

Application of Butler–Volmer equations in the modelling of activation polarization for PEM fuel cells

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Abstract

Proton exchange membrane (PEM) fuel cells have been under development for many years and appear to be the potential solution for many electricity supply applications. Modelling and computer simulation of PEM fuel cells have been equally active areas of work as a means of developing better understanding of cell and stack operation, facilitating design improvements and supporting system simulation studies.

In general, fuel cell models must be capable of predicting values of the activation polarization at both the anode and the cathode. Since the magnitude of an activation polarization for a particular electrode depends on the inverse of the chemical (or electrochemical) reaction rate at that electrode, reaction rate expressions are normally required for each electrode. The reaction rate is commonly expressed as an ‘exchange current density’, typical symbol i_0 , and mechanistic expressions to predict i_0 are, therefore, components of an ideal model.

Most expressions for i_0 are based on the Butler–Volmer (B–V) equation or on more approximate equations derived from the B–V equation. Many publications use one of these B–V equations without a critical determination of the applicability or accuracy of the particular equation being used. The present paper examines these questions and makes some recommendations regarding the applicability of each equation in the ‘B–V family of equations’.

In addition, terminology and symbols have been modified, where possible, to make modelling based on B–V equations more easily understood and applied by those without an extensive background in electrochemistry.

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1. Introduction

Introductory material on the proton exchange membrane fuel cell, PEMFC, has been recently summarized [1]. General PEMFC and electrode processes reviews are available [2–18] as are papers on PEMFC modelling. Much of this has been cited and used in previous publications from our group [19–26] and was recently summarized [27,28].

The earliest of our related publications [19–21] covered the development and application of a simple but mechanistic steady-state electrochemical model for two particular PEM fuel cells. Subsequently [22], this work was extended to a generalized steady-state electrochemical model, suitable for application to

any PEM fuel cell up to the onset of serious mass transfer problems due to accumulation of liquid water at the cathode. Later [23] improvements to the ohmic and activation polarization terms were proposed. The emphasis in all of our PEM modelling work has been to keep the model as mechanistic as possible yet as simple as possible so that it could be understood, programmed and applied relatively easily. The parameter evaluation for these models was, however, based on data from PEM cells or stacks where the activation polarization was primarily from cathode losses. The models, therefore, did not adequately address anode losses and did not deal separately with anode and cathode losses.

The present paper attempts to summarize the important theoretical background, primarily based on the Butler–Volmer equation, that is common to the development of modelling capability for both anode and cathode activation polarization terms in any fuel cell. This will be generally applicable to the development of any fuel cell model but the emphasis is on the PEMFC. A

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Nomenclature

A	Arrhenius pre-exponential in Eq. (2) (A cm^{-2})
A_{act}	area of the actual fluid—active catalyst interface (the ‘reaction surface’) (cm^2)
A_{geo}	geometric area of the electrode (such as a ‘plane’ Pt disc electrode) or the geometric area of a single cell (such as the so-called ‘active cell area’ of a fuel cell incorporating a finely divided dispersed array of Pt particles, essentially the 2D projection of the gas-diffusion-layer on the cell membrane) (cm^2)
b	Tafel slope, $2.3RT/(\alpha F)$ (V decade $^{-1}$)
B	Arrhenius slope in Eq. (2) (K)
B–V	Butler–Volmer
c	concentration (mol cm^{-3})
c_{H_2}	concentration of dissolved hydrogen ($\text{mol H}_2 \text{ cm}^{-3}$)
C_{M}	concentration of active Pt sites (in sites cm^{-2} (order 10^{15}) or moles of sites cm^{-2} (order 10^{-8}))
E	thermodynamic emf (the maximum, equilibrium, voltage theoretically possible for the particular temperature and reactant partial pressures)
f	a combined conversion factor and catalyst utilization/efficiency factor in Eq. (18) (moles of active Pt sites per mg of Pt)
$f_i(\theta, \theta_0)$	functions of θ and θ_0 in the general Butler–Volmer equation
f_θ	a general Langmuir–Hinshelwood term in Eq. (3) to quantify the fraction of the active catalyst sites that are ‘vacant’ and able to participate in the gas–catalyst interaction
F	Faraday’s constant (96,487 C equiv. $^{-1}$)
HER	hydrogen evolution reaction (reverse of HOR)
HOR	hydrogen oxidation reaction
i	current density (A cm^{-2})
i_0	exchange current density (A cm^{-2})
L–H	Langmuir–Hinshelwood
MEA	membrane electrode assembly
n	number of electrons being transferred for one act of the overall reaction
n_a	number of electrons being transferred ‘after’ the rds
n_b	number of electrons being transferred ‘before’ the rds
N	mol of active Pt sites
ORR	oxygen reduction reaction
p	gas partial pressure (atm)
PEM	‘polymer electrolyte membrane’ or ‘proton exchange membrane’
PEMFC	PEM fuel cell
Q	general symbol in the Butler–Volmer equation and equal to i/i_0
r	ratio $A_{\text{act}}/A_{\text{geo}}$ (Eq. (16))
rds	rate-determining-step in the reaction sequence at an electrode

