Short Communication

Measurement, semi-process and process modeling of proton exchange membrane fuel cells

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ABSTRACT

Despite the extensive use of electrochemical impedance spectroscopy (EIS) in diagnosing proton exchange membrane fuel cells, the differences between EIS-based measurement and process models are still not clear, causing often dubious interpretations. These differences, mainly related to the approach used in obtaining the equivalent circuit, are discussed here. The procedure for obtaining the equivalent circuit from the analytical solution and the importance of such a procedure, which distinguishes the process models from other analytical models, are also outlined. In addition, the paper presents the new semi-process model category, presenting the equivalent circuit in a different way than the process models.

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Introduction

The electrochemical impedance spectroscopy (EIS) method is used extensively in proton exchange membrane (PEM) fuel cell studies and diagnosis. The EIS method is often used as a supplementary method to verify the predicted physical phenomena observed using other methods (e.g., polarization curves and cyclic voltammetry) [1—3]. Generally in EIS modeling, the impedance values measured at different operating conditions are used to determine the values of the elements of an equivalent circuit obtained based on either assumption or a set of governing equations. The latter method is called the "process model" and the former is referred to as the "measurement model" [4,5]. Despite the similarity that exists between the two ways of determining the equivalent circuit, the measurement and process models can produce quite different results in a sense that the circuit obtained from the governing equations has a physical meaning (presenting the phenomena that occur in the cell) and can be applied to a wide range of operating conditions; whereas the assumed equivalent circuit does not possess these properties. Despite this difference, measurement and process models are often

not distinguished from each other in the literature, which results in reaching to dubious conclusions.

Measurement modeling approach

Except for a few studies published in the past [e.g.6–18], all the equivalent-circuit-based studies conducted on PEM fuel cells can be categorized as the measurement models [e.g.,19–28]. In a measurement model, basically, the impedance of the fuel cell is first measured and then an equivalent circuit with the impedance characteristics similar to those of the measurements is assumed. There is a wide range of different impedance modeling packages (EC-Lab, ZView, etc.) which present different pre-built equivalent circuits that can be used to model the measured impedances. All of these models have to be classified as measurement models.

The concept of the measurement model was first presented by Agarwal et al. [4,5] as a better way of quantifying the measured impedances compared to other regression methods (such as polynomial fitting) [4]. The significance of the measurement model (compared to other regression methods) is that the assumed equivalent circuit satisfies the Kramer–Kronig relations [4,29] and simplifies the detection of stochastic errors [5], guarantying the accuracy of the measured impedances. Thus, the measurement models can be used as a tool for estimating the accuracy of the measured impedances. In fact, if the impedance of the assumed equivalent circuit fits well to the measured impedance, it can be concluded that the measured impedance satisfies the Kramer–Kronig relations (see the detailed discussion presented by Agarwal et al. [4,5]). Despite this advantage of the measurement models over other regression methods, it is still not wise to perform any physical or chemical interpretations from the changes in the values of the elements of the assumed circuit [1,4,5,13,30]. In fact, there is no physical or theoretical relation between the elements of these hypothetical equivalent circuits and the physical and chemical properties of the PEM fuel cell. For instance, the values of the elements of the equivalent circuit assumed for the measurement model of a cell can change due to the change in the measured impedance of the cell occurring by replacing the membrane. In this case, no physical or theoretical interpretations should be concluded based on the change in the value of the elements of the equivalent circuit since it is not certain whether this change is due to the change in the membrane thickness, conductivity, or an unknown effect that might not be even related to the membrane (e.g., oxygen transfer to the catalyst layer). Thus, most physical discussions conducted this way could be considered as misinterpretations and need to be re-evaluated [1]. Although the measurement-model approach was not essentially presented for concluding these kinds of physical discussions, majority of different models were presented in literature as a result of this misinterpretation, which all can be categorized as measurement models. Despite this conflict, the measurement-model approach still presents a strong methodology for quantifying and studying the measured impedances. It can also be used as a stepping stone to derive the equivalent circuit from the process models [4].

Process modeling approach

In the process-model approach, the impedance of the cell is analytically determined by perturbing the governing equations which is finally converted to an equivalent circuit. The equivalent circuit has the same impedance characteristics as the impedance obtained analytically. The most famous example is the Randles process model determined based on a set of governing equations (i.e., the linear diffusion and Butler–Volmer equations), modeling the reaction of a metal ion in an aqueous solution [31]. Since the Randles equivalent circuit was not derived from measurement models, there is a clear mathematical relation between the physicochemical properties of the system and the elements of the equivalent circuit. Thus, the resulting equivalent circuit can be used for all similar systems and for all various operating conditions.

Procedure for obtaining the analytical solutions

The final goal of the analytical calculations in the process model is to find the analytical solution for the impedance of the cell [31–34]. The approach is similar to the procedure used in the measurement of the impedance of the cell. A small harmonic perturbation is applied to the system resulting in perturbing the parameters in the governing equations which are related to the cell characteristics. The perturbation parts are assumed to be small enabling the linearization of the equations in which the second order terms are neglected. The impedance can then be determined as the ratio of the perturbed part of the potential to the perturbed part of the current. It has to be mentioned that in this impedance relation there is no perturbed parameters. The time derivatives of the perturbed parts of the parameters in the equations are also replaced by the perturbed part itself multiplied by ($i\omega$), where ω is angular frequency and $i = \sqrt{-1}$. These ($i\omega$) terms result in the capacitive and inductive elements in the final equivalent circuits which will be discussed later in Section 3.3.

Importance of the equivalent circuit

After obtaining the analytical relation for the impedance, the equivalent circuit can be determined. The equivalent circuit is not derived to solve or verify the analytical model. The sole purpose of deriving the equivalent circuit is to represent the equations in an alternative way. It can be considered as a transformation to another domain which makes the interpretations easier (conceptually, similar to Laplace or Fourier transforms). In addition, the derivation of the equivalent circuit has several advantages:

i) It is considerably easier to deal with an equivalent circuit rather than the final analytical solution. While the impedance equation does not highlight the physicochemical effects, the equivalent circuit can be interpreted physically and its elements can be labeled or even recognized from prior theoretical studies.

ii) It presents an excellent way to combine the parameters included in the final analytical equation and present them as components that are physically or chemically