

# Henry's Law and the solubilities of reactant gases in the modelling of PEM fuel cells

R.F. Mann\*, J.C. Amphlett, B.A. Peppley, C.P. Thurgood

*Department of Chemistry and Chemical Engineering, Royal Military College of Canada, P.O. Box 17000, Station Forces, Kingston, Ontario K7K 7B4, Canada*

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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 able to predict both activation and concentration polarizations at both anode and cathode. Normally these predictions require values of the concentration of the reactant gases (i.e.  $H_2$  and  $O_2$ ) at the interface between the catalyst and the electrolyte. Electrolytes of interest could include various dilute acids or polymeric membranes such as Nafion<sup>TM</sup> so that gas solubilities, in the form of Henry's Law constants, could be required for a diverse group of solvents.

Published solubility data have been evaluated and a number of Henry's Law correlations are proposed.

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## 1. Introduction

Over the years, there has been an extensive literature on the theory and practice of fuel cells in general and proton exchange membrane (PEM) fuel cells in particular. Several good broad references exist to give an overview of this literature [1–5]. There is also an extensive literature on modelling of PEM fuel cells. Much of this has been cited and used in previous publications from our group [6–12] and was recently summarized [13,14]. Our modelling work has primarily dealt with the development of the 'Generalized Steady State Electrochemical Model' (GSSEM).

In general, all fuel cell models must be able to predict both activation and concentration polarizations, both of these loss terms generally being a function of the concentration of the reactant gas in the electrolyte. These polarizations would generally require prediction at both the anode and the cathode. For a PEM fuel cell, therefore, these predictions would normally require

values of the concentration of both of the reactant gases (i.e.  $H_2$  and  $O_2$ ) at the interface between the respective catalyst and the electrolyte.

For the initial development of a database for the prediction of cell parameters, research results are typically obtained in single electrode studies in lab-type electrochemical cells. Electrolytes of interest at this stage could include various dilute acids such as  $H_2SO_4$  or  $HCl$  and possibly concentrated acids such as  $H_3PO_4$ . The subsequent application of such a database to the modelling of a PEM fuel cell requires knowledge of reactant concentrations in polymeric membrane–electrolytes such as Nafion<sup>TM</sup>. Gas solubilities, in the form of Henry's Law constants, could therefore be required for a diverse group of solvents.

Published solubility data have been evaluated and a number of Henry's Law correlations are proposed. Procedures to use such correlations are summarized.

## 2. The PEM fuel cell (PEMFC)

The PEM fuel cell has been extensively described in the literature. Briefly, there are three major components that are of interest to all PEM fuel cell models:

\* Corresponding author. Tel.: +1 613 541 6000x6055; fax: +1 613 542 9489.  
E-mail address: [mann-r@rmc.ca](mailto:mann-r@rmc.ca) (R.F. Mann).

**Nomenclature**

$A$	Arrhenius pre-exponential in Eq. (6) ( $A \text{ cm}^{-2}$ )
$B$	Arrhenius slope in Eq. (6) (K)
$c$	concentration ( $\text{mol cm}^{-3}$ )
$c_{\text{gas}}$	concentration of dissolved reactant gas in the electrolyte ( $\text{mol cm}^{-3}$ )
$C_M$	concentration of active Pt sites in sites $\text{cm}^{-2}$ or moles of sites $\text{cm}^{-2}$
$E$	thermodynamic emf (the maximum, equilibrium, voltage theoretically possible for the particular temperature and reactant partial pressures)
$f_{\theta}$	‘function of $\theta_{i,o}$ ’ parameter in Eq. (7) (dimensionless)
GSSEM	Generalized Steady State Electrochemical Model
$H$	Henry’s Law ‘constant’ ( $\text{atm cm}^3 \text{ mol}^{-1}$ )
HOR	hydrogen oxidation reaction (Eq. (1))
$i$	current density ( $A \text{ cm}^{-2}$ )
$i_o$	exchange current density ( $A \text{ cm}^{-2}$ )
MEA	membrane electrode assembly
ORR	oxygen reduction reaction (Eq. (2))
$p$	gas partial pressure (atm)
PEM	‘polymer electrolyte membrane’ or ‘proton exchange membrane’
PEMFC	PEM fuel cell
RH	relative humidity (expressed as %)
$T$	temperature (K)
$V$	voltage that appears across the fuel cell terminals (V)

