

Incorporation of voltage degradation into a generalised steady state electrochemical model for a PEM fuel cell

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Abstract

Currently there has been very little reliability or end-of-life analysis conducted for polymer electrolyte membrane fuel cell (PEM) stacks, and detailed designs of PEM systems are still in a rapid evolutionary stage. Voltage degradation as a fuel cell ages is a widely observed phenomenon and results in a significant reduction in the electrical power produced by the stack. Little systematic information has been reported, however, and this phenomenon has not been included in electrochemical models. An earlier work described the development of the generalised steady state electrochemical model (GSSEM) which accepts as input the values of the operating variables (anode and cathode feed gas pressure and compositions, cell temperature and current density), and cell design parameters such as the active area and Nafion membrane thickness. This work will introduce new terms to the model to account for membrane electrode assembly (MEA) ageing, which is a factor in the durability of the stack. One term is based on the concept that the water-carrying capacity (a principal factor in membrane resistance) of the membrane deteriorates with time-in-service. A second term involves the apparent catalytic rate constants associated with the reactions on the anode and cathode side, and the changes in catalytic activity or active site density due to catalyst degradation. A third term deals with the decrease in the rate of mass transfer within the MEA. The resulting model is largely mechanistic, with most terms being derived from theory or including coefficients that have a theoretical basis, but includes empirical parameters to deal with the changing performance. Changes in the polarisation curve predicted by the generalised steady state electrochemical degradation model (GSSEDM) are demonstrated from the data for the performance of typical PEM fuel cell hardware. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PEM fuel cell; Voltage degradation; PEM reliability; Electrochemical model

1. Introduction

Fuel cell performance at ‘beginning-of-life’ (BOL) is well described and has been modelled in a number of different manners. However, two of the most important considerations in an electrical power system are reliability and life, therefore fuel cell performance at ‘end-of-life’ (EOL) is of great interest.

As the development of fuel cell stacks approaches full commercialisation, more interest will be placed on reliability and life of the stacks. For commercial applications, the EOL performance is usually specified, and thus estimates for reliability, and performance degradation require development. Performance degradation of a fuel cell is an observed phenomenon but there is little reported in this area.

The operational history of the stack will influence fuel cell stack degradation and performance characteristics at the EOL. The development of a model and a better understanding of the degradation mechanisms, especially those related to the materials in the electrochemical system, will also be of interest for the development of control systems. Over the life of the fuel cell stack, the control system must adjust to both long-term process changes (i.e. stack performance degradation) and fast process transients (i.e. load changes). Monitoring of fuel cell performance and diagnosing fuel cell deterioration will also be aided through the development of a degradation model. Users need to be able to estimate the remaining lifetime in a cell in order to be able to decide whether to replace or repair the fuel cell stack prior to an unacceptable power loss. This type of modelling can be used as a performance diagnostic tool to assist in monitoring and prediction of polymer electrolyte membrane (PEM) fuel cell stack performance, and as a diagnostic tool for identification of areas for design improvement.

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Nomenclature

A	cell active area (cm^2)
$c_{\text{H}^+}^*$	proton concentration at the cathode membrane/gas interface (mol cm^{-3})
$c_{\text{H}_2}^*$	liquid phase concentration of hydrogen at anode/gas interface (mol cm^{-3})
$c_{\text{H}_2\text{O}}^*$	water concentration at the cathode membrane/gas interface (mol cm^{-3})
$c_{\text{O}_2}^*$	oxygen concentration at the cathode membrane/gas interface (mol cm^{-3})
E_{Nernst}	thermodynamic potential (V)
F	Faraday's constant (96487 C eq.^{-1})
i	current density (A cm^{-2})
k_a^0, k_c^0	rate constants for the anode and cathode reactions, respectively (cm s^{-1})
k_{cell}	empirical term accounting for the apparent rate constants for the anode and cathode reactions
k_{DR}	empirical term representing the ageing in of the overall catalytic activity ($\text{V h}^{-1} \text{K}^{-1}$)
l	thickness of membrane layer (cm)
r_{M}	membrane specific resistivity for the flow of hydrated protons ($\Omega \text{ cm}$)
T	cell temperature (isothermal assumption in degrees K)
ΔG_e	standard state free energy of the cathode reaction (J mol^{-1})
ΔG_{ec}	standard state free energy of chemisorption from the gas state (J mol^{-1})
<i>Greek letters</i>	
α_c	chemical activity parameter for the cathode
ε	diffusivity correction factor
$\eta_{\text{act,a}}, \eta_{\text{act,c}}$	the anodic and cathodic contributions to the cell activation overvoltage (V)
η_{ohmic}	Ohmic contribution to cell overvoltage (V)
$\xi_1, \xi_2, \xi_3, \xi_4$	empirical coefficients for calculation of activation overvoltage
λ	semi-empirical parameter representing the equilibrium water content of the membrane, $\text{H}_2\text{O}/\text{SO}_3^-$
λ_{DR}	empirical parameter representing the ageing of the polymeric membrane (h^{-1})

The goals of the present work are to:

- extend the application of the GSSEM;
- introduce an age or a voltage degradation terms into the model; and,
- discuss some possible issues associated with voltage degradation in PEM fuel cell stacks.

