mu_2}\left[\mu_0 + \mu_1\left(1 - \frac{L}{d}\right)\right] - \xi_1 c_i \sqrt{\frac{\alpha}{1+\beta}}\left(\frac{L}{2dz}\right) \quad (25)$$

$$\text{where } \mu_0 = \frac{c_d}{c_0} - \xi_1 c_i \left[1 - \cosh\left(\sqrt{\frac{\alpha}{1+\beta}}\frac{L}{d}\right) + \sqrt{\frac{\alpha}{1+\beta}}\left(\frac{L}{2dz}\right)\sinh\left(\sqrt{\frac{\alpha}{1+\beta}}\frac{L}{d}\right)\right] - 1 \quad (26)$$

$$\mu_1 = \xi_2 \left[\xi_1 c_i \sqrt{\frac{\alpha}{1+\beta}} \sinh\left(\sqrt{\frac{\alpha}{1+\beta}}\frac{L}{d}\right) - \left(\frac{\alpha \xi_1 c_i}{1+\beta}\right)\left(\frac{L}{2dz}\right) \cosh\left(\sqrt{\frac{\alpha}{1+\beta}}\frac{L}{d}\right) \right] \quad (27)$$

$$\text{and } \mu_2 = \xi_2 \left(1 - \frac{L}{d}\right) + \frac{L}{d} \quad (28)$$

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Electrical power is given by the Eq. (29)

$$P = \frac{\bar{P}d^2}{RT[G_0]D_G L} = \frac{\alpha z[\bar{G}]\left(\ln \frac{c_L}{c_d}\right)}{2(1+\beta[\bar{G}])} \quad (29)$$

The kinetic response of an enzymatic fuel cell depends on concentrations of $[\bar{G}]$ and \bar{c}_{H^+} . The concentrations of the species depend upon concentration of the substrate $[\bar{G}]$. However, the substrate $[\bar{G}]$ also depends on two factors which are α and β . K_M is the Michaelis-Menten constant, an intrinsic character of an enzyme.

5. Limiting case results

5.1. Saturated (zero order) catalytic kinetics

We initially consider the situation where the concentration of glucose is very much greater than Michaelis-Menten constant K_M . In this case $\beta > 1$ and Eqs. (12) and (13) reduced to:

$$\frac{d^2 \bar{c}_{H^+}}{d\bar{X}^2} + \frac{\alpha \xi_1 c_i}{\beta} = 0 \quad (30)$$

$$\frac{d^2 [\bar{G}]}{d\bar{X}^2} - \frac{\alpha}{\beta} = 0 \quad (31)$$

Solving the Eqs. (30) and (31) using boundary conditions (Eqs. (15) - (20)), we can obtain the concentration of glucose and hydrogen ions inside the enzyme layer ($0 < \bar{X} < L/d$) as follows;

$$[\bar{G}](\bar{X}) = 1 - \left(\frac{\alpha}{\beta} \right) \left(\frac{L}{2dz} \right) \bar{X} + \frac{\alpha}{2\beta} \bar{X}^2 \quad (32)$$

$$\bar{c}_{H^+}(\bar{X}) = 1 + \left[\frac{\alpha \xi_1 c_i}{\beta} \left(\frac{L}{d} \right) - \frac{1}{\mu_2} \left(1 + \frac{\alpha \xi_1 c_i}{2\beta} \left(\frac{L}{d} \right)^2 - \frac{c_d}{c_0} \right) \right] \bar{X} - \frac{\alpha \xi_1 c_i}{2\beta} \bar{X}^2 \quad (33)$$

Solving the Eq. (13) using boundary conditions (Eqs. (15) - (20)), we can obtain the concentration of hydrogen ions outside the enzyme layer ($L/d < \bar{X} < 1$) as follows;

$$\bar{c}_{H^+}(\bar{X}) = \frac{1}{\mu_2} \left(\xi_2 \left(\frac{\alpha \xi_1 c_i}{2\beta} \left(\frac{L}{d} \right)^2 + 1 - \frac{c_d}{c_0} \right) \right) (1 - \bar{X}) + \frac{c_d}{c_0} \quad (34)$$

The current density becomes

$$I = \frac{j d}{z F D_{H^+} c_0} = \left(\frac{d \bar{c}_{H^+}}{d \bar{X}} \right)_{\bar{X}=0} = \frac{\alpha \xi_1 c_i}{\beta} \left(\frac{L}{d} \right) - \frac{1}{\mu_2} \left(\frac{\alpha \xi_1 c_i}{2\beta} \left(\frac{L}{d} \right)^2 + 1 - \frac{c_d}{c_0} \right) \quad (35)$$

where μ_2 is defined by Eq. (28). In this case electrical power becomes:

$$\text{Electrical power } p = \frac{\bar{P}d^2}{RT [G_0]D_G L} = \frac{\alpha z \left(\ln \frac{c_L}{c_d} \right)}{2\beta} \quad (36)$$

5.2. Unsaturated (first order) catalytic kinetics

Now we consider the second major limiting situation found in practice, when the glucose concentration is less than Michaelis-Menten constant K_M . This situation will pertain when $\beta \leq 1$.

Hence Eqs. (12) and (13) are reduced to:

$$\frac{d^2 \bar{c}_{H^+}}{d\bar{X}^2} + \alpha \xi_1 c_i [\bar{G}] = 0 \quad (37)$$

$$\frac{d^2 [\bar{G}]}{d\bar{X}^2} - \alpha [\bar{G}] = 0 \quad (38)$$

Hence, the nonlinear Eqs. (12) and (13) have been reduced to one equation which is linear. By solving the Eq. (37) and Eq. (38) using boundary conditions (Eqs. (15) - (20)), we can obtain the concentration of glucose and hydrogen ions inside the enzyme layer ($0 < \bar{X} < L/d$) as follows;

$$[\bar{G}](\bar{X}) = \cosh(\sqrt{\alpha} \bar{X}) - \left(\frac{\sqrt{\alpha} L}{2dz} \right) (\sinh(\sqrt{\alpha} \bar{X})) \quad (39)$$

$$\bar{c}_{H^+}(\bar{X}) = 1 + \frac{1}{\mu_2} \left[\mu_3 + \mu_4 \left(1 - \frac{L}{d} \right) \right] \bar{X} + \xi_1 c_i \left[1 - \cosh(\sqrt{\alpha} \bar{X}) + \left(\frac{\sqrt{\alpha} L}{2dz} \right) \sinh(\sqrt{\alpha} \bar{X}) \right] \quad (40)$$

