Clarifying the Butler–Volmer equation and related approximations for calculating activation losses in solid oxide fuel cell models

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Abstract

This paper shows the importance of including the activation losses in a model designed to accurately predict the voltage–current relationship of a modern solid oxide fuel cell. The governing equation for voltage drop due to activation losses, the Butler–Volmer equation, is discussed and the derivation and applicability of several approximations is investigated. Finally, the assumptions required to combine the separate anode and cathode activation loss calculations into a single-term equation are clarified.
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1. Introduction

The potential promise of electricity generation with higher efficiency, lower cost, and lower pollution using solid oxide fuel cell (SOFC) power systems has fuelled an unprecedented wave of research focused on developing and commercializing this technology. Computational models are being developed by many research groups [1–17] to study the behavior of complex SOFC power systems and to help direct efforts for increasing stack performance and lowering installation costs. The level of detail and applicability of these models depends on the intended purpose. Some are used for high level design-point and off-design system scoping studies, while others are focused on system behavior during transient operation. Lower level models are developed to better understand detailed reaction mechanisms within each cell to guide improvements in materials selection and stack manufacturing processes. Regardless of the intended application, a common goal is necessary to accurately characterize the voltage–current relationship of the SOFC unit.

When the SOFC is not connected to an external load, there is no current flow outside of the stack and the operating voltage is equal to the open-circuit voltage. The open-circuit voltage for an individual cell is typically assumed to be equivalent to the equilibrium Nernst potential for the overall reaction $H_2 + 1/2O_2 \rightarrow H_2O$.

$$V_{oc} \approx V_{Nernst} \equiv \frac{-\Delta G}{n_e F} = \frac{-\Delta G^0}{n_e F} + \frac{R_u T}{n_e F} \ln\left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}}\right) \quad (1)$$

This assumes any irreversible processes occurring at the open-circuit condition are negligible, such as reactant and electronic electrolyte crossover (i.e., internal short-circuiting) [1,18] and electrode–electrolyte parasitic reactions (e.g., corrosion-type reactions that can significantly reduce the open-circuit voltage of other types of fuel cells) [2,19].

As the stack begins to supply current to an external load, it moves away from a state of equilibrium and the operating voltage drops due to irreversibilities associated with internal charge transfer, conduction, and diffusion processes. These irreversibilities are separately categorized as activation, ohmic, and concentration losses (it should be noted the term "loss" used here is equivalent to the

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terms "overpotential" and "polarization" commonly found in electrochemistry literature). Activation losses are associated with overcoming reaction energy barriers at the electrode–electrolyte interfaces. Ohmic losses are associated with electron and ion conduction processes occurring in the electrodes, electrolyte, and interconnects, as well as the contact resistances across each material interface. Concentration losses are associated with reactant and product diffusion limitations between the bulk flow and reaction sites.

$$V_{operating} = V_{OC} - \Delta V_{act} - \Delta V_{ohmic} - \Delta V_{conc} \qquad (2)$$

The purpose of this paper is to compare several methods found in literature for calculating the activation loss and to clarify some common misconceptions. Methods for calculating the ohmic and concentration losses are equally important and highly dependent on cell geome-

try and manufacturing processes. The reader is directed to several good references on these subjects [1–17, 20–23].

A common assumption made in the past SOFC models was to neglect the activation loss all together. Two main reasons typically given were: (a) SOFCs operating around 1000 °C have very rapid chemical kinetics, which tends to significantly lower activation losses, and (b) the ohmic losses are much greater in magnitude and dominate the overall cell behavior under normal operating current densities. These assumptions may be valid for the older tubular geometries which were originally designed to operate at this high temperature and had relatively long current paths, but modern stacks are being designed to operate at, or below, 800 °C and utilize planar geometries with very short conduction paths. This results in activation losses closer in magnitude to, or even greater than, the other two loss mechanisms (see Fig. 1).

Another potential pitfall for modelers is the common misconception that the predominantly linear profile of many SOFC voltage–current curves is the result of ohmic loss domination. Since ohmic losses are a linear function of current density and both activation and concentration losses are logarithmic functions of current density, the danger is to assume these latter two losses do not significantly contribute to the overall voltage drop when the voltage–current curve is nearly linear.

$$\Delta V_{ohmic} \propto i \qquad (3)$$

$$\Delta V_{act} \propto \ln\left(\frac{i}{i_0}\right) \qquad (4)$$

$$\Delta V_{conc} \propto \ln\left(1 - \frac{i}{i_L}\right) \qquad (5)$$

where i_0 (equilibrium exchange current density) is defined as the equal forward and reverse flow of electrons across the electrode–electrolyte interface under open-circuit conditions and i_L (limiting current density) is defined as the maximum possible current density, in which the reactants are consumed at their maximum possible replenishment rates.

