



Process modeling of electrodes in proton exchange membrane fuel cells



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ABSTRACT

The impedance characteristics of the activation and mass transport overpotentials in a proton exchange membrane fuel cell are determined analytically using a process model. The anode and cathode electrodes are studied separately. The governing equations are solved analytically and the resultant impedances and hence the equivalent circuits are extracted. The results show an excellent agreement between the analytical model and different measured impedances reported in the literature for various operating conditions and anode/cathode feedings. It is shown that the high frequency arc is the result of the anode impedance and is not a function of the current density. On the other hand, the mid-frequency arc consisting of two convoluted depressed semi-circles is the result of the cathode impedance. The solution clarifies the reason for an initial decrease followed by an increase in the diameter of the mid-frequency arc as the current density increases. The results also show that cathode starvation can be studied clearly from the mid frequency arc.

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1. Introduction

The electrochemical impedance spectroscopy (EIS) has attracted much attention during the last decade as a fast, accurate and non-destructive method to study the proton exchange membrane (PEM) fuel cells [1,2]. In this method, a small harmonic electrical perturbation is applied to the cell and the response is measured and analyzed [3,4]. Two types of the EIS method have been practiced: the measurement and process models have been implemented for determining the required equivalent circuit which is used for quantifying and analyzing the measured impedances [2,5,6]. In the measurement model approach, a conventional equivalent circuit is presented which has the same impedance characteristics as the measured impedance [7,8]. In the process model approach, however, the governing equations of the cell are studied and the equivalent circuit is analytically determined [6,9].

The measurement models are extensively used in PEM fuel cell studies [1,2]. However, the elements of the measurement-model-based equivalent circuits are not functions of physicochemical properties of the cell, and hence there are concerns about the validity of physical and chemical interpretations concluded from these models [2,5]. Moreover, these models are only valid in the neighborhood of the measured impedances and cannot be employed in

other operating conditions [2,5,10,11]. The process model approach, on the other hand, does not have this limitation and has been used to model different electrochemical systems [6,9,12,13].

There have been attempts made towards presenting a process model for PEM fuel cells [14–20]. Springer et al. [14] derived the governing equations for the catalyst and gas diffusion layers and obtained a set of equations which was solved numerically using Newton–Raphson method. They fitted simultaneously all the measured impedances at different current densities to the predicted ones obtained from their numerical solutions. The best fit to all the measurements presented in the Nyquist plot resulted in estimating the unknown physicochemical parameters. This work can be considered as the most extensive study conducted towards presenting a process model for PEM fuel cells. However, since the final solution was obtained numerically, no equivalent circuit could be presented. As a result, different parts of the Nyquist plot were not related to operating conditions or the physicochemical properties of the cell. For other attempts [15–20] made towards presenting a process model for PEM fuel cells, the complexity of the final impedance relation resulted from the analytical solutions led to the use of assumptive equivalent circuits. In other words, the equivalent circuits established are not based on the analytical solutions presented. These equivalent circuits are normally based on the process models presented before for similar electrochemical systems. They mostly include a series connection of two simplified versions of Randles circuits [12] for the anode and cathode and an

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ordinary resistance for the membrane, and hence cannot capture all impedance characteristics of PEM fuel cells which include three separate semi-circles and an inductive characteristic observed in [11,21–24]. Thus, there is still lack of a comprehensive process-model-based equivalent circuit characterizing different elements and phenomena in PEM fuel cells.

Considering the activation, ohmic and mass transport losses separately, the authors have presented [6] the first step towards the development of a process-model-based equivalent circuit by analytically solving the ohmic-loss governing equations and determining the resultant equivalent circuit. In this paper, the activation and mass transport losses are studied and the resultant equivalent circuits are determined. The governing equations for the anode and cathode electrodes are solved separately, and the results are verified against measured impedances reported in literature [11,21,22]. It is shown that the so-called high frequency (HF) arc [21] is due to the anode double layer. On the other hand, the mid-frequency (MF) arc is shown to be the result of the cathode impedance and a function of the current density. It can also be employed to study cathode starvation.