**Greek letters**

$\eta$	polarization (i.e. overvoltage or loss) (V)
$\theta$	fractional surface coverage (e.g. of chemisorbed hydrogen atoms for the HOR)

**Subscripts**

a	anode
av	average
act	activation or actual
c	cathode
ch	channel
conc	concentration (as related to ‘concentration polarization’, the voltage loss due to slow mass transfer)
$H_2$	hydrogen
H	hydrogen atom
$H_3O^+$	hydrated proton (i.e. $H + \cdot H_2O$ )
$i$	at the gas–aqueous interface or species (e.g. $H_2$ , $O_2$ , H, etc.)
$O_2$	oxygen
ohmic	related to ohmic (iR) losses
$o$	at zero polarization and zero net current condition (i.e. at equilibrium)

**Superscripts**

*	at the interface of the Pt catalyst and the surrounding aqueous medium (the ‘reaction interface’)
sat	saturated (e.g. water vapour at RH of 100%)

- (i) The anode is the electrode where the fuel, hydrogen, is converted to protons and where electrons are released to travel through the external circuit and perform electrical work. The overall half-cell reaction is

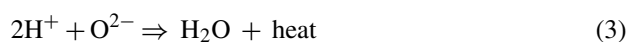


The anode reaction occurs in the presence of a catalyst, typically Pt (although mixtures such as Pt/Ru may be used if there are carbon-containing species in the anode feed). Dissolved hydrogen gas must be present adjacent to the catalyst surface. The ‘hydrogen oxidation reaction’ at the anode is commonly referred to as the ‘HOR’.

- (ii) The membrane, separating the anode and cathode, is a thin layer of a special polymer, commonly Dupont Nafion™, a perfluorinated polymer with sidechains terminating in sulphonic acid groups. The  $H^+$  ions, each hydrated with several water molecules, pass through the membrane from the anode to the cathode, with the membrane serving as the ‘‘electrolyte’’ of the electrochemical cell.
- (iii) The cathode is the electrode where the oxidant, oxygen from a pure-oxygen or from an oxygen-containing stream, first catalytically recombines with the electrons returning from the external circuit



and then permits the completion of the overall half-cell chemical reaction



The ‘oxidation–reduction reaction’ at the cathode is commonly referred to as the ‘ORR’. The cathode, typically, also uses Pt as the catalyst. Dissolved oxygen must be adjacent to the catalyst surface.

**3. The essentials of a fuel cell model**

The shortest form of a general fuel cell model is typically given by:

$$V = E + \eta_{\text{act,a}} + \eta_{\text{act,c}} + \eta_{\text{ohmic}} \quad (4)$$

where the  $\eta$  terms are all losses, i.e. they are negative in Eq. (4). The first two of these,  $\eta_{\text{act,a}}$  and  $\eta_{\text{act,c}}$ , the ‘‘activation polarizations’’, primarily incorporate the chemical kinetic parameters that determine the rates of reaction at the anode and cathode, respectively. The prediction of these activation polarizations typically involves the use of a reaction rate parameter, the exchange current density, itself a function of the concentration of reactant in the electrolyte. The third loss term,  $\eta_{\text{ohmic}}$ , deals with the ‘‘iR’’

electrical loss associated, primarily, with the flow of hydrated  $H^+$  ions through the membrane electrolyte.

Depending on the complexity of the model, the concentrations of reactant gases in a fuel cell can initially be expressed as the inlet partial pressure,  $p_{H_2,i}$  and  $p_{O_2,i}$  (i.e. as the feed enters the particular gas channel) or the average partial pressure in the channel. The average channel parameters would, therefore, be the hydrogen partial pressure in the anode gas channel and the average oxygen partial pressure in the cathode gas channel,  $p_{H_2,ch}$  and  $p_{O_2,ch}$ , respectively. These ‘channel’ partial pressures would, in general, require correction, by appropriate mass transfer calculations in the MEA, to the lower values,  $p_{H_2}^*$  and  $p_{O_2}^*$ , at the ‘reaction interfaces’ where all the participants in the reactions come together. Typically, the latter should actually be expressed as liquid-phase parameters, the dissolved gas concentrations  $c_{H_2}^*$  and  $c_{O_2}^*$ .