T	temperature (K)
V	voltage that appears across the fuel cell terminals
w_{cat}	weight of Pt (mg)
W_{C}	platinum loading (in mg cm^{-2}) where the area used as the basis is the cell ‘active area’ (represented by A_{geo}) (i.e. $W_{\text{C}} = w_{\text{cat}}/A_{\text{geo}}$)

Greek letters

α	transfer coefficient (in Butler–Volmer equation) (defined by Eq. (8))
β	symmetry factor
η	polarization (i.e. overvoltage or loss) (V)
ν	stoichiometric coefficient (number of times that the rds must take place for the overall reaction to occur once)
θ	fractional surface coverage (e.g. θ_{H} for chemisorbed hydrogen atoms in the HOR)

Subscripts

a	anode (or, with n , ‘after’)
act	activation or actual
b	before
c	cathode
ch	channel
conc	concentration (as related to ‘concentration polarization’, the voltage loss due to slow mass transfer)
CO	carbon monoxide
gas	reactant gas (H_2 or O_2)
geo	geometric (as defined for A_{geo})
H	hydrogen atom
H_2	hydrogen
meas	measured, i.e. an experimental value
M	‘metal’ (i.e. Pt) site meas measured, i.e. an experimental value
ohmic	related to ohmic (iR) losses
O_2	oxygen
v	vacant
0	at zero polarization and zero net current condition (i.e. at equilibrium)
2t	2-term series approximation
3t	3-term series approximation

Superscripts

m	order of reaction with respect to C_{M} (Eq. (3))
n	order of reaction with respect to c_{gas} (Eq. (3))
o	general rate constant (function of T only) (Eq. (3))
*	at the interface of the Pt catalyst and the surrounding aqueous medium (the ‘reaction interface’)

recent paper [29] has done a similar analysis in the context of a solid oxide fuel cell. Subsequent papers will develop modelling approaches for the anode activation polarization [30,31] and the cathode activation polarization [32] in a PEMFC.

All symbols and units are described in the Nomenclature.

2. The essentials of a fuel cell model

Mass transfer of the reactant gases can be taken into account in a PEMFC model in at least two ways for a characterized MEA structure. In the first approach, the bulk concentrations of reactants in the feeds (the hydrogen partial pressure in the anode gas channel and the oxygen partial pressure in the cathode gas channel, $p_{\text{H}_2,\text{ch}}$ and $p_{\text{O}_2,\text{ch}}$, respectively) can be corrected, by appropriate mass transfer calculations in the MEA, to the lower values, $p_{\text{H}_2}^*$ and $p_{\text{O}_2}^*$, at the ‘reaction interfaces’ where all the participants in the reactions come together. These interfacial partial pressures are then used in the calculation of the activation polarizations. In the second approach, however, the model includes the mass transfer losses in a more visible way, including concentration polarization terms for each electrode and starting from

$$V = E + \eta_{\text{act,a}} + \eta_{\text{act,c}} + \eta_{\text{ohmic}} + \eta_{\text{conc,a}} + \eta_{\text{conc,c}} \quad (1)$$

