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Improved approximation for the Butler-Volmer equation in fuel cell modelling

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ABSTRACT

This work presents an improved approximation for the explicit form of the Butler-Volmer (BV) equation, which is used in modelling the activation phenomena in fuel cells. Three representations of the BV-equation in the form $x = f(x)$ are presented in this paper, out of which, two forms are reducible to the high field approximation and one is reducible to the hyperbolic sine approximation under certain conditions. It is found that one of the forms offer an excellent approximation for the BV-equation throughout the applicable range. The detailed analysis of the convergence properties, the applicability ranges and comparative studies offer insights into the ranges of relevance. The proposed approximation will be accurate and applicable for a wide range of operation enabling its adaptation into model based algorithms for fuel cell operation and control. The proposed fixed point based iterative method can offer an alternative to the traditional methods that require the Jacobian information.

1. Introduction

Modelling offers an efficient and cheap means of understanding systems and processes and enables the development of controls and algorithms based on it. Fuel cell modelling has been done extensively for purposes ranging from fundamental understanding to design and control. Fuel cell modelling involves representing several phenomena in the electrical, thermal, fluid, chemical, and the electrochemical domains. The heart of the fuel cell is the electrochemical processes that capture the current voltage relationship. The cell voltage is affected by three types of polarisations that result in irreversible voltage losses. Out of the three causes for this irreversibility, the activation over-potential results from overcoming the activation barrier for the electrochemical reactions. The Butler-Volmer (BV) equation is widely used to model the electrochemical kinetics resulting in the activation polarisation in fuel cells.

The BV-equation in its implicit form requires iterative solution for the over-potential given the cell current. However, for some applications, it is preferable that we have an explicit form of this equation. Iterative solution of the BV-equation is not suitable for some purposes, for example, designing observers based on the model (Vijay and Tadé, 2013). Especially, model simplicity is desired in dynamic models that are developed for control design purposes. A simple model may also be more desirable from the point of lesser computational cost. With these motives, several approximations have been used in the literature for modelling the activation over-potential (Bhattacharyya and Rengaswamy, 2009). One of the most popular assumptions used is the Tafel type equation with empirical parameters (Chrysovalantou et al., 2011; Huanget al., 2011). Other approximations like the hyperbolic sine approximation and the high field approximation have also been used extensively (Mueller et al., 2006; Hajimolana and Soroush, 2009; Zhao et al., 2010; Vijay and Tadé, 2013). All of these approximations have limited applicability as they are based on several assumptions. The applicability ranges for the different approximations for the BV-equation were analysed in (Noren and Hoffman, 2005; Mann et al., 2006). In this work an alternate approximation scheme for the BV-equation is presented based on representing it in the form $x = f(x)$. The performance of the proposed form is compared with the common approximations from literature and its convergence properties are investigated using the fixed point theorem.

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2. The BV-equation forms used in fuel cell modelling

The BV-equation for a single step single electron transfer electrochemical reaction is generally given by the following (Noren and Hoffman, 2005).

$$i = i_0 \left[\exp\left(\frac{\beta F\eta}{RT}\right) - \exp\left(\frac{-(1-\beta)F\eta}{RT}\right)\right] \quad (1)$$

where β is the symmetry factor that has values between 0 and 1, i is the current density, i_0 is the exchange current density, η is the activation over-potential, T is the absolute temperature, R is the universal gas constant and F is the Faradays constant. The BV-equation represented in terms of β is referred to as the β case in this paper.

If the electrochemical reactions are based on multistep multi electron transfer assumptions, then the BV-equation is given in the following form.

$$i = i_0 \left[\exp\left(\frac{\alpha_1 F\eta}{RT}\right) - \exp\left(\frac{-\alpha_2 F\eta}{RT}\right)\right] \quad (2)$$

where the α's are the transfer coefficients. If the mechanisms are well known, some methods are suggested to calculate the α's (Noren and Hoffman, 2005). However, since the mechanisms are not very well known, many different values have been suggested for them in the literature (Zhu and Kee, 2008; Klein et al., 2008; Leonidea et al., 2009). The BV-equation in Eq. (2) represented in terms of α's is referred to as the α case in this paper.

3. Common approximations for the BV-equation

For the modelling purposes that require an explicit form of the BV-equation, several approximations are commonly used. Those approximations and their limitations are detailed in the following.