Some modelling approaches include the mass transfer losses in a more visible way, including concentration polarization terms for each electrode and starting from

$$V = E + \eta_{act,a} + \eta_{act,c} + \eta_{ohmic} + \eta_{conc,a} + \eta_{conc,c} \quad (5)$$

In general, modelling of  $\eta_{act,a}$  and  $\eta_{conc,a}$  requires the prediction of  $c_{H_2}^*$  from  $p_{H_2,ch}$  and the modelling of  $\eta_{act,c}$  and  $\eta_{conc,c}$  requires the prediction of  $c_{O_2}^*$  from  $p_{O_2,ch}$ .

## 4. Modelling reactant concentrations in the electrolyte

### 4.1. Introduction—the exchange current density

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

$$i_o = A \exp \left[ \frac{B}{T} \right] \quad (6)$$

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

$$A = A^o C_M^m c_{gas}^n [f_\theta] \quad (7)$$

The parameter  $A^o$  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,  $A^o$  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,  $f_\theta$  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  $f_\theta$  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  $T$ .

The prediction and modelling of  $c_{gas}$  is the focus of this paper.

### 4.2. Solubilities of reactant gases in the electrolyte

#### 4.2.1. Introduction

Published data on exchange current densities and polarization come from studies using a variety of electrolytes, dilute (0.1 or 0.05 M, for example)  $H_2SO_4$  probably being the most common. The major modelling interest for PEMFC, however, is the prediction of electrochemical parameters for all the way from PEMFC designs where the electrolyte phase in direct contact with the Pt catalyst was essentially ‘reactant gas dissolved in water’ to designs where the electrolyte phase was ‘reactant gas dissolved in humidified Nafion<sup>TM</sup>’. In order to make maximum use of published work on electrodes, we must be able to evaluate the previously defined  $A^o$  constant. This requires, according to Eq. (7), the evaluation of  $c_{gas}$ ,  $c_{H_2}$  at the electrolyte/anode interface and  $c_{O_2}$  at the electrolyte/cathode interface. Similarly, in order to properly utilize these  $A^o$  values for modelling of PEMFC, we must be able to predict the values of  $c_{H_2}$  and  $c_{O_2}$  in the membrane electrolyte at the gas–membrane interface and at the operating conditions of the fuel cell.

The solubility of the gaseous reactant in the electrolyte (i.e. the Henry’s Law linkage of  $p_{H_2}$  and  $c_{H_2}$  or  $p_{O_2}$  and  $c_{O_2}$ ) will affect the prediction of activation polarization and the diffusion rate of dissolved reactant gas through the electrolyte will be a factor in the prediction of concentration polarization.

In a relatively simple, 1-D, model, the average hydrogen and oxygen partial pressures in the respective feed channels,  $p_{H_2,ch,av}$  and  $p_{O_2,ch,av}$ , are used to quantify the feed concentrations. In a more complex 2-D or 3-D model, the point values of  $p_{H_2,ch}$  and  $p_{O_2,ch}$  are used to quantify the local reactant partial pressure. Assuming that concentration polarization is estimated in a separate calculation, these  $p_{H_2,ch,av}$  and  $p_{O_2,ch,av}$  or  $p_{H_2,ch}$  and  $p_{O_2,ch}$  become the effective reactant partial pressure,  $p_{H_2}^*$  and  $p_{O_2}^*$ , at the interface of the Pt catalysts and the surrounding aqueous medium. At some point in the system, the ‘gas–aqueous interface’ (subscript i), hydrogen and oxygen gas go into solution. The dissolved reactant concentrations at this interface,  $c_{H_2,i}$ , and  $c_{O_2,i}$ , can now be estimated from the appropriate Henry’ Law expression.

The following form of Henry’s Law will be used

$$c = \frac{p}{H} \quad (8)$$

with  $c$  and  $p$  being appropriately subscripted for the particular interface, typically subscript ‘i’ for the gas–‘aqueous’ interface. The ‘aqueous’ phase could be the dilute acid electrolyte in a single-electrode study or the polymer membrane electrolyte in a PEMFC modelling application.

#### 4.2.2. Quantification of 'p'

A couple of caveats should be kept in mind.

Many published studies report parameter values (such as  $i_o$ , for example) "at atmospheric pressure". Ideally this should mean 'at  $p_{H_2} = 1 \text{ atm}$ ' or 'at  $p_{O_2} = 1 \text{ atm}$ '. In fact it could simply mean than the data were collected in an apparatus open to the atmosphere so that 'atmospheric pressure' was the ambient pressure at that time, probably an absolute pressure between, say, 99 and 103 kPa, i.e. an applied pressure of perhaps  $1 \text{ atm} \pm 2\%$ .