In applying Eq. (1), the $\eta_{\text{act,a}}$ and $\eta_{\text{act,c}}$ terms are quantified using the channel values of the reactant partial pressures.

The present paper primarily concerns only the activation polarization terms, $\eta_{\text{act,a}}$ at the anode and $\eta_{\text{act,c}}$ at the cathode. Modelling of the mass transfer-related concentration polarization terms, $\eta_{\text{conc,a}}$ and $\eta_{\text{conc,c}}$, will be addressed in a later paper.

3. Modelling the activation polarization

3.1. Introduction

The basic theories of polarizations (or ‘overvoltages’) for the hydrogen oxidation reaction and the oxygen reduction reaction have been established for decades. In many PEM fuel cell models, the emphasis is on the contribution from the oxygen reduction reaction (ORR) (i.e. the cathode activation polarization) since the hydrogen oxidation reaction (HOR) is so fast that the anode activation polarization is generally negligibly small. If, however, the concentrations of the reactants for the anode reaction get very low, the HOR could slow down to the extent that the anode activation polarization is also significant. This situation could arise, for example, if the hydrogen partial pressure at the anode is very low or, more likely, the concentration of ‘available’ (i.e. vacant) active Pt catalyst sites on the anode is very low. Similarly, since the anode kinetics are relatively rapid, the anode activation polarization may well be relatively small when compared to the anode concentration polarization. For these reasons, in order to extend the applicability of any PEMFC model, separate anode and cathode polarization terms, both activation and polarization, should be built in.

3.2. The exchange current density

Fuel cell modelling basically involves the prediction of the various voltage losses at a particular current density and at a particular set of operating conditions. Like any process involving chemical reactions, the chemical reaction rate, and the rate equation which predicts this reaction rate, are essential for the

development of a mechanistic model for the prediction of activation polarization at each electrode. Electrochemical energy sources, batteries and fuel cells, commonly use ‘exchange current density, i_0 ’ as the electrochemical version of ‘chemical reaction rate’.

A general correlation for exchange current density, essentially the electrochemical reaction rate, could take the form of a conventional heterogeneous rate equation:

$$i_0 = A \exp \left[\frac{B}{T} \right] \quad (2)$$

where ‘A’ will typically contain one or more rate constants as well as concentration terms to represent all the reactants. This could take the general form:

$$A = A^\circ C_{\text{M}}^m c_{\text{gas}}^n [f_\theta] \quad (3)$$

The parameter A° will contain the kinetic constants and will normally be only a function of temperature. C_{M} would be the catalyst parameter, representing the total concentration of active sites, and could appear to a reaction order, m , other than unity. Often, in heterogeneous catalysis, A° and C_{M}^m are lumped together and are not quantified individually.

The concentration of dissolved reactant gas, c_{gas} , at the electrolyte–catalyst interface could also be raised to some power if the reaction order with respect to this concentration is other than unity. In general, c_{gas} would be a function of the solubility of the reactant gas in the electrolyte and could depend on the solute (e.g. H_2 or O_2), the partial pressure of the solute, the solvent (i.e. the particular electrolyte and its concentration), and the temperature.

Finally, f_θ would be a general Langmuir–Hinshelwood term, common in heterogeneous rate equations, to quantify the fraction of the active catalyst sites that are ‘vacant’ and able to participate in the gas–catalyst interaction. The f_θ term would normally be some function of the equilibrium (zero net current) fractional surface coverage of reaction intermediate and would normally be a function of c_{gas} and T .