1.1. Voltage degradation in a PEM fuel cell

The most likely cause of avoidable severe degradation or failure is contamination of the electrocatalyst or membrane. The impact of CO contamination on the PEM fuel cell anode is well known and studied. Contamination may also be a problem on the cathode side of the fuel cell stack, as the quality of air may not be uniform, and in certain urban settings contamination (e.g. CO, CO₂, sulphur compounds, volatile organic compounds) may be considered unavoidable. Therefore contamination is considered to be a predominant degradation cause, and will certainly contribute to lower stability of performance, if not permanent degradation. Flooding or dehydration are other well-known factors that negatively effect performance of PEM fuel cells, and the temporary degradation effects of a flooded or dry cell are obvious [1]. The model assumes that operating conditions are such that flooding will not take place and that proper water management and hydration does take place for steady state operation. Thus, the model does not yet address stability or reversible performance loss.

A number of references report some observed voltage degradation in PEM fuel cells. Hards et al. [2] conducted life tests with both reformat and pure hydrogen fuel, with a cell that incorporated an air bleed and 10 ppm carbon monoxide. In their study a similar degradation rate to those cells using pure hydrogen, $4 \mu\text{V h}^{-1}$, was found. Nakayama [3] reported a degradation rate of $4.3 \mu\text{V h}^{-1}$ over 4000 h of testing in a laboratory on reformat fuel. Isono et al. [4] reported a degradation rate of $10 \mu\text{V h}^{-1}$ over 2000 h of testing in a laboratory on reformat fuel. Maeda et al. [5] reported a degradation rate of $6 \mu\text{V h}^{-1}$ over 5000 h of testing in a laboratory on reformat fuel, and $20 \mu\text{V h}^{-1}$ over 1000 h on reformat fuel with 1% methanol. Sishtla et al. [6] reported a degradation rate of 1%/1000 h (which is approximately $6 \mu\text{V h}^{-1}$) over 5100 h of testing on reformat fuel, and 1.7% degradation effect from four thermal cycles over 1200 h.

The presentation of the remaining literature review will attempt to classify the observations in three categories: activity loss, conductivity loss, and mass transfer loss. Most of the references did not specifically address the modes or causes of the observed voltage degradation, but this general categorisation leads into further development of the model within the paper.

1.2. Loss of apparent catalytic activity

Wilkinson and Steck [7] briefly discussed the importance of studying lifetime degradation and understanding the sources of degradation, but nothing was reported as to the nature of the sources of degradation. Mitsuda et al. [8] ran endurance tests on PEM fuel cells with simulated methanol reformat gas (H₂: 75%, CO₂: 25%, CO: 100 ppm) and found a degradation of $40 \mu\text{V h}^{-1}$ which was 10 times higher than pure hydrogen. From XRD data Mitsuda con-

cluded that a pure Pt surface layer might grow to cover the surface of Pt-Ru particles. Springer et al. [9] conducted life testing of membranes in order to demonstrate that stability could be achieved over a life test of 4000 h. This paper also reported that significant cathode catalyst agglomeration was observed, but there apparently was no significant effect on cell performance. Wilson et al. concluded that the loss of Pt surface area might be compensated by a higher specific activity per unit surface area [10]. Note that St-Pierre et al. [11] further indicated that the hydration level will effect particle growth in the catalyst (leading to catalyst ripening). Gulzow et al. [12] observed a migration of the platinum catalyst in the interface between the hydrogen electrode and the membrane.

1.3. Conductivity loss

In examining the performance of a new membrane material, Wakizoe et al. [13] found that a reinforced membrane performed better under start and stop cycle testing than unreinforced membranes. In this study, it was concluded that dimensional stability was crucial to the achievement of highly durable fuel cells. From the data presented it appeared that cell internal resistance changed only marginally, while there were large changes in the cell voltage, leading to the conclusion that the changes in the voltage were likely due to catalyst degradation or delamination of the electrode. Delamination of the electrode could very well be a result of dimensional cycling which would correspond to Wakizoe's conclusions. Cleghorn [14] confirmed the conclusion that dimensional stability is critical to membrane electrode assembly (MEA) durability in a work which reported extensive testing but no actual degradation rates. Sakamoto et al. [15] reported a voltage degradation rate of 50–90 μV per start–stop cycle, but does not indicate a cause.

Dvorkin and Kander [16] initiated a study into the morphology changes and their relation to transport properties, but few results were presented. Cell life will be a function of operating temperature, but polymer membrane lifetimes of over 50,000 h can be achieved [17]. Watkins [17] reported that the generally accepted degradation mechanism for Nafion (determined by General Electric) is the result of a metal ion catalyst reaction of an HO_2^\bullet radical which attacks the membrane. Gulzow et al. [18] reported the decomposition of electrode materials under electrochemically stressful conditions.

1.4. Loss of mass transfer

A recent publication by St-Pierre et al. [11] demonstrated the long-term detrimental effects of impurities, and the effect that improper water balance (either too wet or too dry) has on long-term cell degradation rates. They reported that the presence of excess water can negatively effect cell performance by transporting leached contaminants within the cell, depositing them on the catalyst or in the membrane.