A second concern is the correction (or lack of correction) for the partial pressure of water vapour. With ideal behaviour at the low pressures typical of fuel cell operation, we may assume, for pure feeds of reactant gas,

$$p_{H_2} \text{ or } p_{O_2} = P_{\text{total}} - p_{H_2O} \quad (9)$$

and

$$p_{H_2O} = \left( \frac{RH}{100} \right) p_{H_2O}^{\text{sat}} \quad (10)$$

For the typical temperature range of interest to PEMFC, say  $0\text{--}90^\circ\text{C}$ ,  $p_{H_2O}^{\text{sat}}$  will range from 0.006 to 0.69 atm, values ranging from 'insignificant' to potentially 'very significant'. The relative humidity, RH, will typically range from perhaps 40 to 80% in a lab environment, probably close to 100% in the gas space above an aqueous electrolyte in a single-electrode, perhaps 25–100% in the anode gas channel of a PEMFC and close to 100% in the cathode gas channel of a PEMFC. Clearly, therefore, there will be situations where a device run 'at atmospheric pressure' could have a  $p_{\text{gas}}$  ( $p_{H_2}$  or  $p_{O_2}$ ) as low as about 0.3 atm, drastically different from '1 atm'.

#### 4.2.3. Quantification of H

##### 4.2.3.1. Henry's Law constants for aqueous acid electrolytes.

The most common electrolytes in contact with PEM electrodes are water and water-soaked Nafion but published electrode polarization data typically are for various hydrogen or oxygen electrodes where the Pt catalyst is in contact with an aqueous acid electrolyte. Solubility data for hydrogen and oxygen in a variety of acid electrolytes are, therefore, necessary, initially to interpret and correlate published values of exchange current density and finally to apply such  $i_o$  correlations to the prediction of activation polarizations in modelled PEMFC at the operating temperature and reactant compositions of the fuel cell. Recommended expressions for Henry's Law 'constants' for various systems are summarized in the following sections.

**4.2.3.1.1. Henry's Law constants for hydrogen in aqueous acid electrolytes.** For  $H_2$  in water: Analysis of data from various sources [15–19] led to the following proposed correlation for temperatures from 0 to  $100^\circ\text{C}$  and  $p_{H_2}$  up to 10 atm:

$$\text{from } 0 \text{ to } 45^\circ\text{C} : H_{H_2, H_2O} = 7.9 \times 10^6 \exp(-545/T) \\ \times [1 + 0.000071 p_{H_2}^3]. \quad (11)$$

$$\text{from } 45 \text{ to } 100^\circ\text{C} : H_{H_2, H_2O} = 8.34 \times 10^5 \exp(170/T) \\ \times [1 + 0.000071 p_{H_2}^3]. \quad (12)$$

For  $H_2$  in dilute  $H_2SO_4$  electrolyte: Analysis of  $25^\circ\text{C}$  data from the International Critical Tables ([1], p. 145, Fig. 24) led to the recommendation that the above 'pure-water' value can be multiplied by the following concentration correction factor for up to about 4N acid (i.e.  $[N] = 4$ ) or about 2 M acid (i.e.  $[M] = 2$ ):

$$H_{H_2, H_2SO_4} = H_{H_2, H_2O} (1 + 0.1[N]) \quad (13)$$

$$H_{H_2, H_2SO_4} = H_{H_2, H_2O} (1 + 0.2[M]) \quad (14)$$

Lacking any data showing temperature effects, it has been assumed that the temperature effects for the  $H_2$ /dilute  $H_2SO_4$  system are the same as those for the  $H_2$ / $H_2O$  system and are, therefore, already contained in the correlations recommended above. Note that the commonly used 0.05 and 0.1 M  $H_2SO_4$  electrolytes would, therefore, have  $H_{H_2}$  values only about 1–2% above those for water so that the corresponding  $c_{H_2}$  values would only be 1–2% lower in the dilute acids than in water.

For  $H_2$  in dilute HCl or dilute  $HNO_3$  electrolyte: The same ICT reference as above [1] contained data indicating that Eqs. (13) and (14) for dilute  $H_2SO_4$  should be sufficiently accurate for these dilute acids as well. For greater precision,  $H_{H_2, HCl}$  could be  $\sim 5\%$  below  $H_{H_2, H_2SO_4}$  and  $H_{H_2, HNO_3}$  could be  $\sim 8\%$  below  $H_{H_2, H_2SO_4}$ .

