



# Mathematical modelling of an enzymatic fuel cell with an air-breathing cathode



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## ABSTRACT

Multi-dimensional steady-state and dynamic models for an enzymatic fuel cell are developed. In the model system, the biocatalyst (glucose oxidase) is immobilized in a porous electrically conducting anode, while glucose and a mediator are supplied from a solution. A platinum air-breathing cathode and a Nafion membrane complete the cell unit. Detailed mass and charge balances are combined with a model for the ping-pong reaction mechanism in the anode, together with oxygen reduction in the cathode. The effects of enzyme oxidation by dissolved oxygen in the anode (a competing side reaction) are also included. The model is validated against experimental polarization and power curves, and the steady-state performance under different conditions is analyzed and discussed. The simulation results demonstrate some of the possible limitations of enzymatic fuel cells and provide insights into the spatial distributions of the reactants, potentials and current.

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## 1. Introduction

Biofuel cells have been defined as systems capable of direct chemical to electrical energy conversion via biochemical pathways [1–6]. Direct electrochemical conversion is a desirable feature since it avoids the thermodynamic limitations associated with combustion, in addition to being more environmentally friendly.

Enzymatic fuel cells can yield low power densities as a consequence of slow rates of electron transfer from the enzyme active site to the electrode [7]. They can also suffer from short lifetimes as a result of poor stability of the enzyme when it functions in a foreign environment. Much of the current research is directed at alleviating these problems, with particular focus on new methods and materials for enzyme-electrode (and possibly mediator) integration, often in highly ordered three-dimensional structures. Developments in the overall system design have also led to more efficient systems. For example, removing the separator membrane without a significant loss in the power output, and the emergence of single chamber, air-breathing systems using compact membrane electrode assemblies (MEAs).

Mathematical models can reduce the burden on laboratory-based design, testing and characterization. At the cell level, models can capture the potential, reactant, and temperature distribution, as well as global information such as the cell potential. For

many important quantities, local information such as potential and current density profiles can only be gained from detailed and rigorously validated models, particularly during *in-situ* operation. For these reasons, a great deal of effort has been invested in modelling polymer electrolyte membrane (PEM) and solid oxide fuel cells and solid-oxide fuel cells [8]. Numerical modelling of enzymatic and microbial fuel cells, on the other hand, is not a well-developed area [9,10]. With a few notable exceptions [11–13], models are highly simplified, neglecting crucial features such as transience, spatial non-uniformity, ion migration, fluid flow and heat transport. In this paper, a transient, two-dimensional model for a glucose-oxidase based fuel cell is developed. The ping-pong mechanism of the biocatalyzed reactions is treated explicitly and the model is validated against experimental results. The approach can be applied to other biofuel cell systems and in a companion paper a model of a fully biological (anode and cathode) fuel cell is developed.

## 2. Fuel cell model

### 2.1. Reaction kinetics

The system under consideration was reported by Fischback et al. [14] (see also [15,16]). The developed miniature fuel cell (12 mm × 12 mm × 9 mm) comprised a Nafion membrane/cathode electrode assembly (MCEA) stacked with an enzymatic (glucose oxidase) carbon felt anode, as depicted in Fig. 1. Glucose oxidase was covalently attached to functionalized carbon nano-tubes (CNTs) before excess GOX was made to precipitate near the CNTs. Finally, a cross-linking

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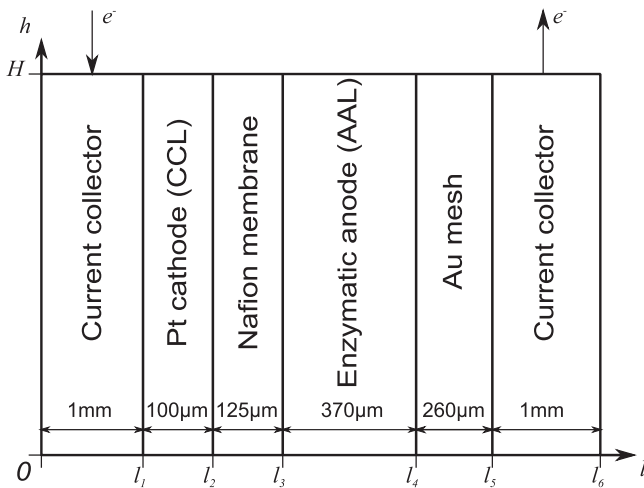
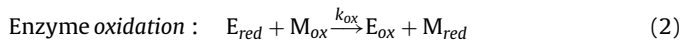
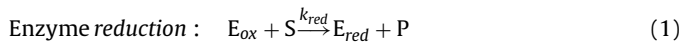


Fig. 1. A schematic of the modelled cell [14].

agent was added to form crosslinked enzyme clusters on the surface of the CNTs. This mixture was then cast on a carbon felt. The anode was placed between the MCEA and a gold mesh, for improved electrical conductivity. The current collectors were made from titanium plates, with current being drawn from the top side (Fig. 1). Slits were machined into these plates to provide the anolyte on the anode side and air on the cathode side. The anode was continuously fed with a solution containing glucose and the mediator benzoquinone. The air-breathing Pt/Nafion cathode was prepared by applying a Nafion/Pt-black layer on a Nafion 115 membrane [14]. The fuel cell was capable of operating continuously at maximum power for 16 h with no significant drop in performance.