A general predictive (i.e. modelling) expression for i_0 should, therefore, contain values of the ‘constants’ A° , C_{M} and B plus expressions for the evaluation of f_θ and c_{gas} .

Most modelling expressions that link the current density, i , and the activation polarization, η_{act} , incorporate i_0 or an expression for i_0 . Most of these $\eta_{\text{act}}(i, i_0)$ expressions are derived from the so-called Butler–Volmer equation or from an expression derived from the B–V equation.

3.3. The Butler–Volmer equation and B–V ‘derivative’ equations

3.3.1. The Butler–Volmer equation

The common starting point for the development of a prediction of an activation polarization for a particular current density is the Butler–Volmer equation (for example, Eq. (5.75) in Austin [4]):

$$i = i_0 Q \quad (4)$$

Here i and i_0 must both be based on the same area of reaction surface. The exchange current density is the value of the current density at zero net current where the reaction is at an equilibrium, subscript 0, condition. This situation is also characterized by zero activation polarization (i.e. $\eta_{\text{act,a}} = \eta_{\text{act,c}} = 0$).

As may be seen elsewhere [30–32], a general expression for this Q may appear in one of the following forms.

For a ‘simple’, one-electron, process, where θ (e.g. θ_{H} in the HOR) is low (i.e. $1 - \theta \approx 1$) or where θ does not differ significantly from θ_0 , the familiar Butler–Volmer expression applies:

$$Q = \exp\left[\frac{\beta F\eta}{RT}\right] - \exp\left[\frac{-\{1 - \beta\}F\eta}{RT}\right] \quad (5)$$

The symbol β in Eq. (5) is commonly used to represent the ‘symmetry factor’ (see Ref. [7], Section 8.2.4, pp. 869–873, in particular Fig. 8.21), a parameter which represents the ratio of ‘distance across double layer to summit’ to ‘distance across whole double layer’ (requiring, therefore, a value between 0 and 1). The physical meaning and numerical value of β are discussed in many sources with considerable support for a value close to 0.5, a commonly used assumption for much data analysis.

Two conditions must be met to make Eq. (5) valid: the coverage of the electrode surface by adsorbed intermediates must be low and the heat of adsorption must be independent of the coverage (i.e. Langmuir rather than Temkin adsorption).

For higher values of θ (i.e. $1 - \theta \neq 1$), or where θ does vary considerably from θ_0 , the following, more general, version of Eq. (5) applies:

$$Q = f_1(\theta, \theta_0)\exp\left[\frac{\beta F\eta}{RT}\right] - f_2(\theta, \theta_0)\exp\left[\frac{-\{1 - \beta\}F\eta}{RT}\right] \quad (6)$$

The $f_i(\theta, \theta_0)$ parameters commonly take the form of ratios such as θ/θ_0 or $(1 - \theta)/(1 - \theta_0)$.

For more complex overall reactions, where other elementary reactions may precede or follow the rds and where the transfer of more than one electron may be involved, the following more general version of Eq. (6) is commonly used:

$$Q = f_1(\theta, \theta_0)\exp\left[\frac{\alpha F\eta}{RT}\right] - f_2(\theta, \theta_0)\exp\left[\frac{-\{1 - \alpha\}F\eta}{RT}\right] \quad (7)$$

For such multistep processes, various authors (such as Refs. [7,8]) suggest that the commonly used empirical parameter, the ‘transfer coefficient’ (symbol α), be defined as follows:

$$\alpha = \frac{\beta(n - n_b - n_a) + n_b}{\nu} \quad (8)$$

and

$$1 - \alpha = \frac{(1 - \beta)(n - n_b - n_a) + n_b}{\nu} \quad (9)$$

Eqs. (8) and (9) apply if the steps occurring before the rds (in both directions) are considered to be in pseudoequilibrium.