Solving the Eq. (14) using boundary conditions (Eqs. (15) - (20)) we can obtain the concentration of hydrogen ions outside the enzyme layer ($L/d < \bar{X} < 1$) as follows;

$$\bar{c}_{H^+}(\bar{X}) = \frac{1}{\mu_2} \left(\xi_2 \mu_3 - \left(\frac{L}{d} \right) \mu_4 \right) (\bar{X} - 1) + \frac{c_d}{c_0} \quad (41)$$

In this case current density becomes represented by the following Eq. (42):

$$I = \frac{jd}{zFD_{H^+} c_0} = \left(\frac{d\bar{c}_{H^+}}{d\bar{X}} \right)_{\bar{X}=0} = \frac{1}{\mu_2} \left[\mu_3 + \mu_4 \left(1 - \frac{L}{d} \right) \right] + \xi_1 c_i \left(\frac{\sqrt{\alpha} L}{2dz} \right) \quad (42)$$

where μ_2 is defined in Eq. (28) and μ_3 and μ_4 are described by Eqs. (43) and (44) as follows:

$$\mu_3 = \frac{c_d}{c_0} - \xi_1 c_i \left[1 - \cosh\left(\sqrt{\alpha} \frac{L}{d}\right) + \sqrt{\alpha} \left(\frac{L}{2dz} \right) \sinh\left(\sqrt{\alpha} \frac{L}{d}\right) \right] - 1 \quad (43)$$

$$\mu_4 = \xi_2 \left[\xi_1 c_i \sqrt{\alpha} \sinh \left(\sqrt{\alpha} \frac{L}{d} \right) - (\alpha \xi_1 c_i) \left(\frac{L}{2dz} \right) \cosh \left(\sqrt{\alpha} \frac{L}{d} \right) \right] \quad (44)$$

Therefore, by re-organising those equations, the electrical power becomes as:

$$P = \frac{\bar{P} d^2}{RT [G_0] D_G L} = \frac{\alpha z [\bar{G}] \left(\ln \frac{c_L}{c_d} \right)}{2} \quad (45)$$

6. Results and discussion

Here Eqs. (22) – (24) are the analytical expressions of concentration of glucose, hydrogen ions inside of the enzyme layer ($0 < \bar{X} < L/d$) and hydrogen ions outside of the enzyme layer ($L/d < \bar{X} < 1$). For an enzymatic fuel cell to be analytically useful, its response must be quantitatively related to the substrate concentration. Based on this principle, $\beta > 1$ is not the proper case for an enzymatic fuel cell, because in the zero order reaction, hydrogen ions concentration is independent of the glucose concentration. Eq. (22) represents the most general approximate new analytical expression for the glucose concentration profiles for all values of parameter α (or distance between electrodes) and β (or initial concentration of glucose).

Dimensionless concentration of hydrogen ions (\bar{c}_{H^+}) inside the enzyme layer ($0 < \bar{X} < L/d$) and outside the enzyme layer ($L/d < \bar{X} < 1$) versus dimensionless distance from the anode \bar{X} using Eq. (23) and Eq. (24) is plotted in Fig. 2. From this figure it is inferred that the concentration of Hydrogen ion increases absurdly from the anode surface and reaches the maximum near the boundary of the enzyme layer ($\bar{X} = L/d$) and then decreases slowly to c_d/c_0 in the bulk solution. Because the hydrogen ions are generating on the anode, moving towards the cathode and consumed on the cathode. Also this is due to the effect of c_d/c_0 as an individual term in the equations (23) and (24).

Dimensionless concentration of hydrogen ions \bar{c}_{H^+} in the inside the enzyme layer as a function of distance from the anode \bar{X} are plotted in Figs. 3(a)-3(e) for various values of $\alpha, \beta, c_i, \xi_1$ and ξ_2 and some fixed values of other parameters using Eq. (23) and Eq. (40). From Figs. 3(a)-3(e), it is inferred that the concentration of hydrogen ions in the interface between

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4 inside the enzyme layer and outside the enzyme layer ($\bar{X} = L/d$) is high because generation of
5 hydrogen ions.
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10 Figs. 4(a)-4(b) represent dimensionless concentration profiles of the concentration of hydrogen
11 ions \bar{c}_{H^+} ($L/d < \bar{X} < 1$) versus distance from the anode surface \bar{X} for various values of
12 parameters using Eq. (24) and Eq. (41). From this figures, it is observed that the concentration of
13 the hydrogen ions decreases in outside the enzyme layer due to consumption of the hydrogen
14 ions in this layer.
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22 Eq. (25) represents the simple closed form of analytical expression of current density. Figs.
23 5(a)-5(d) represent the dimensionless current density I versus dimensionless parameter α for
24 various values of other parameters. From this figures it is observed that the current density is
25 directly proportional to enzyme concentration or square of the distance between electrodes. Also
26 current density is linear with respect to dimensionless thickness of enzyme layer and ratio
27 between diffusion coefficient of glucose and hydrogen ions (ξ_1) (Fig. 6(a)-6(c)).
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35 Figs. 7(a)-7(c) to 9(a)-9(c) represent dimensionless power versus dimensionless glucose
36 concentration $[\bar{G}]$, dimensionless parameter α and β for various values of parameters using Eq.
37 (29). From this figures it is observed that the power density increases when concentration of
38 glucose, enzyme, initial concentration of glucose and c_L/c_d . Also from this figures it is also
39 observe that power density p attains the maximum value and then remains constant because of
40 external resistance and consequence of a current reduction. Increasing the enzyme concentration
41 or distance between electrodes has an important effect on the fuel cell (Fig. 7(a)). Power does not
42 differ significantly give to due to increase of glucose concentration.
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52 **7. Conclusions**

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54 The time independent nonlinear reaction-diffusion equations have been formulated and solved
55 analytically for the first time. The analytical expressions for glucose, hydrogen ions inside and
56 outside the enzyme layer, current density and power are derived for all parameters using a new
57 approach of Homotopy perturbation method. In addition, these analytical solutions are compared
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with zero order analytical solutions. This analytical result is useful to investigate the effects of various parameters of the fuel cell on power. A good agreement with limiting case results for the experimental values of the all parameters is also noted.