For  $H_2$  solubility in concentrated  $H_3PO_4$ : Data from PAFC studies, although in a different acid and generally at temperatures well above PEM operating temperatures, could be applicable to PEM modelling. Although data for  $H_2$  have not yet been located, solubility data for  $O_2$  in aqueous acids [see below] could imply  $H_{H_2, H_3PO_4}$  values  $\sim 20\%$  below  $H_{H_2, H_2SO_4}$ .

**4.2.3.1.2. Henry's Law constants for oxygen in aqueous acid electrolytes.** For  $O_2$  in water: Correlating data from various sources [15–19], the following are recommended:

$$\text{from } 0 \text{ to } 45^\circ\text{C} : H_{O_2, H_2O} = 1.34 \times 10^8 \exp[-1540/T] \quad (15)$$

$$\text{from } 45 \text{ to } 100^\circ\text{C} : H_{O_2, H_2O} = 5.08 \times 10^6 \exp[-500/T] \quad (16)$$

For  $O_2$  in dilute  $H_2SO_4$  electrolyte: Correlating solubility data at  $25^\circ\text{C}$  [1,15], the following concentration correction factors were obtained for concentrations below 2N (i.e.  $[N] = 2$ ) or 1 M (i.e.  $[M] = 1$ ):

$$H_{O_2, H_2SO_4} = H_{O_2, H_2O} (1 + 0.125[N]) \quad (17)$$

$$H_{O_2, H_2SO_4} = H_{O_2, H_2O} (1 + 0.25[M]) \quad (18)$$

Lacking any data showing temperature effects, it has been assumed that the temperature effects for the  $O_2$ /dilute  $H_2SO_4$  system are the same as those for the  $O_2$ / $H_2O$  system and contained in Eqs. (15) and (16) correlations.

For  $O_2$  solubility in  $H_3PO_4$ : Published data ([1], p. 144, Fig. 43) for solubilities up to about 85 wt.%  $H_3PO_4$  have been utilized as follows:

For the dilute region: For wt.% (C) from 0 to 60,

$$H_{O_2, H_3PO_4, 25^\circ\text{C}} = 0.78 \times 10^6 \exp(0.0157C) \quad (19)$$

For  $\sim 100$  wt.%  $H_3PO_4$ ,  $H_{O_2, H_3PO_4, 25^\circ\text{C}} = 6.9 \times 10^6$  (extrapolated estimate).



For  $O_2$  in dilute HCl or dilute  $HNO_3$  electrolyte: From ICT ([1], p. 145, Fig. 44), these solubilities at 25 °C lie in between those of  $O_2$  in  $H_2SO_4$  and  $O_2$  in dilute  $H_3PO_4$ ,  $H_{H_2,HCl}$  being ~5% above  $H_{O_2,H_2SO_4}$  and  $H_{O_2,HNO_3}$  being about 10% above  $H_{O_2,H_2SO_4}$ . Since the earlier recommended correlations for  $H_{O_2,H_2SO_4}$  included the assumption of the same temperature variation as  $H_{O_2,H_2O}$ , that assumption is automatically carried forward to these acids as well.

**4.2.3.2. Henry's Law constants for Nafion™ membrane electrolytes.** There are a number of ion-exchange membranes which have been applied to the development of 'proton-exchange membrane', PEM, fuel cells. Nafion™ is the membrane of major interest in the present work although reference will be made to other related materials.

**4.2.3.2.1. Henry's Law constants for hydrogen in Nafion.** Yeo and McBreen [20] are often cited as an early source of hydrogen solubility data in Nafion.

Ogumi et al. [21], in their major report on oxygen solubility in Nafion 120 (see Section 4.2.3.2.2 for more details), include a 25 °C value of  $24.50 \times 10^{-3}$  M for the solubility of hydrogen in Nafion 120, apparently from Yeo and McBreen [20]. This probably is equivalent to an  $H_{H_2,Nafion}$  value of about  $4.08 \times 10^4$ .