Unique to their work is the finding of how contaminant transport is facilitated in overhydrated conditions (which will impact the mass transport of reactants), and that mass transport properties will degrade as a result of poor water management. St-Pierre reported a number of degradation rates under various conditions of stress, and for different cell designs. The paper reported degradation rates a value of 60 $\mu\text{V h}^{-1}$ for the Ballard Mk5 design, but a vastly improved rate of 1 $\mu\text{V h}^{-1}$ for the Mk 513 design that included better water management.

1.5. PEM fuel cell modelling

Much work has been done on modelling of PEM fuel cell performance, but none of the models attempt to address voltage degradation over time. Many mechanistic models and empirical models can be found in the literature, and the level of complexity associated with these models varies considerably (Mann et al. [19] for a more detailed summary of PEM modelling work). The recent work of Lee et al. [20] presents the most comprehensive form of an empirical model produced to date to predict the current–voltage relationship for the typical PEMFC. Eikerling et al. [21] have recently presented a mechanistic model that considers variable interrelationships. Springer et al. [22,23] as well as, Gottesfeld and Zawodzinski [24] have also achieved considerable success in PEMFC modelling over the last decade, resulting in increasingly complex predictors of cell performance based on interdependencies of process variables and the nature of transport processes.

In a previous paper [19], a generalised steady state electrochemical model (GSSEM) was proposed. It contains the capability of dealing with PEM fuel cells of any active area and Nafion membrane thickness, up to relatively high current densities. Equilibrium membrane water content is considered, in a simplified way, via a single semi-empirical parameter, λ , and the resistance is described with an empirical correlation incorporating the current density.

The variability, and the continual improvement in the nature, preparation and distribution of catalytic material over the electrode and membrane, means that the activation overvoltage term in the GSSEM will also be semi-empirical in nature and it will vary depending on the active surface area. This term will vary depending on the catalyst preparation, the actual surface area of catalyst on the electrode, and the catalyst in contact with the membrane material. The practice of the physical and chemical preparation of MEA electrodes is improving constantly, thus it is expected that these better-prepared MEAs would result in higher effective activity (or allow for lower Pt content).

Much less significant in the model (and also semi-empirical) is the term representing the resistance to electron flow. With continual changes in flow field plate material and contact resistance, the ohmic overpotential term is also expected to decrease with the development of new fuel cell designs.

The usefulness of the GSSEM stems from its largely mechanistic basis, giving it flexibility in application to a wide range of operating conditions. The empirical expression for membrane resistance, through the adjustment of the coefficient, λ , and the adjustment of the effective activity term, k_{cell} , should suffice for modelling all cells using Nafion membranes over a limited period in the age of the membrane. The simplifications (weaknesses) of the GSSEM are: the assumption of an isothermal stack, the assumption that the gas flow rate and the design of the gas flow fields are sufficient to guarantee removal of excess liquid water at an appropriate rate, and the assumption that effective proton and water concentration at the cathode interface ($c_{\text{H}^+}^*$ and $c_{\text{H}_2\text{O}}^*$) change relatively little with changes in current density for specific stack. The GSSEM is an extremely useful tool for simulation and design analysis of fuel cell power systems that allows the adjustment of parameters for fuel cell area and membrane characteristics in the design process.

2. Discussion of the generalised steady state electrochemical model

2.1. General

The basic structure of the GSSEM can be found in the reference by Mann et. al. [19], and will only be summarised here. The basic expression for the voltage for a single cell is:

$$V_{\text{cell}} = E_{\text{Nernst}} + \eta_{\text{act,a}} + \eta_{\text{act,c}} + \eta_{\text{ohmic}} + \eta_{\text{concentration}} \quad (1)$$

where E_{Nernst} is the thermodynamic potential, $\eta_{\text{act,a}}$ the anode activation overvoltage (a measure of the voltage loss associated with the anode), $\eta_{\text{act,c}}$ the cathode activation overvoltage (a measure of the voltage loss associated with the cathode), and η_{ohmic} the ohmic overvoltage (a measure of the IR losses associated with the proton conductivity of the solid polymer electrolyte and electronic internal resistances). Within the GSSEM the concentration overvoltage $\eta_{\text{concentration}}$ is addressed with Stefan–Maxwell multicomponent mass transfer equations for the reactants through the porous electrodes (this is described by Amphlett et. al. [25] and will not be addressed here in detail). All quantities in Eq. (1) are in units of volts and the overvoltage terms are all negative.

2.2. The activation overvoltage

As proposed by Berger [26] and described earlier [19], the total activation overvoltage can be represented by the following expression:

$$\eta_{\text{act}} = \zeta_1 + \zeta_2 T + \zeta_3 T [\ln(c_{\text{O}_2}^*)] + \zeta_4 T [\ln(i)] \quad (2)$$

where

$$\zeta_1 = -\frac{\Delta G_{\text{ec}}}{2F} - \frac{\Delta G_{\text{e}}}{\alpha_{\text{c}} n_{\text{c}} F} \quad (2a)$$

$$\zeta_2 = \frac{R}{\alpha_{\text{c}} n_{\text{c}} F} \ln [nFAk_{\text{c}}^0 (c_{\text{H}^+}^*)^{(1-\alpha_{\text{c}})} (c_{\text{H}_2\text{O}}^*)^{\alpha_{\text{c}}}] + \frac{R}{2F} \ln [4FAk_{\text{a}}^0 c_{\text{H}_2}^*] \quad (2b)$$

$$\zeta_3 = \frac{R(1-\alpha_{\text{c}})}{\alpha_{\text{c}} n_{\text{c}} F} \quad (2c)$$

$$\zeta_4 = -\left(\frac{R}{2F} + \frac{R}{\alpha_{\text{c}} n_{\text{c}} F}\right) \quad (2d)$$