Neglecting the second exponential term in the BV-equation (Eq. (2)), we get the following form:

$$i = i_0 \left[\exp\left(\frac{\alpha_1 F\eta}{RT}\right)\right] \quad (3)$$

which may be rearranged to:

$$\eta = \frac{RT}{\alpha_1 F} \ln\left(\frac{i}{i_0}\right) \quad (4)$$

This assumption is called the high field approximation and is good for values of $i/i_0 > 4$. In some cases, the terms before the logarithmic term are lumped together as a constant, A, known as the Tafel slope and can be derived from i Vsη curves obtained experimentally. Then the Tafel equation will approximate the straight portion of the i Vsη curve.

$$\eta = A \ln\left(\frac{i}{i_0}\right) \quad (5)$$

The Eq. (5) may be rearranged to obtain the value of A as a slope of the i Vsη curve as follows.

$$A = \frac{\eta - 0}{[\ln(i) - \ln(i_0)]} \quad (6)$$

From this equation, we can understand that the point where the slope of the curve intercepts the 'i' axis will give us the value of i_0, providing a method for measuring i_0.

A linear approximation is obtained be expanding the BV-equation as a power series and neglecting the higher order and nonlinear terms. This is called as the low field assumption as it is only valid for $i/i_0 < 1$.

$$\eta = \frac{RT}{F}\left(\frac{i}{i_0}\right) \quad (7)$$

Another very popular assumption for the BV-equation is the hyperbolic sine approximation. This is derived by assuming$\alpha_1 = \alpha_2 = \alpha$. In such a case, we can use the exponential relation for the hyperbolic sine function to arrive at the following approximation for the BV-equation.

$$\eta = \frac{RT}{\alpha F}\sinh^{-1}\left(\frac{i}{2i_0}\right) \quad (8)$$

This assumption in general is not given a range of applicability and has been widely used in a variety of models in the literature mainly due to the convenience it offers. This assumption is perfectly valid when the two transfer coefficients are equal or nearly equal. In other cases, this is a very poor assumption as will be shown in the following sections. Since a number of very different values for α's are reported in the literature and considering that the activation over-potential is very sensitive to the transfer coefficient, there is a need for a better approximation that is valid for the whole applicable range of the BV-equation.

4. Approximations based on modified forms of the BV-equation

In the following, we present three representations of the BV-equation in form $x = f(x)$. Though these are not explicit forms of the equation, the idea is that we can utilise these forms to devise a better approximation to the BV-equation and to construct efficient numerical methods for an iterative solution.

The following terminology is used in deriving the first form of the BV-equation and will also be used in discussions about the other two forms.

Let,

$$\alpha_1 + \alpha_2 = \alpha_{tot} \quad (9)$$

This implies:

$$\alpha_1 = \frac{\alpha_{tot}}{2} + x; \alpha_2 = \frac{\alpha_{tot}}{2} - x \quad (10)$$

Therefore,

$$x = \alpha_1 - \tfrac{\alpha_{tot}}{2} = \tfrac{\alpha_{tot}}{2} - \alpha_2. \quad (11)$$

In other words, x denotes the deviation of α from the mid value $\frac{\alpha_{tot}}{2}$. Using this terminology, the BV-equation is represented as:

$$i = i_0 \left[\exp\left(\frac{\left(\frac{\alpha_{tot}}{2} + x\right)F\eta}{RT}\right) - \exp\left(\frac{-\left(\frac{\alpha_{tot}}{2} - x\right)F\eta}{RT}\right)\right] \quad (12)$$

Taking the common exponent in these two terms outside of the parenthesis and using the exponential relation for the hyperbolic sine function, this equation can be converted to the following form.

$$\eta = \frac{RT}{\frac{\alpha_{tot}}{2}F}\sinh^{-1}\left(\frac{i}{2i_0}\exp\left(\frac{-xF\eta}{RT}\right)\right) \quad (13)$$

It is interesting to note that this form will reduce to the hyperbolic sine assumption if the value of η on the right hand side of the equation is assumed to be zero. For the sake of using this equation as an approximation, we write it in the following form.

$$\eta = \frac{RT}{\frac{\alpha_{tot}}{2}F}\sinh^{-1}\left(\frac{i}{2i_0}\exp\left(\frac{-xF\eta_{app}}{RT}\right)\right) \quad (14)$$

where the η_{app} will be the given by one of the previous approximations presented in Section 3. In later sections, two options will the explored for this initial assumption. The form of the equation presented in Eq. (13) is suitable for fixed point iteration schemes. In the following, other possible forms of the BV-equation that are amenable for fixed point iteration are provided.