Sakai et al. [22] reported solubilities of  $H_2$  in dried Nafion 125, acid  $H^+$ -form and  $K^+$ -form. In the 0–45 °C region, the two sets of data, when converted to Henry's constants, had Arrhenius temperature coefficient terms of  $\exp(-363/T)$  and  $\exp(-411/T)$ , respectively. These compare reasonably with the corresponding  $H_{H_2,H_2O}$  coefficient of  $\exp(-545/T)$ . From 45 to 100 °C, there were only  $K^+$ -form data and the temperature coefficient term is  $\exp(-1040/T)$  with the corresponding term for  $H_{H_2,H_2O}$  being  $\exp(+170/T)$ . The Nafion appears to behave water-like below 45 °C but not above that temperature. At the typical temperatures for PEMFC operation (the 45–100 °C range),  $H_{H_2,H_2O}$  values appear to be from  $3\frac{1}{2}$  to  $6\frac{1}{2}$  times  $H_{H_2,Nafion 125,K^+-dried}$  values, the latter being given by:

$$H_{H_2,Nafion 125,K^+-dried} = 5.6 \times 10^6 \exp(-1040/T) \quad (20)$$

The Henry's Law recommendations by Bernardi and Verbrugge [23] were: "Yeo and McBreen [20] report the solubility of hydrogen at 25 °C in Nafion 120. Data at higher temperatures were not reported. Since the solubility of hydrogen in water is only weakly dependent on temperature in the 25–100 °C temperature range, the Henry's constant is assumed to be independent of temperature." (Support for this last statement is a reference to 'Berger, p. 143' [1,2]. See above for further detail re this reference.) Using this argument, their  $H_{H_2,Nafion,25\text{ °C}}$  of  $4.5 \times 10^4$  atm cm<sup>3</sup> mol<sup>-1</sup> should be combined with the temperature dependence for  $H_{H_2,H_2O}$  given by Eqs. (11) and (12) to give, for the 45–100 °C temperature range:

$$H_{H_2,Nafion} = 0.255 \times 10^5 \exp(170/T) \quad (21)$$

i.e. only ~3% of  $H_{H_2,H_2O}$

**4.2.3.2.2. Henry's Law constants for oxygen in Nafion.** Ogumi et al. [21] appear to be widely cited as the first to publish data for oxygen solubility in Nafion. They used Nafion 120, with

0.83 meq g<sup>-1</sup> of exchange capacity, in contact with "prehumidified oxygen ... at atmospheric pressure". It is not completely clear what the value of  $p_{O_2}$  is for their reported solubility results since, for 'prehumidified gas',

$$p_{O_2} = P_{total} - p_{H_2O} \quad (22)$$

and  $p_{H_2O}$  could have any value from 0 up to  $p_{H_2O,sat}$  for the particular test temperature. This does give a range for  $p_{H_2O}$  and, therefore, a range for the calculated values of  $H_{O_2,Nafion}$ . The lower values of the  $H$ -values below are probably the more likely.

$T$ (°C)	$c_o \times 10^3$ (M)	$H_{O_2,Nafion} \times 10^{-5}$ (atm cm <sup>3</sup> mol <sup>-1</sup> )
20	7.20	1.36–1.39
30	6.50	1.47–1.54
40	5.30	1.75–1.89
50	5.90	1.49–1.69

Their membranes were stated to be "pretreated by soaking in boiling water in the  $Na^+$  form for 30 min". There was also the observation reported that "oxygen solubility was almost independent of the sample and pretreatment".

Ogumi et al. [24], for both oxygen and hydrogen in Nafion 125, stated that "solubility,  $c^o$ , was very high compared with the value in aqueous solutions, was of the order  $10^{-2}$  mol dm<sup>-3</sup>, and was almost independent of the water content of the membrane." Assuming that the same experimental apparatus and procedure were used as in the 1984 work [21], there is a small uncertainty in the actual value of  $p_{O_2}$  when converting the solubility to a value of  $H_{O_2,Nafion}$ . At the 25 °C used for the following results, the actual  $H$  could be  $1\frac{1}{2}$ % above or below the value shown:

Nafion form	$H_{O_2,Nafion}$ (atm cm <sup>3</sup> mol <sup>-1</sup> )
Nafion 125-Na	$7.2 \times 10^4$
Nafion 117-Na	$1.14 \times 10^5$
Nafion 125-K	$9.03 \times 10^4$
Nafion 117-K	$9.21 \times 10^4$

Several relevant ratios, for 25 °C, can also be calculated from their results:

$$\begin{aligned} H_{H_2,H_2O}/H_{H_2,Nafion 120} &= 0.032, \\ H_{H_2,H_2SO_4}/H_{H_2,H_2O} &= 1.08, \\ H_{H_2,Nafion 120}/H_{O_2,Nafion 120} &\approx 1, \text{ and} \\ H_{O_2,H_2O}/H_{H_2,H_2O} &= 0.6. \end{aligned}$$

Sakai et al. [25] report extensive data on  $O_2$  and  $H_2$  permeabilities through Nafion 117 and 125 but make no direct mention of solubility data.