The parameters n , n_a , n_b and ν are all defined in the Nomenclature. The HOR is normally based on the consumption of one molecule of hydrogen so that ‘ $n=2$ ’ would apply. For the ORR, the reduction of one molecule of oxygen implies an ‘ $n=4$ ’ situation.

The symbol α is often used instead of β without any clear definition. In addition, α and β are often used interchangeably, sometimes a source of confusion when evaluating and comparing the work of several authors.

Note that when n_a and n_b are equal to 0 and ν equals 1, the multi-step process reduces to the elementary, one-electron, step, Eq. (8) reduces to $\alpha = \beta$, and Eq. (7) reverts to Eq. (6).

Therefore, while β is commonly assumed to have a value of 0.5, α may or may not have this value. Since the HOR and the ORR are multi-step processes, α will be used instead of β in the following discussion of the Butler–Volmer equation.

A general caveat that applies to these B–V expressions is that they are all based on the same reaction mechanism over the range of η_{act} and i being considered (i.e. the same value of α). If a particular process changes rds over the operating range being considered, a single B–V equation will not suffice. This is a particular problem when the ORR is being modelled.

3.3.2. Butler–Volmer approximations

The simpler version of Q in Eq. (7), with the $f_1(\theta, \theta_0)$ and $f_2(\theta, \theta_0)$ terms set to unity, can conveniently be represented as $e^x - e^y$ where x equals $\alpha F\eta/RT$ and y equals $[-(1 - \alpha)/\alpha]x$. There are two approximations regarding Q that are commonly used in the analysis or prediction of polarization data.

3.3.2.1. The ‘high-polarization’ approximation. This is based on the ‘if $e^x \gg e^y$ ’ condition where e^y is dropped out and the following results:

$$\eta \approx \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right) = \left[2.303 \frac{RT}{\alpha F}\right] \log\left(\frac{i}{i_0}\right) \quad (10)$$

This is the Tafel equation and $[2.3RT/\alpha F]$ is the Tafel slope, typically symbol ‘ b ’.

It is important to quantify ‘high-polarization’ and determine both the limits of applicability and the accuracy of the Tafel approximation. The accuracy can be quantified via the ratio e^x/e^y . For a 5% error in the approximation, this ratio should be about 20 and for a 1% error e^x/e^y should have a value of about 100. The latter error goal implies that, for $n=2$ and for ‘room temperature’ of about 296 K, the following tabulation indicates what polarization must be exceeded to keep the Tafel approximation within 1% error for, as an example, the HER.

α	b (V decade ⁻¹)	$\eta_{\text{act,a}}$ (V)
0.25	0.117	>0.059
0.5	0.059	>0.059
0.75	0.039	>0.059

For ~5% error in the Tafel approximation, the minimum polarization for use of the Tafel approximation drops from ~0.059 to ~0.039 V. This voltage threshold will be temperature dependent since b varies directly with temperature.

As mentioned earlier, the application of the B–V equation over a wide operating range requires that the mechanism and rds remain unchanged over that range. For example, the B–V equation cannot apply to the low-temperature ORR where both the theoretical reversible potential and the anode process taking

place on the same material as the cathode process are unavailable. In this situation, only the forward process of the ORR applies and Eq. (10) is essential for modelling the activation polarization.

3.3.2.2. The ‘low-polarization’ approximations. A common approximation used in the literature is based on the ‘if $e^x \approx 1 + x$ ’ approximation, the series expansion being truncated after the first term. This implies, therefore, that this ‘2-term’ approximation leads to

$$e^x - e^y \approx (1 + x) - \left[1 + \left\{ \frac{-(1 - \alpha)}{\alpha} \right\} x \right] \approx x + \left[\frac{(1 - \alpha)}{\alpha} \right] x \quad (11)$$

giving

$$i_{2t} \approx i_0 \left[\frac{\alpha F \eta}{RT} + \left(\frac{1 - \alpha}{\alpha} \right) \left(\frac{\alpha F \eta}{RT} \right) \right] \quad (12)$$

Eq. (12) reduces to the often-used, linear $\eta(i)$, low-polarization approximation:

$$i \approx i_0 \left[\frac{F \eta}{RT} \right] \quad (13)$$

Two questions should now be examined:

- (1) What is the upper polarization limit for this ‘2-term’ approximation to be acceptably accurate?
- (2) What if α is significantly greater or less than 0.5? (As is often implied from published results.)