2. Anode impedance

Fig. 1 shows the schematic view of the anode-membrane interphase. The hydrogen gas (H_2) is diffused through the anode gas diffusion layer and adsorbed on an empty site (A) at the Pt surface and dissociated into the hydrogen atoms (H_{ads}) in a rapid reaction [25]



The adsorbed hydrogen atom is then discharged into a proton (H^+) and electron (e^-) according to the following electrochemical reaction:



The proton (H^+) is then displaced to the Nafion surface (II) and causes a surplus surface density of a positive charge at the plane II (Γ_{H^+}). Similarly, the remaining electron causes a surplus surface density of a negative charge at the plane I (Γ_{e^-}). These couple charges are the origin of the formation of the double layer capacitance which occurs in a layer with a thickness of d (with the order of magnitude of 1 nm [25]). The total resultant electrical current (j_{tot}) presented in Reaction (2) is the summation of the proton transfer current (j_{H^+}) and the displacement current [26].

$$j_{tot} = j_{H^+} + \epsilon_s \frac{\partial E_s}{\partial t} \quad (3)$$

where ϵ_s and E_s are the dielectric permittivity and the electric field strength at the interphase, respectively. On the other hand, the anode overpotential (η_A) can be written as [25]

$$\eta_A = \varphi_I - \varphi_{II} - \mu_{H^+}/F \quad (4)$$

where φ_I , φ_{II} , and F are the electric potentials in the layers I and II, and the Faraday constant (96485 C mol^{-1} [27]), respectively. μ_{H^+} is the chemical potential of transferring protons [25,27]. The electric potential difference ($\varphi_I - \varphi_{II}$) can be determined from the electric field strength (E_s) using the parallel plate assumption for the plates I and II (this parallel plate assumption is revisited in the discussions related to the constant phase element (CPE))

$$\varphi_I - \varphi_{II} = d \cdot E_s \quad (5)$$

where d is the thickness of the so-called interphase layer (Fig. 1). Also, the chemical potential can be determined as [27]

$$\mu_{H^+} = \mu_{H^+}^0 + RT \ln \frac{\Gamma_{H^+}}{\Gamma_{H^+}^0} \quad (6)$$

where $\mu_{H^+}^0$, R , T , Γ_{H^+} and $\Gamma_{H^+}^0$ present the reference chemical potential at the standard state condition, the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ [27]), temperature, the surface density of the protons at the plane II, and the surface density of the protons at the standard state condition, respectively. Neglecting the electric field in the membrane [25], the protons surface density at the plane II (Γ_{H^+}) can be written as

$$\Gamma_{H^+} = -\epsilon_s E_s \quad (7)$$

It has to be mentioned that the above assumption (i.e., neglecting the electric field in the membrane) will be revisited in the discussions related to the constant phase element (CPE).

To specify the impedance characteristics of the electrode, the parameters are perturbed and the impedance is calculated [6]. The perturbed parts of the parameters are presented with the symbol $\tilde{\cdot}$, e.g., $\tilde{\Gamma}_{H^+}$; while the steady-state parts which show the values of the parameters prior to perturbation are shown with the symbol $\bar{\cdot}$, e.g., $\bar{\mu}_{H^+}$ [6]. Using these notations, Eq. (7) can be represented as

$$\bar{\Gamma}_{H^+} + \tilde{\Gamma}_{H^+} = -\epsilon_s (\bar{E}_s + \tilde{E}_s) \quad (8)$$

Considering the validity of Eq. (7) in the steady-state condition ($\bar{\Gamma}_{H^+} = -\epsilon_s \bar{E}_s$), the perturbed part of the proton surface density ($\tilde{\Gamma}_{H^+}$) can be determined as

$$\tilde{\Gamma}_{H^+} = -\epsilon_s \tilde{E}_s \quad (9)$$

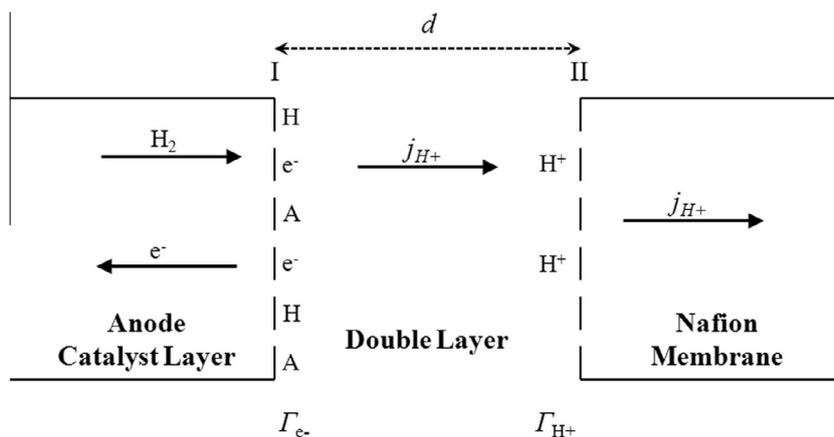


Fig. 1. The schematic view of the anode-membrane interphase.

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