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Modelling diffusion impedance in the sensing of micron-sized particles

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ABSTRACT

Development of electrochemical impedance biosensor with reliable detection output is important for bringing the technology to use in real world applications. The use of increase in charge-transfer resistance, a component of faradaic impedance, as indicator of analyte-sensor interaction is one of the conventional approaches of data interpretation. However, while charge-transfer resistance is very sensitive, it is susceptible to non-specific drifts. This study explored the use of diffusion impedance, another component of faradaic impedance, in sensing applications involving micron-sized analytes such as bacteria. Fick's second law of diffusion and finite element method were used to simulate the effect of binding micron-sized particles on diffusion impedance. Simulations were validated with the measured impedances involving polystyrene beads as analyte model. The results showed good agreement between the simulations and experimental observations. Further analysis has led to the use of apparent diffusion number, which was derived from the diffusion impedance, as the indicator for quantifying particle binding. The experimental results showed the use of diffusion impedance had stronger correlation with electrode coverage by polystyrene beads than the conventional charge transfer resistance approach. The improved data consistency may be attributed from the different drift property of diffusion impedance.

1. Introduction

1.1. Background

Biosensing has important applications in areas such as medical diagnostics, food safety, and agriculture [1–4]. Impedance-based electrochemical biosensors are an example which utilizes electrode as the transducer to detect interactions between the sensor and the target analyte. Interactions that affect the electrochemical properties of the electrode system will modify its impedance; the recognition of this change forms the basic sensing mechanism of impedimetric biosensors. Typically, a sinusoidal voltage excitation is applied to the electrode and the current response is read to deduce the impedance spectrum. The main advantages of impedimetric biosensors include portability, low fabrication cost, and the ability to perform label-free sensing [1,2]. However, like other new biosensing technologies, the reliability of sensor output is a major barrier that prevents the technology from being applied in real world problems.

Impedimetric biosensors have been successfully applied to the detection of bacteria, which involves target species with micron dimensions. In particular, the blocking of faradaic current has been used to detect bacteria captured on electrode surfaces [5,6]. Faradaic current is the result of electron exchange between the electrode and electroactive molecules in the solution. Bacteria bound on to an electrode surface reduce the area available for faradaic current to occur and thus increase faradaic impedance. This observation is typically modelled by an increase in charge-transfer resistance (R_{ct}), which is a faradaic impedance component that reflects the reactivity of the electrode surface with electroactive molecules. However, charge-transfer resistance, being very sensitive, is susceptible to non-specific drifts [7]. This means response data based on the change in R_{ct} must be referenced to a system of control measurements to provide reliable interpretation.

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An alternative explanation for increased faradaic impedance is the obstruction of the mass transfer of electroactive molecules from the bulk solution to the electrode surface. This interpretation suggests that a faradaic impedance component alternative to R_{ct} is involved, namely the diffusion impedance (Z_d). How the diffusion impedance is implicated in biosensing applications have not been explored previously. Diffusion impedance is dependent on a physical process that is distinct to charge transfer, so it is expected to exhibit different properties and drift behaviours. Therefore, we sought to investigate on how diffusion impedance is involved and whether it can be applied in biosensing applications, specifically for micron-sized targets. We have employed finite element method (FEM) as the numerical modelling technique to help with understanding the phenomenon involved.

FEM is a popular mathematical modelling technique used in the study of diffusion processes in electrochemical systems. However, the uses so far have mostly been limited to characterizing the diffusion properties of different electrode designs [8,9]. On the other hand, FEM is commonly used to study how non-faradaic currents respond to the presence of captured bacteria by simulating the electric fields in each situation [10–13]. This is often used for electrode geometry optimization purposes to improve sensor sensitivity.

The theory that underpins the modelling of electrode impedance and more specifically the diffusion impedance is described in Section 1.2. The FEM model implementation for solving diffusion impedance and experimental procedures for model validation are outlined in Section 2. In Section 3, the simulation results are described and validated with experimental data. Subsequently, a data analysis approach for sensing that is based on diffusion impedance is developed from the validated model. This new approach is compared to the conventional R_{ct}-based method to evaluate its advantages and disadvantages.