In reality, the activation losses tend to steadily increase over the operating range of the SOFC due to relatively large values of the equilibrium exchange current density, i_0. In contrast, low temperature fuel cells tend to have smaller exchange current densities and consequently a rapid increase in activation losses at low operating currents followed by a leveling out at higher currents. Also evident in Fig. 1 is the relatively small magnitude of the concentration loss over most of the operating range, thus it does not significantly affect the slope of the operating voltage curve until the limiting current density, i_L, is approached.
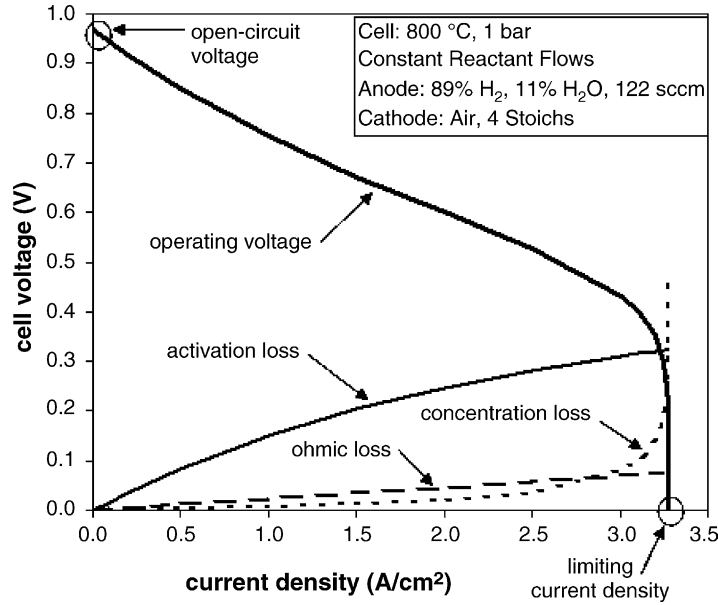
Fig. 1. Example of planar SOFC voltage–current characteristics for a single cell operating at $800\,°C$ (developed using PNNL model [9]).

2. Butler–Volmer equation and approximations

The governing equation for the activation loss at each electrode–electrolyte interface (i.e., the equation is applied separately at the anode and cathode) is the general Butler–Volmer (B–V) equation [19,22]:

$$i = i_0(e^{\alpha_1(F/R_uT)\Delta V_{act}} - e^{-\alpha_2(F/R_uT)\Delta V_{act}}) \quad (6)$$

The equilibrium exchange current density, i_0, is a strong function of cell materials, construction, and temperature and is typically calculated using an Arrhenius-type relation of the form:

$$i_0 = A\,e^{-E_{act}/R_uT} \quad (7)$$

where the pre-exponential term, A, is generally a function of cell temperature and reactant and product partial pressures [1–4,6,8,9,11,15]. The reduction and oxidation transfer coefficients, α_1 and α_2 respectively, are governed by the electron transfer processes occurring across the electrode–electrolyte interface. The net reactions at the anode and cathode are well understood for a hydrogen fueled SOFC and given by [$H_2 + O^{2-} \rightarrow H_2O + 2e$] and [$1/2O_2 + 2e \rightarrow O^{2-}$], respectively. There may be several intermediate steps, however, and the exact reaction mechanisms are difficult to identify. If the mechanisms are known, the published method [19,22] for determining the transfer coefficients is as follows:

$$\alpha_1 = \frac{n - \gamma}{\nu} - s\beta \quad (8)$$

$$\alpha_2 = \frac{\gamma}{\nu} + s\beta \quad (9)$$

where n is the total number of electrons transferred in the overall reaction, γ the number of electrons transferred before the rate determining step (rds), ν the number of times the rds

occurs for one act of the overall reaction, s the number of electrons transferred in the rds (0 or 1) and β the symmetry factor (defined below).