For a mediated enzymatic anode, the two chemical reactions occurring are the two-substrate ‘ping-pong’ reactions involving the reduction and oxidation of the enzyme [17–19]:



where  $E_{ox}$  and  $E_{red}$  (i.e., FAD and FADH<sub>2</sub>) are the oxidized and reduced states of the enzyme (i.e., glucose oxidase) respectively.  $M_{ox}$  and  $M_{red}$  are the oxidized and reduced forms of the quinone mediator: benzoquinone and hydroquinone respectively [17]. S and P are the glucose substrate and glucono-lactone product, respectively. A third electrochemical reaction regenerates the mediator at the electrode:



This reaction is assumed to be a two-proton/two-electron process [20]. There is disagreement in the literature on the chemical pathway of the benzoquinone reduction reaction, and the stability of some of the intermediate radicals [21]. Ions formed by a single-electron transfer are found to be more stable in unbuffered solutions for pH > 2.5 [22]. In this work, the hydroquinone oxidation is assumed to proceed by reaction (3).

When studying the influence of a third substrate, dissolved oxygen ( $O_d$ ), which competes with the mediator for the oxidation of the GOx, a third enzymatic reaction is included:



Unless stated otherwise, the competing enzyme oxidation reaction (Eq. (4)) is neglected.

The anode is treated as an electrically conducting porous matrix in which the immobilized enzyme resides and participates

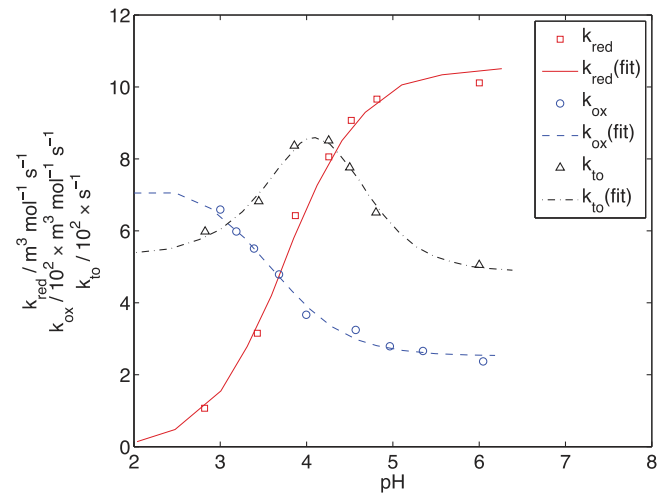


Fig. 2. The pH dependence of enzymatic rate constants (determined from the results in [23,24]).

in the bio-electrochemical reactions. Applying steady-state approximations to the intermediate enzyme complexes (i.e., Michaelis–Menten kinetics), the reaction rates of the two enzymatic reactions (1) and (2) can be expressed as (in the anode active layer (AAL) only):

$$R_{red} = k_{red} c_{gluc} c_{E_{ox}} \quad (5)$$

$$R_{ox} = k_{ox} c_{M_{ox}} c_{E_{red}} \quad (6)$$

respectively, where  $c_i$  represents the concentration of species  $i$  (‘gluc’ representing glucose).  $k_{red}$  and  $k_{ox}$  are the pH dependent bimolecular rate constants, which were interpolated from the experimental data in [23,24] (see Fig. 2).

When assuming the presence of dissolved oxygen the rate of enzyme oxidation by the third substrate is expressed as:

$$R_{O_d} = k_{O_d} c_{O_d} c_{E_{red}} \quad (7)$$

The rate of reaction (3), occurring on the carbon anode, is expressed in Butler–Volmer form, assuming a two-electron reaction:

$$R_{anod} = k_{anod} c_{M_{red}}^{\alpha_a} c_{M_{ox}}^{\alpha_c} \left[ \exp\left(\frac{2\alpha_c F \eta_a}{RT}\right) - \exp\left(\frac{-2\alpha_a F \eta_a}{RT}\right) \right] \quad (8)$$

where  $k_{anod}$  is the rate constant ( $s^{-1}$ ),  $\eta_a$  is the anode overpotential,  $\alpha_a$  and  $\alpha_c$  are the anodic and cathodic charge transfer coefficients, respectively,  $T$  is the system temperature,  $F$  is Faraday’s constant and  $R$  is the molar gas constant.

In the cathode catalyst layer (CCL), oxygen is assumed to undergo a four-electron reduction to water on Pt:



This is the most common assumption made in fuel cell modelling when considering air-breathing cathodes. For alkaline conditions, or for conditions close to neutral pH, this model may not be valid. In the present case, however, the pH remains below 4.75 for all cases considered. The pH of the anolyte was measured by Fischback et al. [14], who recorded values of 3.2 and 3.48 before and after operation, respectively. The same conditions were used as the basis for the simulations. Given the location of the reaction sites (simultaneous contact between ionomer, Pt and carbon [25,26]) it is assumed that the water enters the ionomer phase, i.e., is in a dissolved form (denoted with a subscript ‘(d)’). The rate of reaction (9)

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