1.2. Electrode impedance

This section provides a brief overview of electrode impedance, then a more detailed explanation on diffusion impedance modelling. Lastly, the basis for which diffusion impedance can be applied in sensing is proposed.

1.2.1. Randles circuit

Randles circuit is the conventional model used to interpret electrode impedances (Z). The circuit and its characteristic Nyquist plot are shown in Fig. 1. There are two current paths across the electrode-solution interface in the model, non-faradaic and faradaic. Non-faradaic current is generated by the transient charging and discharging of electric double layer capacitance (C_{dl}) at the electrode-solution interface. Whereas faradaic current occurs via physical electron exchange between the electrode and electroactive molecules in the solution. Faradaic current is commonly modelled with a series combination of charge-transfer resistance (R_{ct}) and diffusion impedance (Z_d). Solution resistance (R_{sol}) models the electrical conductivity of the bulk solution due to mobile ions.

Electrode current is predominantly diffusion controlled at low frequencies. In this study, we focused on investigating how the diffusion impedance Z_d is affected by micron-sized particles immobilized on the electrode surface and subsequently attempt to apply this knowledge to sensing.

1.2.2. Diffusion impedance modelling

The faradaic charge exchange reaction depletes reactants and builds up products near the electrode surface, which need to be replenished or removed for the reaction to continue. This mass transfer can be modelled with simple diffusion when the non-electroactive supporting electrolytes in the solution are in excess of the electroactive species, as the non-electroactive ions shield the effect of electric field that would otherwise exert on the electroactive species. This concentration dependent mass movement is mathematically described by Fick's second law of diffusion (Eq. (1)). The frequency domain representation, obtained from Fourier transformation of Eq. (1), is shown in Eq. (2).

$$\frac{\partial c}{\partial t} = \nabla \cdot -D\nabla c = \nabla \cdot \boldsymbol{J} \tag{1}$$

$$\mathrm{j}\omega c = \nabla \cdot -D\nabla c = \nabla \cdot J \tag{2}$$

c: concentration (mol.m^{-3} mM)
t: time (s)
D: diffusion coefficient (m^2.s^{-1})
$\boldsymbol{J}$: molecule flux density vector (mol.m^{-2}.s^{-1})
j: imaginary number $\sqrt{-1}$
ω: angular frequency of excitation signal (radians.s^{-1})

Fick's law can be solved analytically when the diffusion pattern is semi-infinite and planar for a flat electrode surface, and the solution is the well-known Warburg element (Z_W). A derivation of Warburg element is provided in the book by Bard & Faulkner [14]. In the article by Jacobsen et al. [15], the frequency domain representation (Eq. (2)) was used to derive the diffusion impedance for the general case of planar diffusion in the presence of absorbing or blocking boundaries. Warburg element can be obtained from the general solutions by defining infinite distance between the boundaries and the electrode surface, such that the diffusion pattern is semi-infinite.

Warburg element manifests as a unity-sloped (45°) straight line at the low frequency part of Nyquist plots (Fig. 1B, red line). The equation for Z_W is shown in Eq. (3). Warburg coefficient A_W is

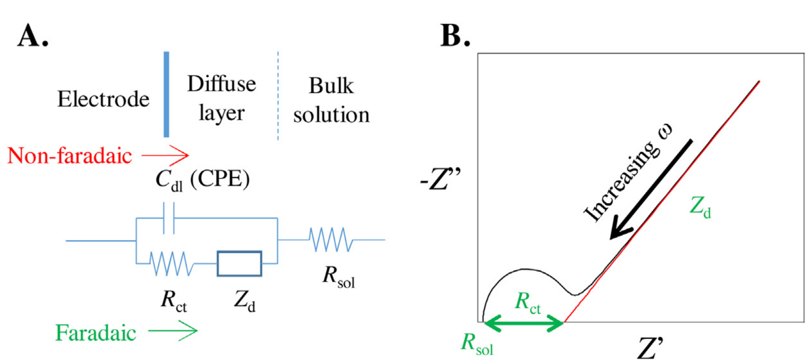

Fig. 1. Randles circuit (A) and its Nyquist plot (B). C_{dl} is often modelled as a constant phase element (CPE). The red line in the Nyquist plot denotes the faradaic impedance components (R_{ct} + Z_d) (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).