To examine the first question, the more accurate, ‘3-term’, series approximation:

$$e^x \approx 1 + x + \frac{x^2}{2} \quad (14)$$

will be used, resulting in the following:

$$i_{3t} \approx i_0 \left(\frac{F \eta}{RT} \right) \left[1 + (\alpha - 0.5) \frac{F \eta}{RT} \right] \quad (15)$$

The square-bracket term in Eq. (15) can be called the ‘3-term correction factor’ as the rest of the equation is the same as the 2-term approximation given by Eq. (13). For an α value of 0.5, this ‘correction factor’ has a value of unity and Eq. (15) reduces to Eq. (13). For α values above or below 0.5, the value of the $[1 + (\alpha - 0.5)(F\eta/RT)]$ ‘correction factor’, i.e. its deviation above or below 1, becomes the parameter for assessing the accuracy of the 2-term approximation. For example, for the ‘room temperature’ calculation as before, Table 1 illustrates the loss in accuracy of the 2-term and 3-term approximations compared to the more rigorous Butler–Volmer equation given by Eqs. (4) and (5) (itself a simplification from the more general Eqs. (4) and (6)).

At an α value of ~ 0.5 , the $<1\%$ inaccuracy is met below ~ 0.015 V and the $<5\%$ inaccuracy below ~ 0.03 V. When α reaches the extremes of the 0.5 ± 0.25 range used for this illustration, the commonly used ‘2-term’ approximation for low-polarization appears to exceed the 1% inaccuracy criteria above

Table 1

The importance of α in the various versions of the Butler–Volmer equation in the low-polarization region at ‘room temperature’

η (V)	i_{2t}/i_{B-V}			i_{3t}/i_{B-V}		
	$\alpha = 0.25$	$\alpha = 0.5$	$\alpha = 0.75$	$\alpha = 0.25$	$\alpha = 0.5$	$\alpha = 0.75$
0.0005	1.0049	1.0000	0.9951	0.9998	1.0000	1.0000
0.001	1.0098	1.0000	0.9902	0.9995	1.0000	0.9999
0.0025	1.0244	0.9996	0.9754	0.9993	0.9996	0.9993
0.005	1.0485	0.9984	0.9507	0.9972	0.9984	0.9972
0.0075	1.0606	0.9975	0.9382	0.9956	0.9975	0.9957
0.01	1.0960	0.9936	0.9008	0.9867	0.9936	0.9892
0.015	1.1419	0.9857	0.8510	0.9739	0.9857	0.9761
0.02	1.1859	0.9748	0.8013	0.9662	0.9748	0.9584
0.025	1.2279	0.9611	0.7522	0.9270	0.9611	0.9365
0.03	1.2675	0.9446	0.7040	0.8949	0.9446	0.9110

~ 0.001 V and the 5% criteria above about 0.005 V polarization. At the same extreme values of the α range, the proposed ‘3-term’ approximation raises the range of applicability up to ~ 0.0075 V for $<1\%$ inaccuracy and up to ~ 0.02 V for $<5\%$ inaccuracy. The ‘3-term’ results therefore represent significant improvements in modelling accuracy over the ‘2-term’ results.

For example, at the suggested upper limit of the ‘micropolarization’ region for the HOR, 0.01 V, the common 2-term approximation is in error by about -1% when α is 0.5 but is about $\pm 10\%$ in error at the example 0.25 and 0.75 extremes in α value. Clearly the value of α must be known before i_0 values are estimated from low-polarization experimental data as Eq. (13) could be quite inaccurate compared to Eq. (15).