For later use the ζ_2 term in Eq. (2b) can be rewritten as the following, in order that all the rate constants for the overall reaction are grouped together in one term (which aids in development of the degradation model):

$$\zeta_2 = \frac{R}{\alpha_{\text{c}} n_{\text{c}} F} \ln [nFk_{\text{c}}^0 (c_{\text{H}^+}^*)^{(1-\alpha_{\text{c}})} (c_{\text{H}_2\text{O}}^*)^{\alpha_{\text{c}}} (k_{\text{a}}^0)^{n_{\text{a}}/2}] + \left(\frac{R}{2F} + \frac{R}{\alpha_{\text{c}} n_{\text{c}} F}\right) \ln(A) + \frac{R}{2F} \ln(4Fc_{\text{H}_2}^*) \quad (2e)$$

2.3. Coefficient values chosen for the GSSEM

From our earlier work on Mark IV and Mark V Ballard hardware [19], the following coefficient values are proposed for the GSSEM in accordance with the above development. Note that these values have been adjusted slightly from earlier publications to reflect that α_{c} must have a value that is consistent across the parameters, and that α_{c} is equal to 0.56 (an average of experimental values).

$$\zeta_1 = -0.948(\pm 0.004), \quad \zeta_2 = k_{\text{cell}} + 0.000197 \ln A + 4.3 \times 10^{-5} \ln c_{\text{H}_2}^*,$$

$$\zeta_3 = 6.8 \pm 0.2 \times 10^{-5}, \quad \zeta_4 = -1.97 \pm 0.05 \times 10^{-4}$$

The parameter k_{cell} includes rate constants for the anode and cathode reactions, as well as some properties specific to the cell design such as effective catalyst surface area, and the concentration of protons and water at the interface. As such, k_{cell} is a measure of the apparent catalytic activity. The actual surface area of the catalyst on the electrode in contact with membrane material (and the electrode current-collecting material, and the gas phase reactant) will effect the overall rate of reaction. The effective catalyst surface area must be included in the overall ζ_2 term, therefore k_{cell} will vary based on the actual catalyst surface area. The practice of the physical and chemical preparation of MEA electrodes is improving constantly, resulting in MEA's with higher active catalyst surface areas, due to better membrane/catalyst/current collector interface. Hence, it is expected that these better-prepared MEAs will have higher values of k_{cell} for equal catalyst loading. As will be discussed later in the paper, it is the active surface area or catalyst activity that will degrade with operational time on a cell. Therefore, it is this term that will change with time within the model in order to represent the degradation of voltage associated with loss of catalyst activity in a fuel cell.

2.4. The Ohmic overvoltage

Ohmic polarisation should result from resistance to electron transfer in the graphite collector plates and graphite electrodes plus resistance to proton transfer in the solid polymer membrane. This could be expressed using Ohm's Law equations such as:

$$\begin{aligned}\eta_{\text{ohmic}} &= \eta_{\text{ohmic}}^{\text{electronic}} + \eta_{\text{ohmic}}^{\text{proton}} \\ &= -i(R^{\text{electronic}} + R^{\text{proton}}) = -iR^{\text{internal}}\end{aligned}\quad (3)$$

For high purity machined graphite plates the actual $R^{\text{electronic}}$ should not be significant in comparison to R^{proton} and can be assumed to be insignificant compared to R^{proton} [22].

Resistance to proton flow will be a function of water content and distribution in the membrane [19], both of which will be further dependent on operating parameters such as T and i . The GSSEM takes an empirical approach to the prediction of R^{proton} .

A general expression for resistance is defined to include all the important membrane parameters:

$$R^{\text{proton}} = \frac{r_{\text{M}}l}{A}\quad (4)$$

where r_{M} is the membrane specific resistivity for the flow of hydrated protons ($\Omega \text{ cm}$), and l the thickness of the polymer membrane (cm), which serves as the cell electrolyte.

In Eq. (4), A and l are known dimensional parameters for a particular cell while r_{M} will be a function of the type and characteristics of the membrane, temperature, water content or degree of hydration of the membrane, and current density. Nafion membrane, a trade-mark preparation of Dupont, is widely used in PEM fuel cells and will be the only membrane considered in this paper.

The following empirical expression for Nafion membrane resistivity was proposed in an earlier publication [19] and modified for this publication:

$$r_{\text{M}} = \frac{181.6[1 + 0.03(i/A) + 0.062(T/303)^2(i/A)^{2.5}]}{[\lambda_{\text{age}} - 0.634 - 3(i/A)]\exp\{3.25[(T - 303)/T]\}}\quad (5)$$

In this work, λ , is being considered as an adjustable fitting parameter, commonly between 10 and 20. The parameter λ will be influenced by the membrane preparation procedure, will be a function of the relative humidity and stoichiometric ratio of the anode and cathode feed gases, and will likely also be a function of the age (time-in-service) and thermal/hydration history of the membrane [27].