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9. Appendixes

Appendix A: Approximate analytical solution of nonlinear Eq. (13) using a new approach to the Homotopy perturbation method (NHPM)

In this appendix, we have indicated how to determine the solution of Eq. (13). To solve Eq. (13), we first construct the Homotopy for the equation as follows:

$$(1-p) \left[\frac{d^2[\bar{G}]}{d\bar{X}^2} - \frac{\alpha[\bar{G}]}{1+\beta([\bar{G}](\bar{X}=0))} \right] + p \left[\frac{d^2[\bar{G}]}{d\bar{X}^2} - \frac{\alpha[\bar{G}]}{1+\beta[\bar{G}]} \right] = 0 \quad (A1)$$

$$(1-p) \left[\frac{d^2[\bar{G}]}{d\bar{X}^2} - \frac{\alpha[\bar{G}]}{1+\beta} \right] + p \left[\frac{d^2[\bar{G}]}{d\bar{X}^2} - \frac{\alpha[\bar{G}]}{1+\beta[\bar{G}]} \right] = 0 \quad (A2)$$

The approximate solution of (A2) is given by

$$[\bar{G}] = [\bar{G}_0] + p[\bar{G}_1] + p^2[\bar{G}_2] + \dots \quad (A3)$$

Substituting Eq. (A3) comparing the coefficient of p^0 we obtain the following differential equation:

$$p^0 : \frac{d^2[\bar{G}_0]}{d\bar{X}^2} - \frac{\alpha[\bar{G}_0]}{1+\beta} = 0 \quad (A4)$$

Solving Eq. (A4) by using boundary conditions Eq. (17) and Eq. (18), we obtain the following equation:

$$[G_0] = \cosh \left(\sqrt{\frac{\alpha}{1+\beta}} \bar{X} \right) - \left(\frac{L}{2dz} \sqrt{\frac{\alpha}{1+\beta}} \right) \left(\sinh \left(\sqrt{\frac{\alpha}{1+\beta}} \bar{X} \right) \right) \quad (A5)$$

Similarly, we can obtain the Eq. (23) and Eq. (24).

Appendix B. Nomenclature and units

Symbols	Definitions	Units and Experimental values
$[G]$	Glucose concentration	0.1M, 0.01M, 0.001M
c_{H^+}	Hydrogen ions concentration	M
x	Distance	m
k_{cat}	Kinetic enzyme reaction rate	10^3 Sec^{-1}
K_M	Kinetic enzyme reaction rate	0.019M
$[E_T]$	Volume enzyme concentration	$0.7 \times 10^{-5} \text{M}$, $0.5 \times 10^{-5} \text{M}$, $0.3 \times 10^{-5} \text{M}$, $0.1 \times 10^{-5} \text{M}$
L	Thickness of an enzyme layer	0.001-0.0005m
d	Distance between electrodes	0.003-0.004m
D_G	Diffusion coefficients of glucose	$10^{-5} \text{m}^2 \text{s}^{-1}$
D_{H^+}	Diffusion coefficients of hydrogen ions	$10^{-5} \text{m}^2 \text{s}^{-1}$
D_{bH^+}	Diffusion coefficients of hydrogen ions in bulk	$10^{-5} \text{m}^2 \text{s}^{-1}$
c_0	Hydrogen ions concentration between the glucose reservoir and an anode	0.002M
$[G_0]$	Glucose concentration in the glucose reservoir	0.001, 0.01, 0.1, 0.19, 1.9 mol m^{-3}
$\frac{c_L}{c_d}$	Ratio between initial concentration of hydrogen ions at $x = L$ and $x = d$.	5×10^3 , 50
$\frac{c_d}{c_0}$	Ratio between initial concentration of hydrogen ions at $x = d$ and $x = 0$.	1

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$P = I^2 R_L$	Power	Watt(W)
\bar{P}	Power density	W/cm ² (or) Watt = J/s=kg*m ² /s ³
R_L	Resistance	0.01 Ω - 1 Ω ($\Omega = V / A = kg * m^2 A^2 s^3$)
$\alpha = \frac{2d^2 k_{cat} [E_T]}{D_G K_M}$	Reaction diffusion parameter	16,50,84,117
$\beta = \frac{[G_0]}{K_M}$	Saturation parameter	0.05, 0.5, 5.2, 10, 100
$c_i = \frac{[G_0]}{c_0}$	Ratio between initial concentration of glucose and hydrogen ions	0.5, 5, 50, 95, 950
$\xi_1 = \frac{D_G}{D_{H^+}}$	Ratio between diffusion coefficients	1
$\xi_2 = \frac{D_{H^+}}{D_{bH^+}}$	Ratio between diffusion coefficients	0.5,0.8,1
$[\bar{G}]$	Dimensionless concentration of Glucose	--
\bar{c}_{H^+}	Dimensionless concentration of Hydrogen ions	--
\bar{X}	Dimensionless distance	--
L/d	Dimensionless thickness of an enzyme layer	--