A simplification made in many SOFC models is to assume each reaction occurrence is a one-step, single-electron transfer process. This results in the following form of the B–V equation:

$$i = i_0(e^{(1-\beta)(F/R_uT)\Delta V_{act}} - e^{-\beta(F/R_uT)\Delta V_{act}}) \quad (10)$$

where the symmetry factor, β, is defined as the fraction of the activation voltage loss that affects the activation energy barrier, and thus the rate of electrochemical transformation. For simplicity, this factor is commonly assumed to be 0.5 for fuel cells, but values ranging from 0.3 to 0.6 have been used to match experimental data [9].

Since the full B–V equation must be solved implicitly for the activation voltage loss, several explicit approximations have been utilized in the literature. It is crucial to understand the range of applicability of each of these equations to minimize modeling inaccuracies. When the activation loss is large ($\Delta V_{act} > 200\,mV$), the first exponential term in the B–V equation is much larger in magnitude than the second. If the second exponential is neglected, the resulting equation is the *high-field approximation* (or sometimes called the *Tafel equation* [1,7,13,18,19,21–23]). This equation is valid when $i/i_0 > 4$, as discussed in the next section:

$$\Delta V_{act} \cong \frac{R_uT}{\alpha_1 F} \ln\left(\frac{i}{i_0}\right) \quad (11)$$

If the exponential terms in the one-step, single-electron transfer process B–V equation are expanded in a power series and the higher-order, non-linear terms are neglected, the resulting equation is the *low-field approximation* (or sometimes called the *linear current–potential equation* [1,7,13,19,21–23]).

This equation is valid when $i/i_0 < 1$, as discussed in the next section:

$$\Delta V_{\text{act}} \cong \frac{R_u T}{F} \left(\frac{i}{i_0} \right) \qquad (12)$$

Another approximation to the B–V equation comes from recognizing the shape of the corresponding ΔV_{act} versus current curve is similar to a hyperbolic sine function. In fact if α_1 and α_2 are assumed to be equal, the activation loss can be explicitly found using [19,22]:

$$\Delta V_{\text{act}} \cong \frac{R_u T}{\alpha_1 F} \sinh^{-1} \left(\frac{i}{2 i_0} \right) \qquad (13)$$

This will be referred to as the *hyperbolic sine approximation*.

3. Applicability of approximations

As stated earlier, the applicability of each explicit approximation to the implicit B–V equation must be analyzed to avoid significant modeling errors. To simplify the analyses, a one-step, single-electron transfer process is assumed and the current density is normalized by the equilibrium exchange current density. Fig. 2 shows a comparison of activation loss calculations for a cell operating at 800 °C and a symmetry factor of 0.5. Note the hyperbolic sine approximation is exactly equal to the B–V equation for this case. The low-field approximation is only applicable when the operating current density is less than or equal to the equilibrium exchange current density. The high-field approximation is only
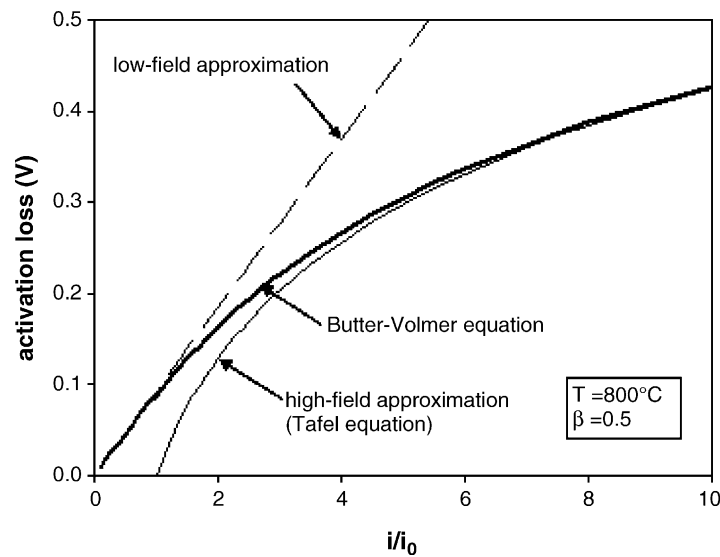