3. Introduction of ageing terms to the model

The objective of this modelling effort is to model the observed behaviour in performance, not to mechanistically model the actual degradation modes. As the fuel cell ages, a number of degradation mechanisms may take place which

will result in voltage degradation at any specific current density of the fuel cell. Therefore, for ease of modelling the observed voltage degradation using the GSSEM, the likely failure causes have been grouped into three different observed degradation modes. There is recognition that the degradation causes may not result exclusively in one category of the degradation, but the generalised steady state electrochemical degradation model (GSSEDM) is only attempting to model the observed behaviour at this time. This work does not attempt to specifically link the specific causes of such behaviours to the observed degradation, simply to summarise some of the degradation modes identified in the literature [28]. The use of stochastic modelling techniques will also allow accommodation for uncertainty and variation in a reliability analysis. Once again the apparent degradation modes will be categorised for ease of modelling.

3.1. Loss of apparent catalytic activity

The first observable degradation mode will be a loss in apparent activity of the catalyst. This activity loss can result from a number of potential causes or mechanisms, including:

- Catalyst sintering or loss of catalyst surface area.
- Loss of catalyst material.
- Degradation of Nafion in contact with active sites rendering those sites inactive.
- Low levels of contaminants binding to active sites.
- Carbon corrosion of the catalyst carbon support resulting in a loss of surface area.

However, the GSSEDM and the proposed experimental method for calibration of the GSSEDM, do not permit differentiation of activity changes on the anode and cathode sides. Therefore, simple alteration of k_{cell} by the ageing rate will adequately change model in the effective catalyst surface area, and thus catalyst activity, in an empirical manner.

3.2. Conductivity loss

The second easily observable degradation mode will be an increase in resistance of the cell or stack. This conductivity loss can result from a number of potential causes or mechanisms, including:

- low levels of cation contamination reducing the proton conductivity (this cause may be accelerated by high hydration levels as the water acts as a source and pathway for contaminants);
- polymer degradation;
- corrosion of the plates leading to increased contact resistance;
- carbon corrosion of the catalyst support or electrode increasing electrical resistance;
- reduction in the water content of the membrane;

- thermal or hydration cycling leading to mechanical stress cycling resulting in delamination of the polymer membrane and catalyst.

A change in the membrane will essentially result in a decrease in the water/proton conductivity across the membrane. Therefore, any increase in resistance across the membrane can be modelled by a decrease in λ . Delamination of the electrode or catalytic material will principally effect the proton conductivity at the immediate catalyst interface, and thus will be modelled by a decrease in the observed value of λ . This increase in contact resistance will effect the proton conductivity immediately at the catalyst interface, and thus be modelled by an increase in $R^{\text{electronic}}$. Experimentally, the separation of the different types of conductivity loss will require techniques such as AC impedance spectroscopy.

3.3. Loss of mass transfer of reactants

The third observable degradation mode category will be a decrease in mass transfer rate of the reactants. This mass transfer loss can result from a number of potential causes or mechanisms, including:

- catalyst particle ripening leading to more tortuosity in the reactant pathway;
- swelling or degradation of polymer materials in the active catalyst layer changing water removal characteristics;
- compaction of the gas diffusion layer due to mechanical stresses; and
- surface chemistry changes in the gas diffusion layer and carbon catalyst support making water removal more difficult.

From the limited perspective of the GSSEDM, changes in the mass transfer will impact the porosity in the diffusion equations, which represents a correction factor for the diffusivity. The porosity will decrease as the materials age and mass flow properties degrade. Most likely the effect will be on a porosity/tortuosity factor for diffusion in the catalytic region. However, the model currently does not account for diffusion limitations in the catalytic region, nor is the GSSEM validated in the region of fuel cell operation where concentration overpotential become significant (i.e. very high current densities). Ridge and White [29] demonstrated that performance of the porous electrode is virtually independent of the porosity and tortuosity of the porous backing layer. Testing of the sensitivity of this model to variations in the porosity term has confirmed this observation. The work by St-Pierre et al. [11] is unique in that it has been able to clearly separate the membrane conductivity and kinetic losses from the mass transport loss, however, this work then concludes that the fundamental mechanisms leading to mass transport losses requires more study. Since the model is not very sensitive to changes in the porosity of the electrode layer, the loss in mass transport is likely to be in

the catalyst agglomerate, which is currently not accounted for in this model. Therefore, at this time there is a simple recognition that the ageing model will likely have to include a parameter that accounts for mass transfer through the catalyst agglomerate, and extension of the GSSEM itself into a region where mass transfer degradation is significant was not attempted in this work.

4. Results: demonstration of the GSSEDM

4.1. Single cell degradation

The predictions of the GSSEM were compared to data for the performance of the single cell in our laboratory. The single cell was produced uses a Nafion 117TM perfluorosulphonic acid membrane with a dry thickness of approximately 0.178 mm (unreinforced 1100 eq. weight perfluorinated copolymer). The MEA active surface area is about 50 cm², and is constructed of heat-bonded, two-catalyst coated, fibre-cloth electrodes (supplied by E-TEK). Prior to entry into the flow channels, anode and cathode gases are saturated with water vapour in a humidifying section. Heated water is fed to the humidification section and through heat transfer channels in the cell itself in order to maintain a uniform cell temperature within ± 0.5 °C. Inlet and exit flow rates are monitored, and controlled through the exit flow meter. Pressures on anode and cathode side are maintained at an equal value.