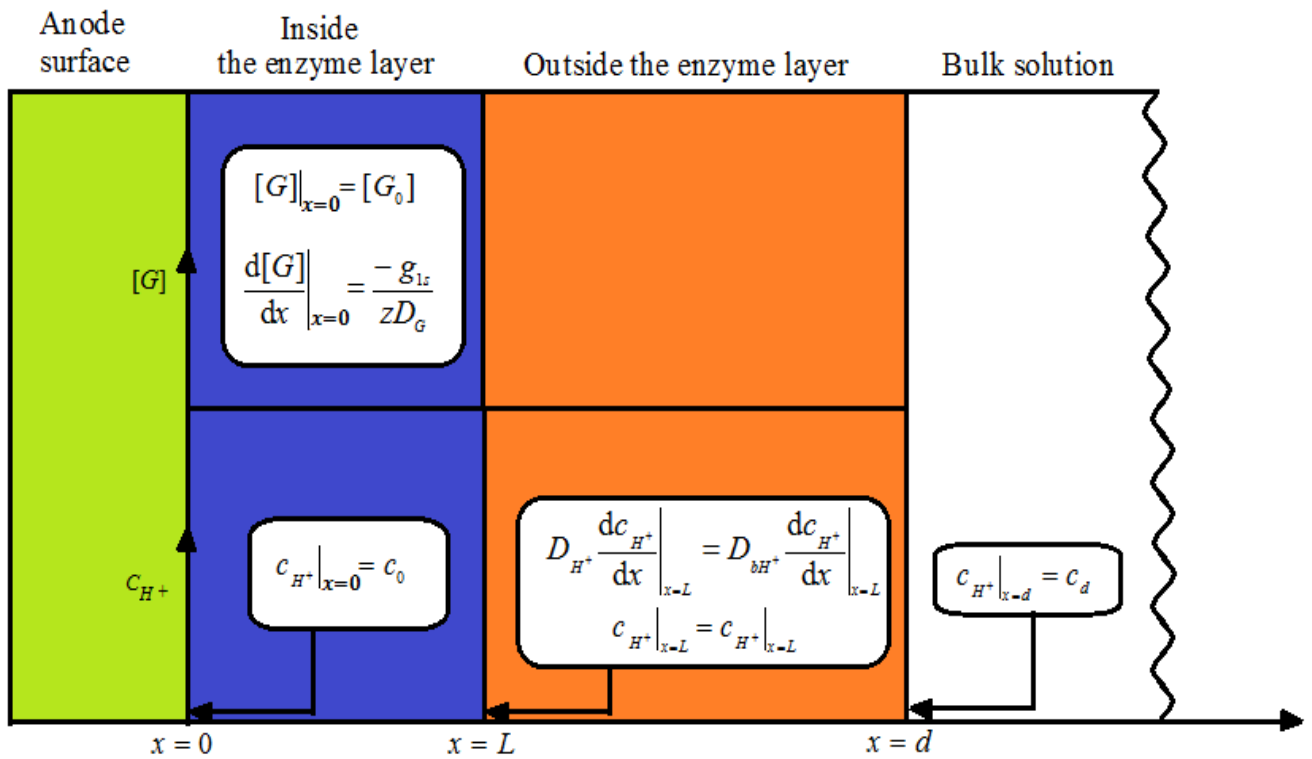


Figure1. Boundary conditions employed in the enzymatic glucose fuel cell for the substrate $[G]$ and product c_{H^+} .

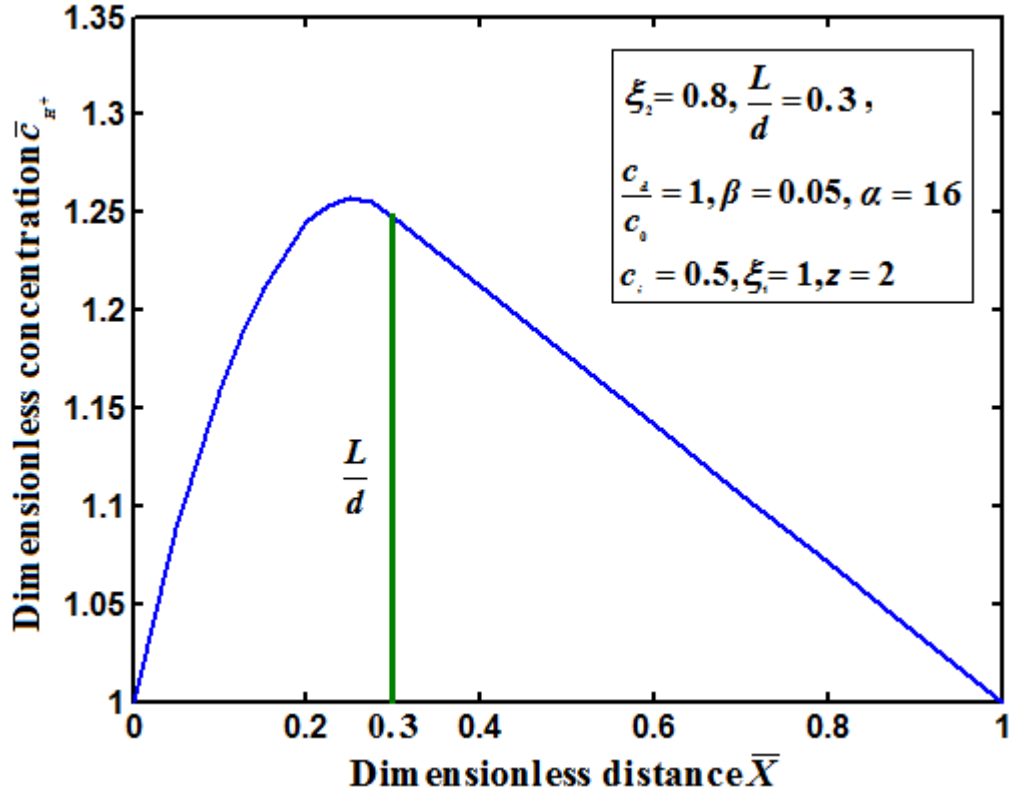


Figure 2. Combined plot of dimensionless concentration of hydrogen ions (\bar{c}_{H^+}) inside the enzyme layer ($0 < \bar{X} < L/d$) and dimensionless concentration of hydrogen ions (\bar{c}_{H^+}) outside the enzyme layer ($L/d < \bar{X} < 1$) versus dimensionless distance \bar{X} using Eq. (23) and Eq. (24). Where L/d is the interface between inside the enzyme layer and outside the enzyme layer.

