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Mathematical Modeling of a Porous Enzymatic Electrode with Direct Electron Transfer Mechanism

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ABSTRACT

1-D model of a porous enzymatic electrode with direct electron transfer mechanism has been developed. As a model reaction, hydrogen peroxide reduction catalyzed by Horseradish Peroxidase has been chosen. The model description includes material and charge balances in different phases as well as detailed kinetics of bioelectrochemical hydrogen peroxide reduction. The model has been solved numerically and validated experimentally under steady state conditions. To investigate the influence of the electrode structure and the immobilization procedure, two types of enzymatic electrodes have been developed. In one procedure (Vulcan-PVDF) enzymes were entrapped into a porous conductive matrix, while in the second one (Vulcan-Gelatin) gelatin was used as a binder and enzymes were cross-linked. The performances of Vulcan-PVDF electrodes were significantly better than of Vulcan-Gelatin electrodes under all studied conditions. According to the model, the main reasons for this observation are higher number of active enzymes and higher diffusivity of hydrogen peroxide in the catalyst layer (CL) in case of Vulcan-PVDF procedure. The model pointed out that the major limitation in both studied systems is mass transfer limitation. Enzyme utilization in both systems is very low.

1. Introduction

Enzymatic electrodes have found applications in different devices, like biosensors, enzymatic fuel cells and enzymatic reactors [1–5]. In all of these applications, enzymes as catalytic elements are combined with electron conducting materials and additional additives forming complex composite structures. In general, the performance of such electrodes is low, specifically in comparison to traditional metal based electrodes [2,4]. Still, due to excellent catalytic properties of enzymes under mild reaction conditions and in complex reaction environments the interest in further development of these systems sustains. In particular, use of such electrodes in enzymatic fuel cells motivates a large amount of research in last years [2,6]. The employment of these electrodes in bioorganic synthesis is also of high importance specifically with respect to partial oxidation or reduction processes where enzymatic catalysts due to their high selectivity have significant advantageous over conventional catalysts [2,5].

Up to date number of preparation methods for fabrication of enzymatic electrodes have been reported [4,6]. Major foci were on enzyme immobilization, testing of different mediators and usage of diverse nanomaterials (like gold and carbon nanoparticles or carbon nanotubes) [4,6]. Due to number of different procedures and materials employed in production of such electrodes, it is difficult to establish general design rules pointing out the correlation between preparation protocol, electrode structure and its performance.

In this respect, in addition to experimental efforts, further progress can be achieved/accelerated by bringing mathematical modeling into play. This can likely provide new insights into the interactions between components of enzymatic electrodes and their performances, reducing number of required experiments.

In general, electrode models can be formulated at different scales (macro, meso, micro) with varying degrees of complexity [7,8]. Among these model presentations macroscale models are still the most “practical” for correlating with experiments. They can be roughly classified into interface models and distributed models. While the interface models neglect the thickness and the morphology of the electrode, the distributed models take into account the electrode structure. In the field of enzymatic electrodes the interface models prevails [9]. In these studies enzymes were freely diffusive, entrapped behind a thin membrane, immobilized inside

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of a non conductive matrix or adsorbed at the electrode surface [9]. In all cases the electrochemical reaction was taking place only at the conductive surface. Accordingly these models do not include spatial distributions of potential fields, but only distribution of concentrations of involved species in different layers. They can be very useful for determination of enzymatic electrode kinetics as shown for e.g. in [10]. However, they are not helpful in cases where the thickness of the electrode can not be disregarded and where electrode structural parameters and interplay between enzyme and electrode kinetics as well as mass transfer limitations inside of the porous electrode start to play a role. In such cases distributed models are better suited. Examples of such studies from literature are works of Lyons [11], Baronas et al. [12], Barton [13], and Chan et al. [14]. Lyons [11] developed a model of a carbon nanotube electrode where enzymes were assumed to be uniformly distributed within a layer of finite thickness considering two cases relevant for practical applications, namely conductive and less conductive porous matrixes. Baronas et al. [12] used a macro-homogeneous 1-D model to investigate the behavior of the amperometric biosensors based on the carbon nanotubes deposited on the perforated membrane. The simulations pointed out that only 0.5% of nominal enzyme loading was able to participate in the direct electron transfer. The model also suggested that the longer linear calibration range of biosensor can be obtained if operating at diffusion limiting conditions and not under enzymatic reaction limiting conditions. A 1-D macro porous model, including additional micro scale along cylindrical fibers where the enzymatic reaction takes place was developed by Barton [13] for an enzyme-catalyzed oxygen cathode. This model pointed out an importance of the enhanced reactant transport for high performance enzymatic electrodes and was able to predict limiting current densities. Chan et al. [14] employed transient material balances along with steady-state charge balances for the electron- and ion- conducting phases, to study the dynamic behavior of a bio fuel cell anode at high mediator concentrations. The rate limiting process in different ranges of applied potentials was determined and the controlled potential range for electrode optimal operation was recommended.