As can be seen in Fig. 1, this particular cell has degraded over the 1350 h continuous operation. Although operation was continuous, this particular experimental cell has undergone operational and maintenance activities which would have ‘stressed’ the cell over its operation:

- it was operated for with 75% H₂/25% CO₂ for about 60 h of it operation;
- it was partial dehydrated (i.e. operated on dry reactant gases), as well as ‘flooded’ for very limited periods of operation (under 30 min);
- the cell was assembled by hand and thus there is high potential for assembly irregularities;
- it was tightened to seal leaks;
- the seals were aged and somewhat degraded (i.e. the seals have over 2000 h of operation by the end of the operation); and
- it was load-cycled many times (including open circuit potential for a total of approximately 10 min), and had limited thermal cycling between 50–80 °C in the first 500 h of operation in order to collect a variety of polarisation curves.

A model 4328A Hewlett-Packard milliohm meter was used to measure the combined resistance of the fuel cell in parallel with the external load, and then a mathematical calculation was used to derive the internal resistance from the combined value. Fig. 2 clearly shows that the resistance

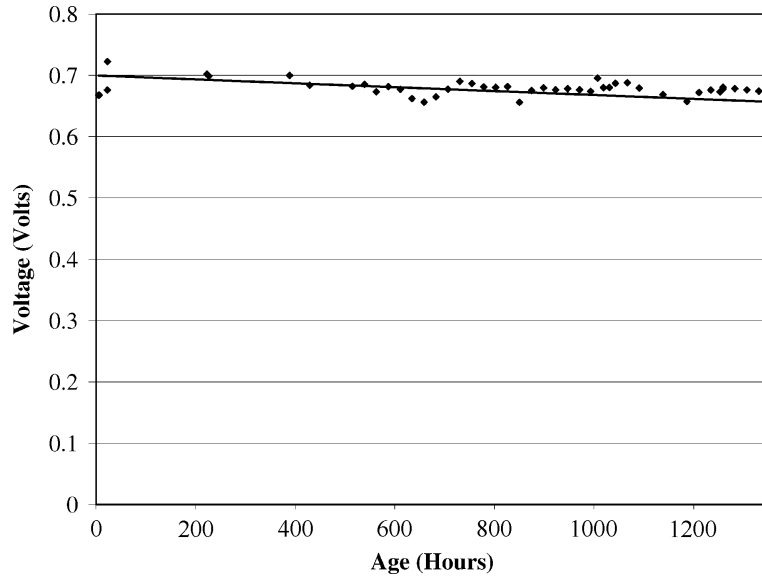


Fig. 1. Voltage degradation curve of a single cell operated at 80 °C, 0.4 A cm⁻², 30 psig/30 psig, H₂/Air—stoichiometric ratios 1.2/2.

increased over the operation period. Since this cell was constructed with high purity machined graphic plates and since the cell clamping pressure remained constant (and $R^{\text{electronic}}$ was considered to be insignificant), the change in resistance has been attributed to changes in the membrane conductivity. Using the GSSEM the membrane conductivity is used to back calculate λ at each data point, and a decline in the derived λ is also shown in Fig. 2.

Since the observed degradation is in a region of operation where concentration overpotential is not significant (as observed from the cell polarisation curve), mass transfer loss was not considered. Due to limitations in the experimental

apparatus this work has not attempted to model the degradation associated with mass transfer loss with is experienced at high current densities. With this consideration, and given that the loss of conductivity is known from the measurement of resistance, the remainder of the overall voltage degradation was attributed to loss of apparent catalyst activity. Using the GSSEM the activity term k_{cell} was determined for each data point over the operating period in order to best fit the observed voltage (less the Ohmic drop). As shown in Fig. 3 there is a decline in activity.

Firstly, the GSSEM adequately models the performance of this cell at beginning-of-life, and the model is fitted

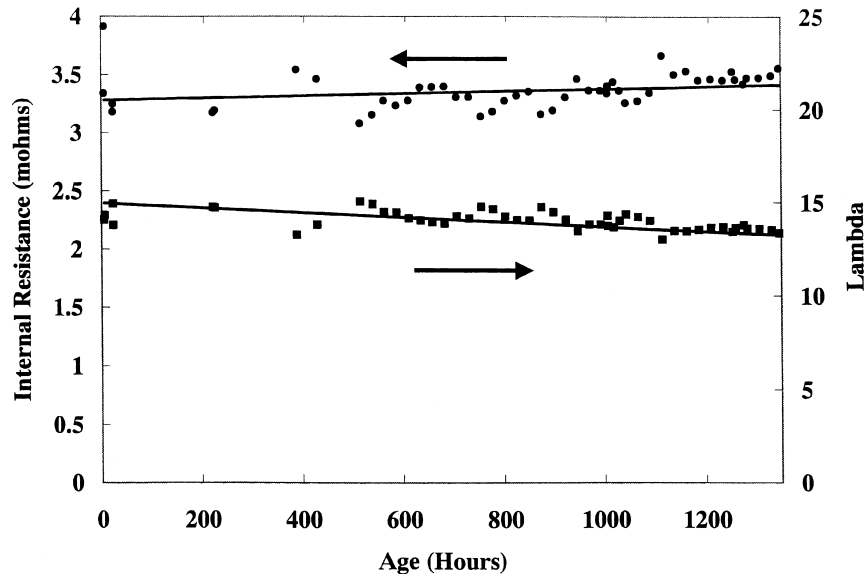


Fig. 2. Resistance increase curve of a single cell operated at 80 °C, 0.4 A cm⁻², 30 psig/30 psig, H₂/Air—stoichiometric ratios 1.2/2.