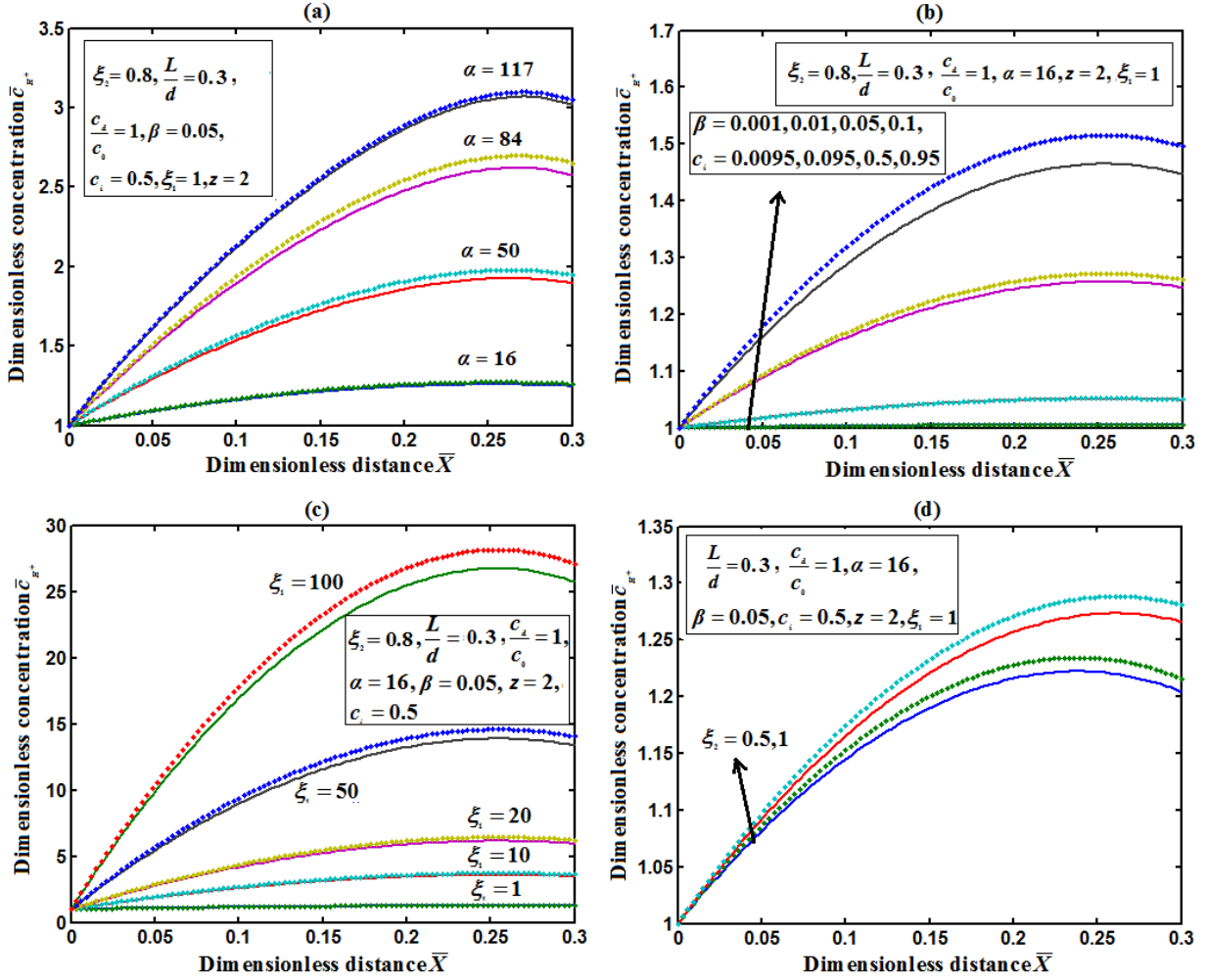


Figure 3(a)-3(e). Comparison of dimensionless concentration profiles of the product \bar{c}_{H^+} versus dimensionless distance \bar{X} for various values of $\alpha, \beta, c_i, L/d, \xi_1$ and ξ_2 and some fixed values of other parameters using Eq. (23) and Eq. (40). The key to the graph: (—) represents the Eq. (23) and (...) represent the Eq. (40).

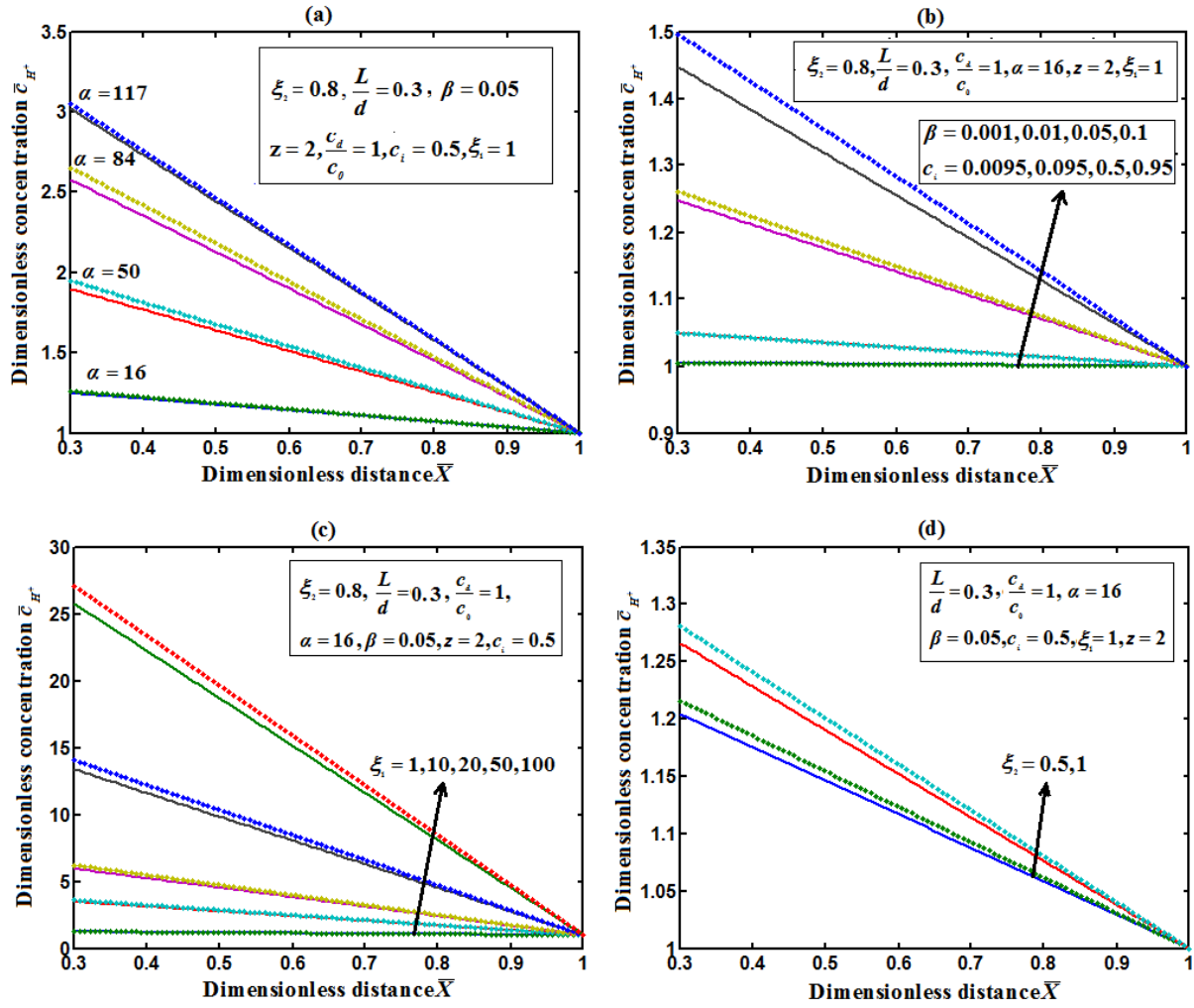


Figure 4(a)-4(e). Comparison of dimensionless concentration profiles of the product \bar{c}_{H^+} versus dimensionless distance \bar{X} for various values of $\alpha, \beta, c_i, L/d, \xi_1$ and ξ_2 and some fixed values of other parameters using Eq. (24) and Eq. (41). The key to the graph: (_) represents the Eq. (24) and (...) represent the Eq. (41).