Sakai et al. [22] reported solubilities of  $O_2$  in dried Nafion 125, acid  $H^+$ -form and  $K^+$ -form, Nafion 117- $K^+$ (dry) and Nafion 117- $H^+$ (wet). The four sets of data, when converted to  $H_{O_2,Nafion-xx}$  and put on an Arrhenius plot, lay in four essentially parallel lines, temperature coefficient  $\exp(-970/T)$ . All the 'dried membrane data, all for 25–100 °C, were fitted by

$$H_{O_2,Nafion-xx} \approx 3.73(\pm 25\%) \times 10^5 \exp(-970/T) \quad (23)$$

while the few ‘wet membrane’  $H$ -values, all taken from data at or below 25 °C, were 50–80% higher than values given by the extrapolated ‘dried membrane’ correlation.

Bernardi and Verbrugge [26] cite the solubility data published by Ogumi et al. [21] (and tabulated above) as the basis of their derived Henry’s constant correlation:

$$H_{O_2, \text{Nafion}} = 1.33 \times 10^6 \exp(-666/T) \quad (24)$$

Strictly speaking, this correlation was based on data from 20 to 50 °C only and, as is clear in the above tabulation, the Arrhenius behaviour of the 40 and 50 °C data is a bit inconsistent with the data below 40 °C. Combining this with observations in other publications that there is commonly an inflection point in the 40–50 °C range of an Arrhenius plot of Nafion membrane characteristics (water content, dissolved gas content, etc.), the above Bernardi and Verbrugge correlation probably should not be used above 40 °C. Nevertheless, their Table 3 includes an 80 °C value consistent with Eq. (24) correlation. In a subsequent paper [23], Bernardi and Verbrugge quote their 1991 paper but suggest the correlation

$$\ln K_{O_2} = -(666/T) + 14.1 \quad (25)$$

which, since  $H$  and  $K_{O_2}$  have identical definitions, is consistent with their 1991 correlation. However, their 1992 Table II [23] includes two values of Henry’s constant: an 80 °C value of  $2.0 \times 10^5$  (which is consistent with the above Eqs. (24) and (25)) and a 95 °C value of  $8.1 \times 10^6$  (which is far from being consistent with Eqs. (24) and (25)).

Parthasarathy et al. [27,28] reported extensive data on water content and oxygen solubility in Nafion from 25 to 80 °C and at an oxygen pressure of 5 atm. The  $H_{O_2, \text{Nafion}}$  values range from  $3.12 \times 10^5$  at 25 °C to  $1.13 \times 10^6$  at 80 °C with a major change in slope on an Arrhenius plot at  $8.7 \times 10^5$  and 40 °C. They do comment, however, that “the high solubilities (i.e. low  $H_{O_2, \text{Nafion}}$ ) at low temperature (<50 °C) do not persist after the first heating cycle. After the polymer has imbibed sufficient water at the higher temperature, lowering the temperature does not enhance the oxygen solubility. This indicates that water imbibed by the Nafion is permanently associated with the structure of the polymer.” This conclusion suggests the possibility that many published solubility data are at Nafion conditions not representative of the operating conditions of a PEM fuel cell and raises a warning flag about the interpretation and use of published solubility data. Subsequently, Gottesfeld and Zawodzinski [29] state that the above solubility results, utilizing Pt/bulk ionomer rather than Pt/recast ionomer, ‘do not mimic precisely the interfacial compositions in a Pt/C/recast ionomer composite’.

Broka and Ekdunge [30] reported results from extensive oxygen and hydrogen permeation and water uptake studies on Nafion membrane but did not report any gas solubility results.