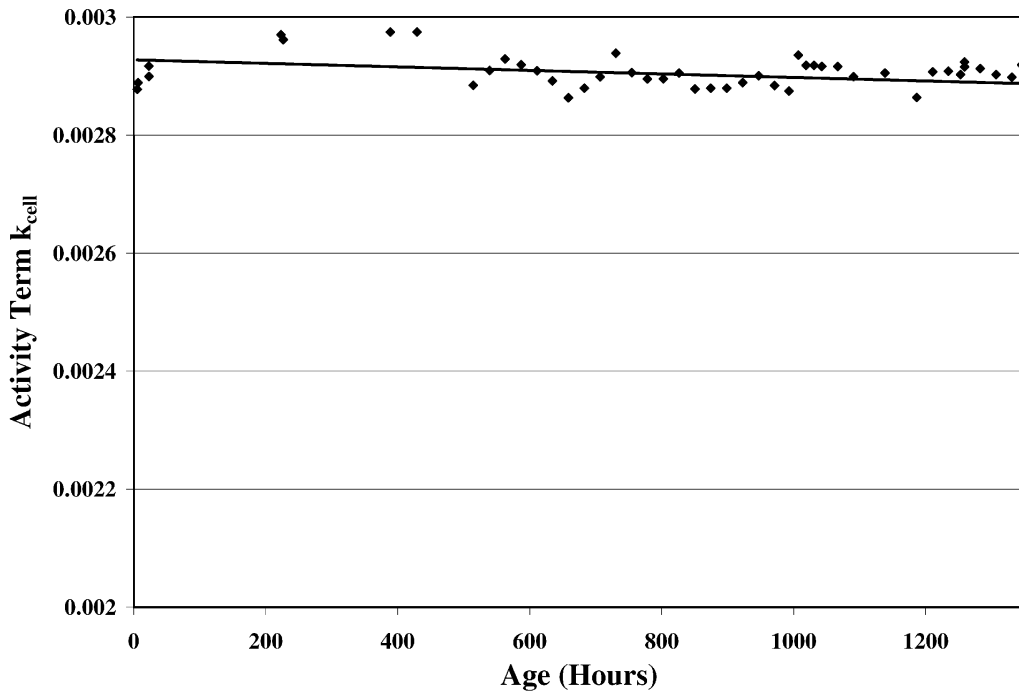


Fig. 3. Activity term k_{cell} (from the GSSEM) of a single cell operated at 80 °C, 0.4 A cm⁻², 30 psig/30 psig, H₂/Air—stoichiometric ratios 1.2/2.

with model parameters of $\lambda = 14.6$ and k_{cell} of 0.00295 which are within a predicted range of other modelling efforts using the GSSEM [19]. The experimentally observed overall ‘ageing’ rate is (11 $\mu\text{V h}^{-1}$), is consistent with many of those reported in the literature. For example, for a related style of cell, Watkins [30] reported a specific value decay rate of 6 $\mu\text{V h}^{-1}$ based on 33:00 h

of testing, and in 1990 Watkins [31] measured a decay rate of 7 $\mu\text{V h}^{-1}$ based on 36:00 h (with some start–stop cycles).

From the data, and as represented by the use of the model, it can be seen that the cell has progressively lost effective catalyst activity since the beginning-of-life over 13:50 h of operation.

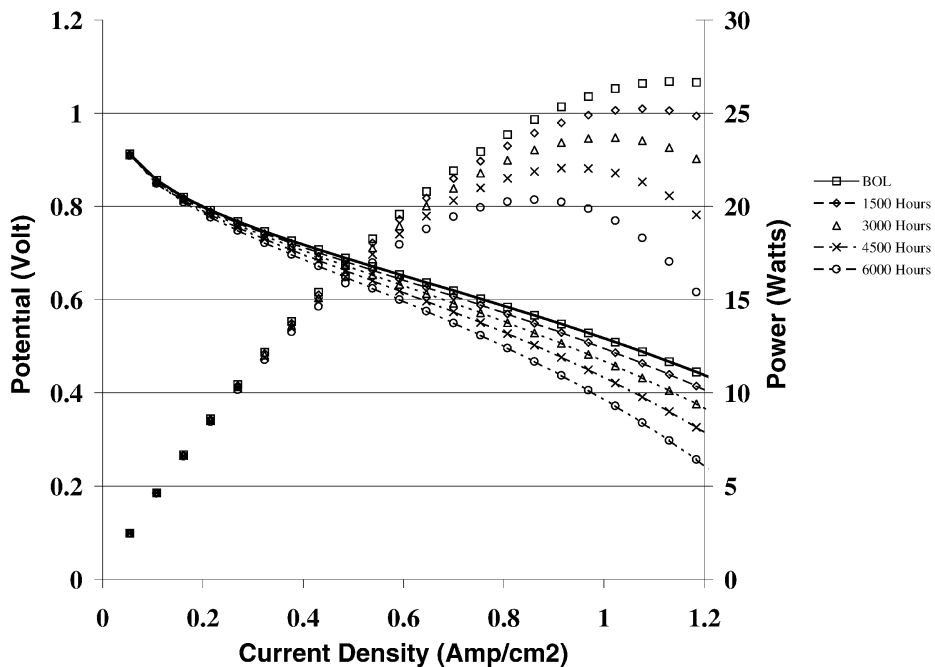


Fig. 4. Simulation of single-cell ageing using the GSSEDM and experimentally determined ageing rates.