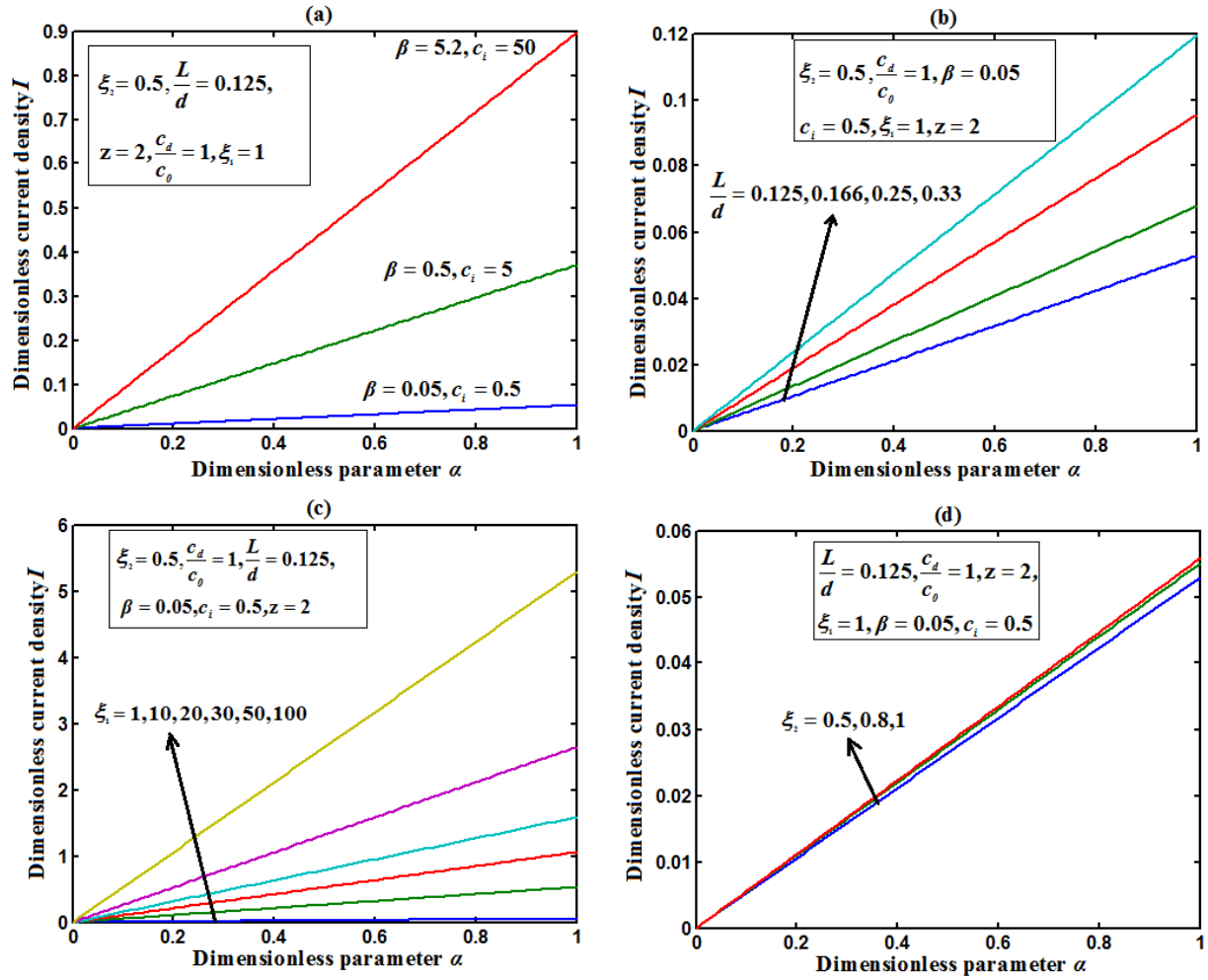


Figure 5. Plot of dimensionless current density I versus dimensionless parameter α for various values of $\beta, c_i, L/d, \xi_1$ and ξ_2 and some fixed values of other parameters using Eq. (28).