Most of literature studies consider porous electrodes with mediated electron transfer. These studies provide indications that the electrode response is significantly influenced by electrode structural parameters like porosity and thickness. However, an attempt of investigating these parameters in simulations which is validated further by experimental data can not be found in literature.

In this contribution one dimensional (1-D) porous electrode model has been formulated based on porous electrode theory [8]. The balance equations for potential fields in the electron- and ion-conducting phases as well as concentration field have been developed and solved numerically. The enzymatic kinetics has been described in agreement with Michaelis-Menten mechanism, followed by direct electron transfer to the electrode [10]. To justify the necessity of distributed model formulation, spatial model reduction has been performed, resulting in reduced 1-D model. The comparison of reduced (1-D) and reference (1-D) models provided further understanding about the importance of inner mass transfer limitations. The main goal of the present study is to get more insight into interplay between reaction and diffusion resistances inside of the porous layer. While the former one is governed by enzyme kinetics and the total number of immobilized enzymes (which in turn is influenced by structural parameters/enzyme immobilization), the latter one is impacted by the porous electrode structural parameters like porosity, internal active surface area and thickness. In the present study it is assumed that the porous electrode structure influences only the number of active enzymes, while intrinsic enzyme kinetics remains largely unchanged. The validity of this assumption is discussed later on in the text. The electrode structural parameters are assumed to be influenced by the preparation procedure. Some of these parameters can be readily measured (like thickness), while some are more insecure (internal active surface area). In the present study these parameters have been varied in experiments and their impact has been assessed in simulations.

The 1-D model has been experimentally validated in different concentration ranges, at varying electrode thicknesses and by following two different protocols for the preparation of enzymatic electrodes, giving valuable insights into electrode preparation/performance relationship.

2. Mathematical model

A schematic representation of modeling domains is shown in Fig. 1. The first modeling domain (from $z=0$ to $z=L$) is the catalyst layer (CL). Here electron- and ion- conducting phases are modeled as distinct phases characterized by respective void fractions "ε" with electrochemical reaction taking place at the interface between two phases, defined further as internal active surface area "$a = A_{act}/(A_{geo}L)$" (in $m_{act}^2 m_{geo}^{-3}$), where A_{act} is active surface area, A_{geo} geometrical surface area and L thickness of the porous electrode. Balance equations for potential distributions in the electron- ($\phi_E^{CL}(z,t)$) and ion- ($\phi_I^{CL}(z,t)$) conducting phases as well as the potential distribution $E(z,t)$ at the interface of these two phases have been formulated. To complete the model description mass balance equations for species involved in enzymatic and electrochemical reactions have been introduced.

In the balance equations, all fluxes are related to superficial quantities by multiplying the interstitial flux with the corresponding void fraction ε.

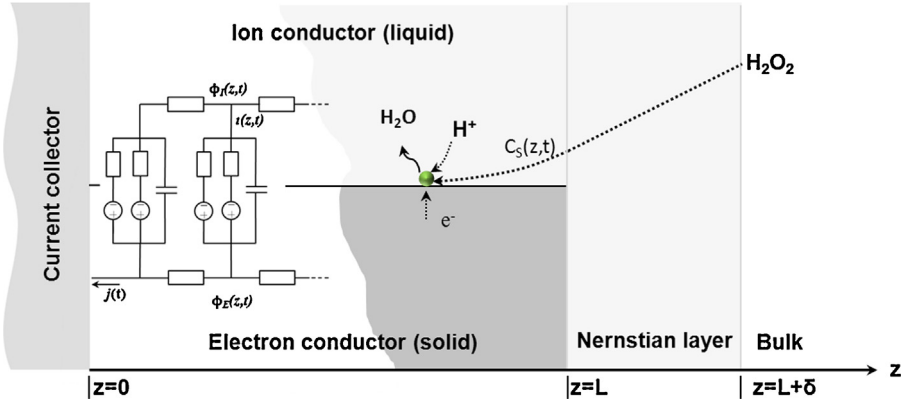

Fig. 1. Schematic representation of modeling domains.