3.3.3. The electrode catalyst

The parameter A in Eqs. (2) and (3) is normally a function of C_M . For a particular electrode, in the absence of any transient phenomena such as catalyst poisoning or deactivation, C_M should be constant.

For present purposes, the electrode catalyst of interest is a polycrystalline Pt. Following the practice that is common in catalytic kinetics, the catalyst will be considered as a ‘reactant’ and will appear in kinetic expressions as a ‘concentration’. For example, if C_M is the maximum number of active Pt sites (typically of the order 10^{15} sites cm^{-2} Pt), this concentration term will typically be used with units of mol cm^{-2} (normally, therefore, with a value of about 2×10^{-9}).

Taking this a step further, a published value of exchange current density, i_0 (or $i_{0,\text{meas}}$) is normally the ratio of the measured exchange current, I_0 , to the measured or calculated geometric area of the electrode, A_{geo} (whether this is a ‘plane’ Pt disc electrode or a finely divided dispersed array of Pt particles in an MEA):

- (i) Considering first a ‘plane’ Pt disc electrode or a Pt wire electrode, the probable source of most fundamental measurements of the exchange current density, the actual fluid–catalyst interface will generally follow a slightly larger surface, A_{act} , resulting from a surface that is ‘rough’ and/or porous. This is often characterized by a ‘roughness

factor', r , defined by

$$r = \frac{A_{\text{act}}}{A_{\text{geo}}} \quad (16)$$

so that an 'actual' kinetic parameter $i_{0,\text{act}}$ would be defined by

$$i_{0,\text{act}} = \frac{i_{0,\text{meas}}}{r} \quad (17)$$

In this case, the parameter ' r ' could be called ' $r_{\text{electrode}}$ ' for further clarity. Such a 'rough' or 'porous' electrode surface could perhaps be expected to have an ' r ' value in the range $1 < r < 10$. For example, Ayad et al. [33] reported roughness factors on smooth Pt of ~ 3 while Ho and Piron [34], in their study of surface area determination of Pt in KOH, summarized roughness factors for 'bright Pt wire' determined by three different methods, in both 5 M KOH and 0.5 M H₂SO₄, and showing good agreement, ' r ' values ranging from 1.7 ± 0.0 to 1.8 ± 0.1 . Mitsushima et al. [35], from their work with a Pt disk microelectrode on Nafion, reported roughness factors from 1.5 to 1.8. Parthasarathy et al. [36], for a 100 μm diameter Pt wire electrode, reported 'apparent roughness factors' of 9.2 for a Pt/Nafion combination and 9.6 for a Pt/H₃PO₄ combination.

- (ii) Extending this to a 'real' fuel cell electrode, where typically there will be a finely divided dispersed array of Pt particles in an MEA, the amount of Pt catalyst is probably most-commonly expressed as W_C , the 'platinum loading'. A number of other catalyst parameters (N , w_{cat} and f) are defined in the Nomenclature. Although these parameters often have the same values for both anode and cathode, this need not be so. Normally, therefore, they would be subscripted to denote 'anode' or 'cathode'. The parameter ' r ' could, for clarity, now be written as r_{MEA} to distinguish it from $r_{\text{electrode}}$ although it is still defined by Eq. (16). These various catalyst parameters are related by expressions such as