Fig. 2. Comparison of high-field and low-field approximations to the Butler–Volmer equation for a one-step, single-electron transfer process.
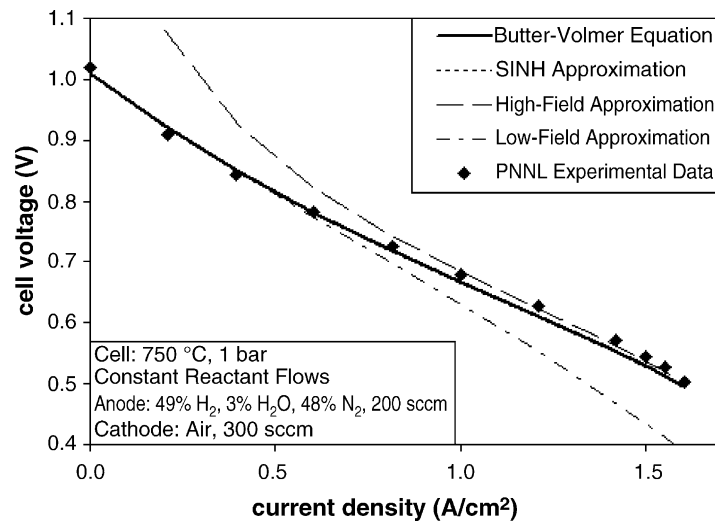

Fig. 3. Comparison of experimental voltage–current data [9] and model-based curves using different activation loss equations.
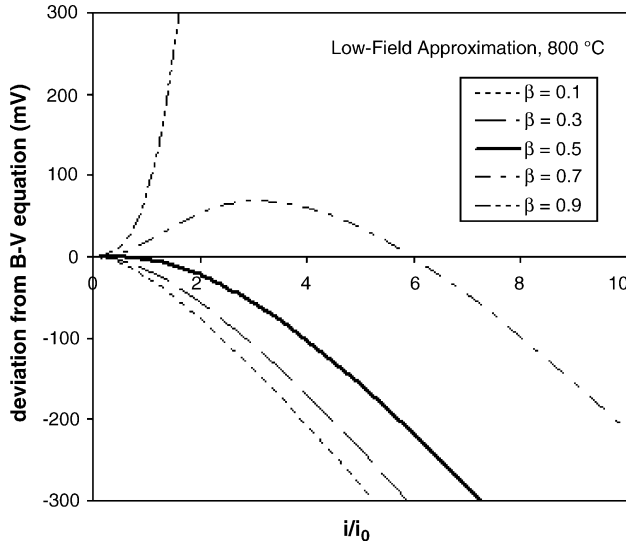
Fig. 4. Deviation from B–V equation using low-field approximation.

Fig. 6. Deviation from B–V equation using hyperbolic sine approximation.

applicable when the operating current density is greater than four times the equilibrium exchange current density. There is a significant gap $(1 < i/i_0 < 4)$ where neither of these approximations adequately determines the activation loss.

Fig. 3 shows the applicability of each activation loss equation used in a cell model validated with experimental data from a modern planar SOFC. The model results using the B–V equation and hyperbolic sine approximation are nearly identical and match well with the experimental data. The model results using the high-field and low-field approximations deviate significantly from the experimental data, except in very limited ranges of current density.
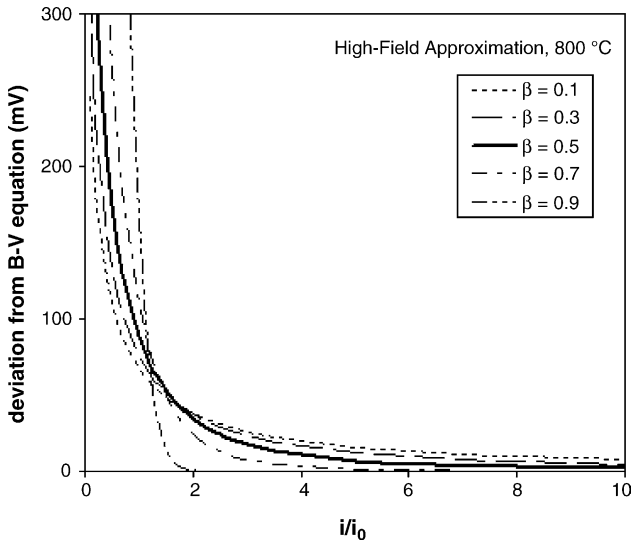