4.2. Development and demonstration of the GSSEDM

With a current lack of a complete mechanistic understanding of the degradation associated with the conductivity loss, and based on the observed results shown above, a simple linear relationship is proposed:

$$\lambda_{\text{age}} = \lambda^0 + \lambda_{\text{DR}} \times \text{age} \quad (6)$$

where ‘age’ is an operating time (h). From the data presented in Fig. 2, a membrane conductivity degradation rate can be determined, and the value for λ_{DR} would be -0.0007 h^{-1} .

A degradation term can be introduced to the equation for ξ_2 , where k_{DR} is the degradation rate of the fuel cell due to the changes in catalytic activity. A first-order decay rate is proposed (once again a better fit than a second-order model).

$$\begin{aligned} \xi_2 = & k_{\text{DR}} \times \frac{\text{age}}{T} + k_{\text{cell}}^0 + 0.000197 \ln A \\ & + 4.3 \times 10^{-5} \ln c_{\text{H}_2}^* \end{aligned} \quad (7)$$

For use in the model, the proposed ageing rate (k_{DR}) is $-0.055 \mu\text{V K h}^{-1}$, which is an experimental observed rate under reasonably controlled laboratory conditions and near continuous operation. This will vary depending on operating conditions and catalyst type.

As more experimental data becomes available, age units may be more suited as a number of start–stop cycles, load or thermal cycles, or total power output; or each cycle can be converted into an equivalent age. Contaminant accelerated degradation, thermal shocking or hydration cycling may accelerate the ageing of the membrane itself. Both rates of degradation will vary with temperature and operating conditions, including start–stop, load, hydration and thermal cycling. If a stack is to be operated at extreme temperatures and/or operating conditions a degradation rate for these conditions should be established and applied to the cell for the length of time at those conditions.

Fig. 4 demonstrates the use of the GSSEDM using the experimental cell data as presented. The performance of the cell has been modelled over a 60:00 h expected life. Unfortunately, the other aspect of PEM fuel cell reliability (and likely more critical reliability aspect), catastrophic failure, appeared prior to an end-of-life polarisation curve being collected. The membrane developed a pinhole and hydrogen crossover was at unacceptable levels.

5. Summary and conclusions

The preliminary GSSEDM proposed in this paper is broader in applicability than the earlier proposed GSSEM model [19]. It now contains the capability of dealing with PEM fuel cells of any active area and Nafion membrane thickness within a range of likely operational current densities over the life of the cell. Average membrane water

content/resistance of the membrane is considered, in a simplified way, via a single semi-empirical parameter, λ . The effective activity of the catalyst is considered via a single semi-empirical parameter, k_{cell} . The model can be extended over the life of a fuel cell so that performance can now be predicted as the fuel cell ages.

The usefulness of the GSSEDM lies in its largely mechanistic basis, giving it flexibility in application over a wide range of operating conditions. The empirical expression for membrane resistance, through the adjustment of the coefficient, λ , and the adjustment of the effective activity term, k_{cell} , should suffice for modelling all cells using Nafion membranes. Currently, there are little data available for the establishment of degradation rates for the membrane and catalytic activity. However, it has been demonstrated how the model could be adapted to accommodate an ageing cell. The simplifications that were made in development of the GSSEDM are:

- the assumption of an isothermal stack;
- the assumption that the gas flow rate and the design of the gas flow fields are sufficient to guarantee removal of excess liquid water. This is a result of the assumption that flooding is a controllable operational issue that will not ‘age’ the stack but only effect performance during the specific period of those poor operating conditions;
- this model does not yet account for the impact of specific contamination or poisons on the stack;
- this model does not yet quantify the impact of operation in a poorly hydrated (high or low) manner, which will impact the ageing rate; and
- this model can provide an extension to ‘cycling’ of the stack, but no estimated decay rate is yet developed. It would be proposed, with the appropriate experimental data, that the ageing effect of a ‘cycle’ could be translated into an equivalent ‘age’ addition to the stack.

This paper also discussed the causes and failure modes that effect voltage degradation in a fuel cell stack. Clearly more analysis is needed to clearly define mechanistic linkages (i.e. well-defined chemical and physical processes) between the causes and failure modes. Diagnostic modelling will assist in this analysis.

In conclusion, the GSSEDM is an extremely useful tool for simulation and design analysis of fuel cell power systems that allows the addition of parameters for fuel cell area and membrane characteristics in the design process. With the addition of an ageing parameter, this model can be used in simulations of fuel cell performance over the life of the stack.

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