$$f = \frac{N}{w_{\text{cat}}} \quad (18)$$

$$C_M = fW_C \quad (19)$$

In utilizing published rate data (e.g. exchange current densities from fundamental studies on Pt electrodes) to model 'real' PEM electrodes, the area 'basis' must be kept in mind. In a 'real' fuel cell MEA, the ratio of the actual active Pt area to the 'plane' cell area, r_{MEA} , could probably range from several 'tens' to several hundred. For example, Ayad et al. [33] reported $A_{\text{act}}/A_{\text{geo}}$ for Pt/Nafion PEM electrodes of ~ 160 . (These values were determined by hydrogen ads/des voltametry which also revealed that these ratios were greater for the HOR on the anode than for the ORR on the cathode.) Gasteiger et al. [37] presented correlations of PEM anode polarization data which employed r_{MEA} values of 26 and 210. Appleby and Foulkes [12], in discussing PAFC in their Chapter 2, state: "With low-loading high-surface area Pt catalysts (0.25 mg cm^{-2} , $100 \text{ m}^2 \text{ g}^{-1}$), the ratio of

true catalyst area to electrode geometrical area will be about 250." Xie et al. [38], for gas diffusion electrodes which had 3-zone Pt/Nafion catalyst layers, measured electrochemical surface areas and reported roughness factors from 335 to 446.

In kinetic expressions involving catalyst concentration, the fraction of the Pt sites that are vacant is often required. This leads to the introduction of the common Langmuir–Hinshelwood parameter, θ_V , the fraction of the active sites that is vacant and therefore able to participate in the chemisorption/dissociation reactions on each electrode. This parameter can, therefore, appear in a kinetic expression (such as exchange current density) in combination with, for example, C_M . For the HOR, for example, the fraction vacant, θ_V , could simply depend on the fraction of the sites occupied by H atoms, θ_H , i.e.

$$\theta_V = 1 - \theta_H \quad (20)$$

or it could also reflect the effects of adsorbed impurities, chemisorbed CO poison, other intermediates in the reaction, etc, such that, for example

$$\theta_V = 1 - \theta_H - \theta_{\text{CO}} - \theta_{\text{impurities}} - \theta_{\text{intermediates}} \quad (21)$$

Parameters W_C would be determined by the manufacturing process, f would be determined by both manufacturing and subsequent operating history (including ageing and permanent poisoning processes), and the L–H chemisorption parameter, θ_V , would be a function of reactant gas partial pressure, gas composition, temperature, mechanism of the electrode process, and the process kinetics.

3.3.4. Solubilities of reactant gases in the electrolyte

As introduced in Eq. (3), the exchange current density will normally be some function of c_{gas} , either c_{H_2} or c_{O_2} . The quantification of this variable has been recently dealt with in detail elsewhere [1].

4. Summary and conclusions

In general, modelling of activation polarization, when the rate-determining-step involves electron transfer, should be based on Eqs. (4) and (6).

At low-polarizations, or when other system characteristics justify the assumptions that the $f_1(\theta, \theta_0)$ and $f_2(\theta, \theta_0)$ parameters can both be assumed to have a value of close to unity, the simpler Butler–Volmer equation, given by Eqs. (4) and (5), can be used.

When the particular electrode experiences a multi-step reaction and when one or more of the steps involve electron transfer, Eqs. (8) and (9) should be applied to replace β and $(1 - \beta)$ by α and $(1 - \alpha)$ in Eqs. (5) and (6). This will require complete knowledge of all the fundamental steps involved in the overall electrode reaction.

When the activation polarization for a particular electrode is sufficiently high that the Tafel approximation is acceptably accurate, and if a value of α is known for the particular reaction and reaction conditions, Eq. (10) can be applied to predict η_{act} .

At very low current densities (and very low activation polarizations), and if a value of α is known for the particular reaction and reaction conditions, the ‘3-term approximation’, Eq. (15), should generally be used for modelling. If α has a value close to 0.5, however, the simpler Eq. (13), the ‘2-term approximation’, may be used.

In general, expressions such as Eqs. (2) and (3) must be derived to provide i_0 , essentially the kinetic rate equation for the rate-determining step(s). These expressions will require values of exchange current density parameters such as A^0 and B , a surface coverage parameter such as f_θ , catalyst parameters such as C_M and r , and interfacial concentrations derived from reactant partial pressures and solubility information.

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