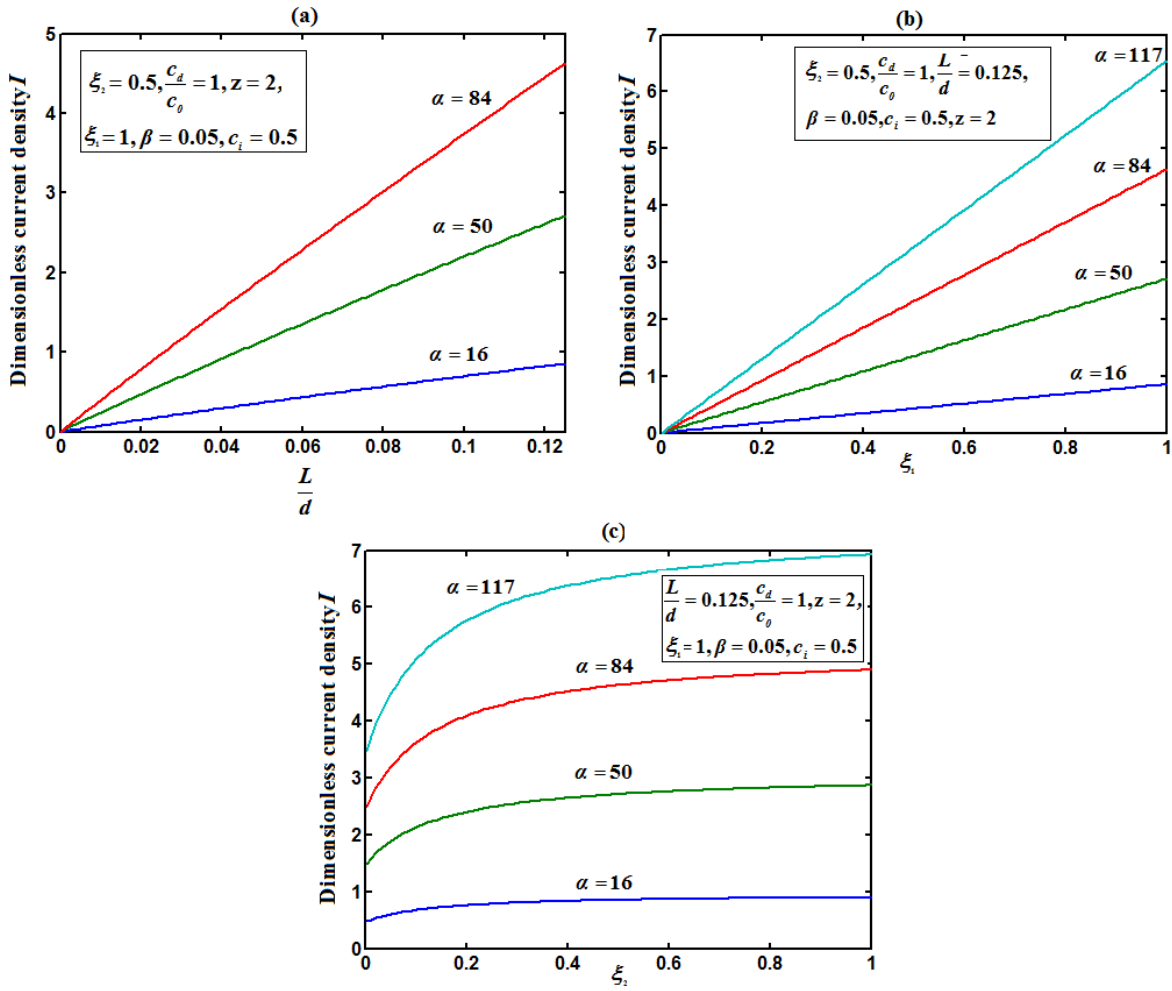


Figure 6(a)-6(c). Plot of dimensionless current density I versus $L/d, \xi_1$ and ξ_2 for various values of α and some fixed values of other parameters using Eq. (28).

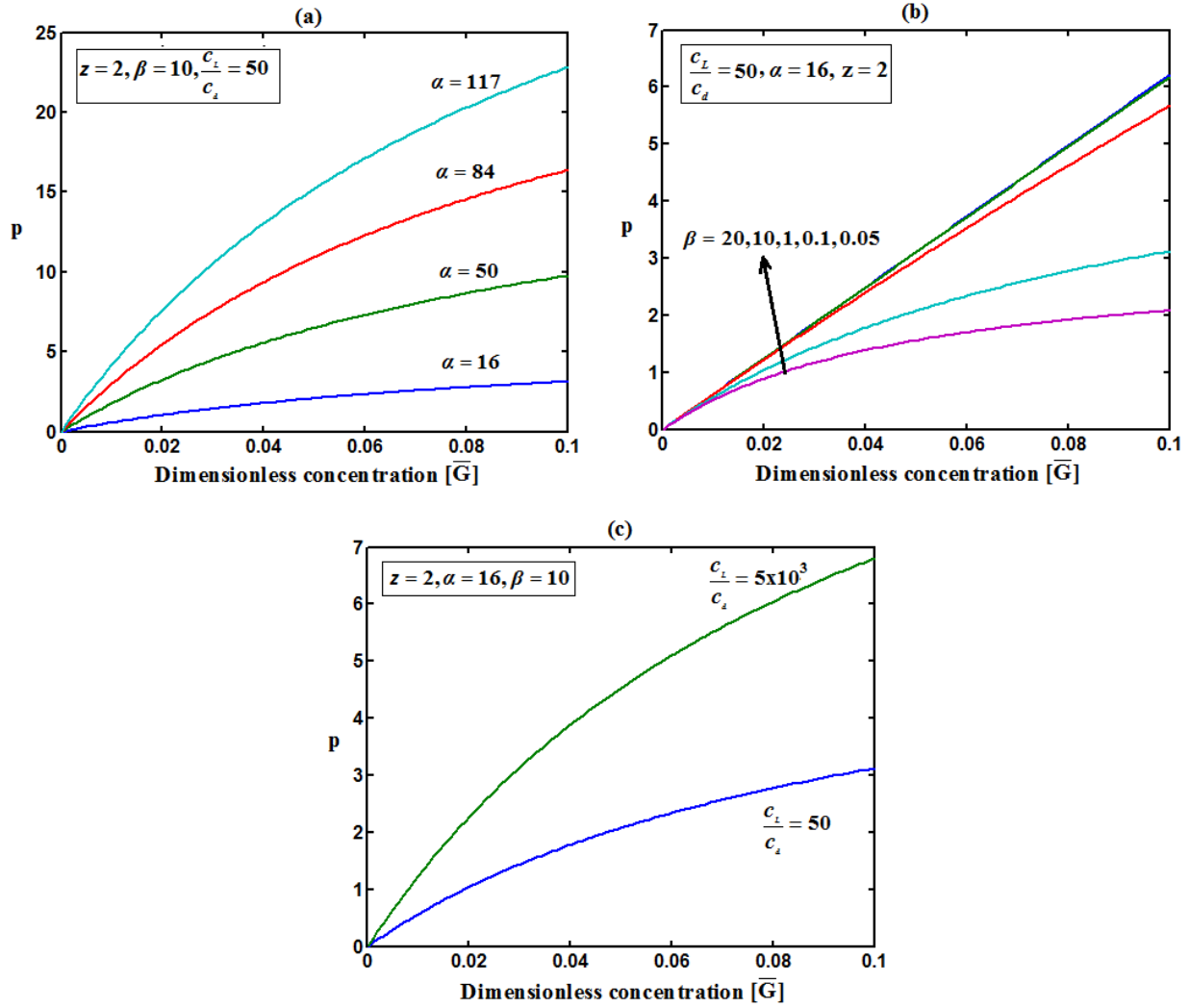


Figure 7(a)-7(c). Plot of dimensionless power versus p dimensionless concentration $[\bar{G}]$ for various values of α, β and c_L/c_d and some fixed values of other parameters using Eq. (29).