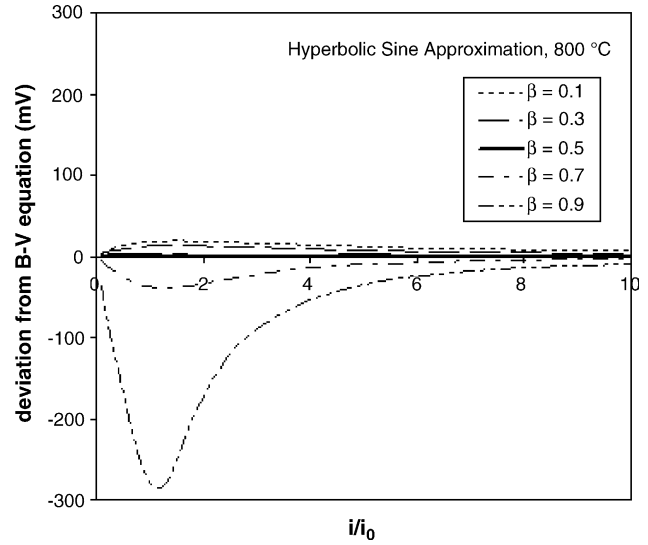Fig. 5. Deviation from B–V equation using high-field approximation.

To better understand the validity of each approximation relative to the B–V equation as a function of symmetry factor, an analysis was performed where the activation loss error is calculated over a wide range of current density ratios and symmetry factors. Fig. 4 illustrates the error using the low-field approximation, which shows increasingly severe inaccuracies as i/i_0 exceeds 1, especially when the symmetry factor deviates from 0.5 in either direction. Fig. 5 shows significant errors using the high-field approximation for $i/i_0 < 4$ and $\beta < 0.5$. The range of applicability increases for $\beta > 0.5$. Fig. 6 indicates small error over the entire operating regime using the hyperbolic sine approximation for $\beta < 0.7$.

4. Combining anode and cathode activation losses

Another questionable practice in some SOFC models is to represent the combined anode and cathode activation losses with a single-term equation. For example, starting with the hyperbolic sine approximation, the total cell activation loss is:

$$\Delta V_{\text{act,total}} = \Delta V_{\text{act,A}} + \Delta V_{\text{act,C}}$$
$$= \frac{R_u T}{\alpha_{1,A} F} \sinh^{-1}\left(\frac{i}{2i_{0,A}}\right)$$
$$+ \frac{R_u T}{\alpha_{1,C} F} \sinh^{-1}\left(\frac{i}{2i_{0,C}}\right) \tag{14}$$

There are two ways to reduce this two-term equation down to the following single-term equation and retain the physical meanings of α and i_0:

$$\Delta V_{\text{act,total}} = \frac{R_u T}{\alpha_{\text{eff}} F} \sinh^{-1}\left(\frac{i}{2i_{0,\text{eff}}}\right) \tag{15}$$

Method 1: Assume identical activation loss behavior for the anode and cathode (i.e., $\alpha_{1,A} = \alpha_{1,C}$ and $i_{0,A} = i_{0,C}$, which yields $\alpha_{eff} = \alpha_{1,A}/2$ and $i_{0,eff} = i_{0,A}$). This method is extremely questionable, since the activation loss is dependent on electrode materials and local reactants and products, which are completely different for the anode and cathode of a SOFC.

Method 2: Assume one of the equilibrium exchange current densities (i.e., anode or cathode) is sufficiently larger than the other, thus allowing the corresponding activation loss to be neglected (e.g., $i_{0,A} > 100i_{0,C}$ is required to neglect the anode activation loss and keep the resulting error below 2%). If this is not the case and experimental data is used to develop curve-fits for values of α_{eff} and $i_{0,eff}$, then the model's predictive capabilities should be considered suspect outside the operating conditions of the test unit.

5. Conclusions

For the relatively low temperature SOFCs being developed today, it is no longer reasonable to neglect the activation losses when building models to predict the cell voltage–current characteristics. The Butler–Volmer equation, or an appropriate approximation, should be implemented to accurately predict these losses. If an explicit equation is desired for functional reasons (e.g., quick parametric studies or severe computational speed requirements) and the charge transfer reaction is assumed to be a one-step, single-electron transfer process, then the hyperbolic sine approximation (Eq. (13)) is recommended for its superior accuracy over the majority of operating current densities and symmetry factors of interest. Otherwise, the implicit Butler–Volmer equation is easily solved using any one of a variety of standard numerical technique (e.g., the basic secant method typically converges within five iterations). High-field and low-field approximations, such as Eqs. (11) and (12), should be avoided unless the model's range of i/i_0 values is clearly established to be within the approximation's range of applicability. Finally, if a single-term equation is used to combine the anode and cathode activation losses, then the applicability of this model should be scrutinized outside of the range of the experimental data used for validation.

Acknowledgement

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