Evaluation of Tafel–Volmer kinetic parameters for the hydrogen oxidation reaction on Pt(1 1 0) electrodes

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ABSTRACT

Modelling of PEM fuel cells has long been an active research area to improve understanding of cell and stack operation, facilitate design improvements and support simulation studies. The prediction of activation polarization in most PEM models has concentrated on the cathode losses since anode losses are commonly much smaller and tend to be ignored. Further development of the anode activation polarization term is being undertaken to broaden the application and usefulness of PEM models in general.

Published work on the kinetics of the hydrogen oxidation reaction (HOR) using Pt($h\,k\,l$) electrodes in dilute H_2SO_4 has been recently reassessed and published. Correlations for diffusion-free exchange current densities were developed and empirical predictive equations for the anode activation polarization were proposed for the experimental conditions of the previously published work: Pt(1 0 0), Pt(1 1 0) and Pt(1 1 1) electrodes, p_{H_2} of 1 atm, and temperatures of 1, 30 and 60 °C. It was concluded that the HOR on Pt(1 1 0) electrodes followed a Tafel–Volmer reaction sequence.

The aim of the present paper is to generalize these Tafel–Volmer correlations, apply them to published data for Pt(1 1 0) electrodes and further develop the modelling of anode activation polarization over the range of operating conditions found in PEMFC operation.

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1. Introduction

The background for the present paper has been recently published [1–3]. Our long-term aim is to further develop our generalized steady-state electrochemical model, the GSSEM, which consists of a simple, 1-dimensional, model of a PEM fuel cell (PEMFC) based on

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

The specific goal of the present paper is to further evaluate previously published work which studied the hydrogen oxidation reaction on Pt($h\,k\,l$) electrodes in dilute H_2SO_4 and to develop the results into a modelling approach for $\eta_{act,a}$, the anode activation polarization, in PEMFCs. The quantitative prediction of this particular loss is generally not given much attention in a PEMFC model since it is, normally, much less significant than the corresponding loss at the cathode. There are situations, however, where the anode activation polarizations could become significant and a modelling capability is therefore desirable.

Our present interest is the anode activation polarization related to the 'hydrogen oxidation reaction' (HOR) for which the overall half-cell reaction is

$$H_2 \Rightarrow 2H^+ + 2e^- \qquad (2)$$

The reverse of reaction (2) is the 'hydrogen evolution reaction' (HER).

The anode reaction occurs in the presence of a catalyst, typically Pt if the anode feedstock is pure hydrogen.

There is broad support in the literature for the HOR on Pt to proceed via a Tafel–Volmer reaction sequence, fully described recently [3]. There is not, however, complete agreement on the kinetic model as literature support exists for both 'rds Tafel–fast Volmer' kinetics and for 'fast Tafel–rds Volmer' kinetics. These were respectively referred to as 'Mechanism I' and 'Mechanism II' in our recent reassessment [3] of a body of work published by what we chose to call the 'Markovic Group' [4–9]. This group of publications included extensive results for rotating disk electrode (RDE) studies of the HOR on single-crystal Pt(1 0 0), Pt(1 1 0) and Pt(1 1 1) electrodes in dilute sulphuric acid electrolyte at 1, 30 and 60 °C and 'corrected to a p_{H_2} of 1 atm'. These publications [4–9] concluded that the Pt(1 1 0) results were best explained by 'rds Tafel–fast Volmer' kinetics, our so-called 'Mechanism I'.

The present paper, in Section 2, will review the detailed development of thermodynamic and kinetic equations for 'Mechanism