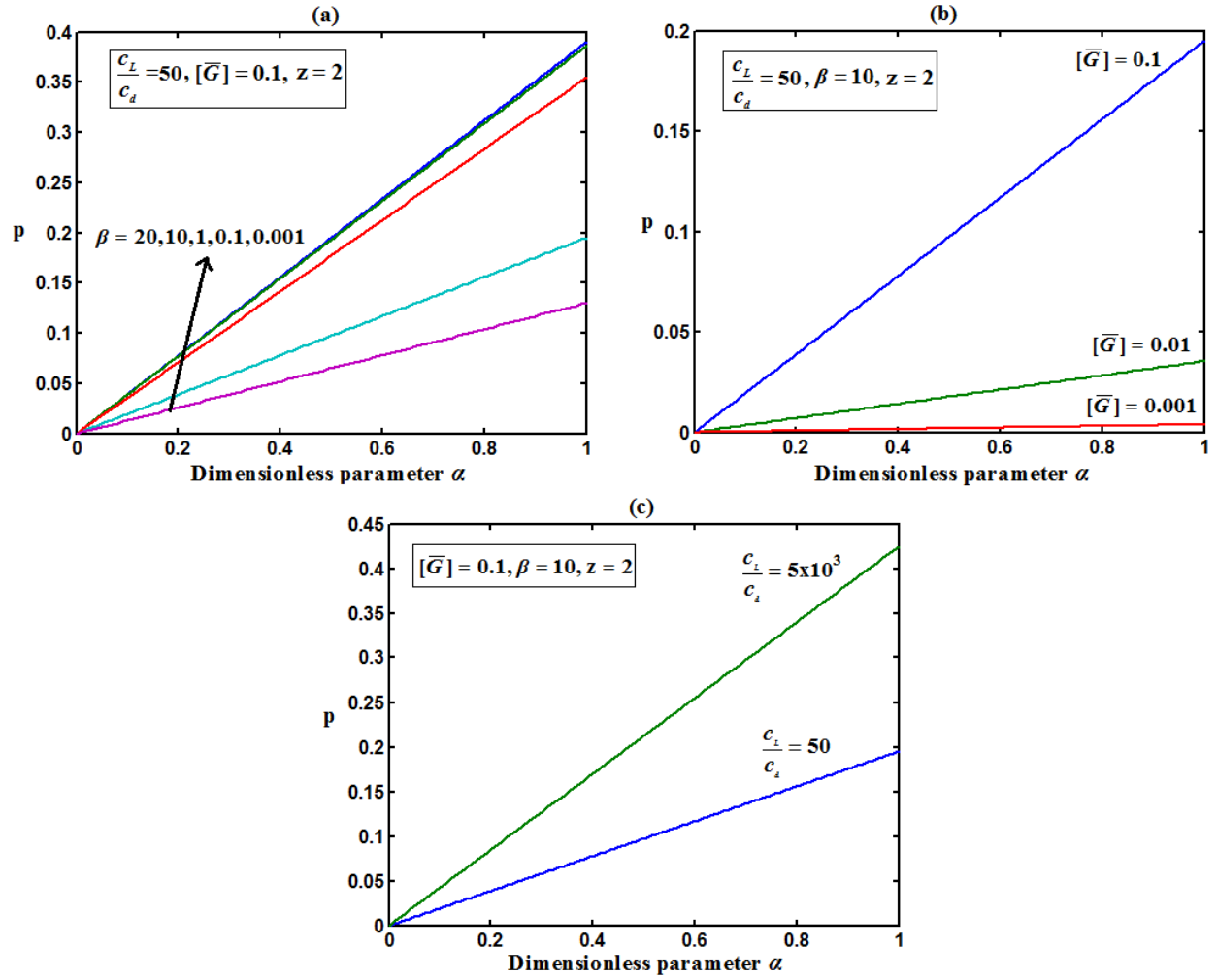


Figure 8(a)-8(c). Plot of dimensionless power p versus dimensionless parameter α for various values of $\beta, [\bar{G}]$ and c_L/c_d and some fixed values of other parameters using Eq. (29).

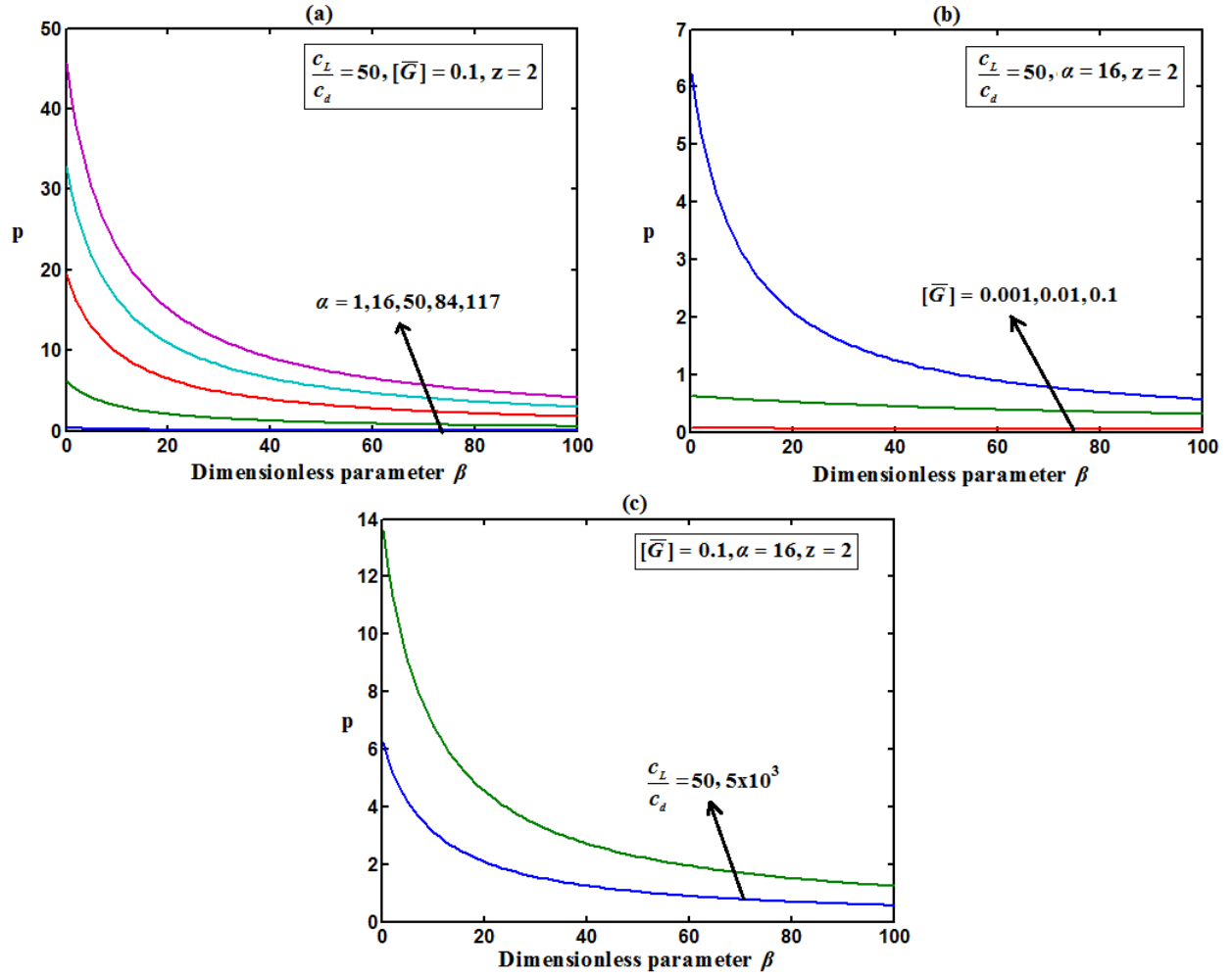


Figure 9(a)-9(c). Plot of dimensionless power p versus dimensionless parameter β for various values of $\alpha, [\bar{G}]$ and c_L/c_d and some fixed values of other parameters using Eq. (29).