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Nomenclature

b	Tafel slope, $2.3RT(\alpha F)^{-1}$ (V dec^{-1})
B–V	Butler–Volmer
c	concentration (mol cm^{-3})
c_{H_2}	concentration of dissolved hydrogen at the reaction interface (mol H$_2$ 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	equilibrium EMF of a cell (V) or total anode polarization, $\eta_{act,a} + \eta_{conc,a}$, in Refs. [4–9] (V)
$f_I(\theta,\theta_0)$	functions of θ and θ_0 in the general Butler–Volmer equation (see following Eq. (25))
F	Faraday's Constant (clbs equ't^{-1})
GSSEM	generalized steady state electrochemical model
H	Henry's Law 'constant' (atm cm^3 mol^{-1})
HER	hydrogen evolution reaction (reverse of Eq. (2))
HOR	hydrogen oxidation reaction (Eq. (2))
i	current density (A cm^{-2})
i_o	exchange current density (A cm^{-2})
k	chemical rate constant
k_{ads}	rate constant for the 2-site dissociative chemisorption of a hydrogen molecule [cm^5 s^{-1} (mol of vacant Pt sites)$^{-2}$]
k_{des}	rate constant for the hydrogen molecule desorption reaction [(mol H$_2$) cm^2 s^{-1} (mol of occupied Pt sites)$^{-2}$]
$k_{et,fwd}$	forward rate constant for the electron transfer (Vogel) reaction
$k_{et,rev}$	reverse rate constant for the electron transfer (Vogel) reaction
K_{ads}	adsorption equilibrium constant for chemisorbed hydrogen molecules (also equal to k_{ads}/k_{des}) [cm^3 (mol H$_2$)$^{-1}$, the reciprocal of the units of c_{H_2}]
$K_{et}c_{H_3O^+,o}$	equilibrium 'constant', representing $\{k_{-et}c_{H_3O^+,o}(k_{et})^{-1}\}$, for the electron transfer reactions, Eqs. (8) and (9)
Mechanism I	the 'rds Tafel–fast Volmer' HOR process
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
p	partial pressure of a gas component (atm)
r	chemical reaction rate
rds	rate-determining-step in the reaction sequence at the anode
RDE	rotating disk electrode
V	cell voltage (V)

Greek letters

α	transfer coefficient
β	symmetry factor
η	polarization (i.e. overvoltage or loss) (V)
θ	fractional surface coverage (generally of chemisorbed hydrogen atoms)
ν	stoichiometric coefficient in Eq. (5) (number of times that the rds must take place for the overall reaction to occur once)

Subscripts

a	anode or activity
act	activation
ads	adsorption
b	bulk
c	cathode
conc	concentration (relating to mass transfer losses)
des	desorption
et	electron transfer (as in the Volmer reaction)
expl	experimental
fwd	forward
H$_2$	hydrogen molecule
H	hydrogen atom
H$_3$O$^+$	hydrated proton (i.e. H$^+$:H$_2$O)
i	interface
I	Mechanism I
MG	Markovic Group (authors of Refs. [4–8])
ohmic	relating to ohmic (i.e. iR) losses
o	at zero polarization and zero net current condition (i.e. at equilibrium)
pred	predicted
rev	reverse
sat	saturated
T	Tafel reaction
V	Volmer reaction
vac	vacant

I', the 'rds Tafel–fast Volmer' HOR process. Then, in Section 3, these equations will be applied to the further analysis and correlation/recorrelation of some published results for the HOR on Pt(1 1 0) electrodes and evaluation of the Tafel–Volmer, T–V, parameters. Section 4 will then deal briefly with the generalization of these correlations to values of p_{H_2} and temperatures that are more representative of PEMFC modelling applications.

2. Development of mechanistic equations for a 'Tafel–Volmer' HOR reaction

2.1. Introduction

The basic theories of activation polarizations for the HOR and, especially, overvoltages for the HER have been established for decades. This section will summarize the development of a correlation and modelling approach for the anode activation polarization that is as mechanistic as possible yet as simple to understand and apply as possible. The goal is to develop a relationship linking the anode activation polarization to the current density and the other operating parameters of the fuel cell.

The literature dealing with both the HOR and the HER is vast but there appears to be general agreement on the main features of the process. Much of the following development has benefited from the previous work of Parsons [10], Austin [11,12], Bockris and Reddy [13], Gileadi et al. [14], the 'Markovic Group' [4–9], Springer et al. [15], Camara et al. [16], Breiter [17] and Lasia [18].

2.2. Fundamental steps in the HOR

Various possible steps in the overall HOR have been suggested, one combination being the so-called 'Tafel–Volmer sequence'. Using 'M' to represent an active Pt atom and 'e$^-$' to represent an electron, the steps in this sequence are:

(i) H$_2$ + M $\Leftrightarrow$ M.H$_2$
(ii) M.H$_2$ + M $\Leftrightarrow$ 2M.H
    with (i) + (ii), the 'Tafel step', often simply
(iii) H$_2$ + 2M $\Leftrightarrow$ H$_{ad}$ + H$_{ad}$