Gottesfeld and Zawodzinski [29] include (in their Table 2, p. 205) some solubilities which permit the following semi-quantitative comparisons:

$$H_{O_2, \text{recast Nafion ionomer film}} / H_{O_2, 0.5 \text{ M H}_2\text{SO}_4} \approx 0.36$$

$$H_{O_2, \text{bulk Nafion ionomer}} / H_{O_2, 0.5 \text{ M H}_2\text{SO}_4} \approx 0.07\text{--}0.13$$

This clearly shows the large difference between the bulk and recast Nafion ionomer but also can be used, in conjunction with our earlier correlations for  $H_{O_2, \text{H}_2\text{SO}_4}$  and  $H_{O_2, \text{H}_2\text{O}}$ , to suggest  $H_{O_2, \text{Nafion}}$  correlations that are perhaps more applicable to modern PEMFC:

$$\text{from 0 to 45 °C : } H_{O_2, \text{recast Nafion}} \approx 5.43 \times 10^7 \exp[-1540/T] \quad (26)$$

$$\text{from 45 to 100 °C : } H_{O_2, \text{recast Nafion}} \approx 2.06 \times 10^6 \exp[-500/T] \quad (27)$$

It is worth noting that these ‘synthesized’  $H_{O_2, \text{Nafion}}$  correlations lie in the middle of the Arrhenius plot of all the literature data summarized in the present paper and about a factor of  $2\frac{1}{2}$  above the often-used 1991 and 1992 correlations of Bernardi and Verbrugge [26,23]; that is, predicted oxygen solubilities in Nafion would be about 40% of the Bernardi and Verbrugge predictions. Such a 40% difference in  $c_{O_2, \text{Nafion}}$  would effectively mean a 40% difference in the predicted exchange current densities at the cathode.

Um et al. [31] quantified the oxygen solubility in Nafion membrane at 80 °C by an  $H_{O_2, \text{Nafion}}$  value of  $\sim 2 \times 10^5 \text{ atm cm}^3 \text{ mol}^{-1}$ . This appears to be simply an acceptance of the above-mentioned recommendations of Bernardi and Verbrugge [26,23].

Mitsushima et al. [32] reported considerable solubility data for four membranes of different exchange capacities, one of them being Nafion 117 at  $\sim 0.91 \text{ meq g}^{-1}$ , at a  $p_{O_2}$  of 5 atm. As noted elsewhere, there is the uncertainty as to whether or not the partial pressure of water vapour has been allowed for in stating the value for  $p_{O_2}$  but this uncertainty is minor at 5 atm. The authors do state, however, that “measurements carried out with the feed gas at saturated relative humidity”. The solubilities, on conversion to Henry’s constants, are:

$T$ (°C)	$H_{O_2, \text{Nafion}}$ ( $\text{atm cm}^3 \text{ mol}^{-1}$ )
20	$7.24 \times 10^5$
30	$7.8 \times 10^5$
50	$1.54 \times 10^6$
70	$5.55 \times 10^6$

A number of PEM modelling papers by Broka (Dannenberg) et al. [30,33,34] include considerable data for  $O_2$  permeability in Nafion, “based on solubility measurements” but only say “the solubility of the oxygen is higher in PTFE than in water”. They refer to several earlier publications [22,24,25], all discussed above.

*Comments and conclusions re  $H_{O_2, \text{Nafion}}$ :* If all the above-cited results are put on an Arrhenius plot, a huge spread in the published numerical values of  $H_{O_2, \text{Nafion}}$  is apparent, ranging from about an order of magnitude at low temperatures to approaching two orders of magnitude at 100 °C. There are probably several contributing factors to this apparent major obstacle to the accurate prediction of  $c_{O_2, \text{Nafion}}$  in modelling of PEMFC.

Gottesfeld and Zawodzinski, in their major publication on all aspects of PEMFC [29], dwelt at length on the importance of

using data for the appropriate form of Nafion, some properties of bulk ionomer being significantly different than those for the recast ionomer commonly used in PEM MEAs.

The appropriate water content in the membrane is also very important as gas solubilities are certainly dependent on the actual ‘imbibed water/Nafion matrix system’ used to measure solubilities on the one hand or to model particular PEMFC on the other hand. The recent work by Fimrite et al. [35], although containing no solubility data, gives a good overview of a modelling framework for the evaluation of physical properties in water/Nafion systems.

The solubility data in the literature could also be subject to a variation based on the experimental details, often not considered important enough to report completely. The preparation of the membrane prior to each run, the humidification procedure followed, the sequence of the experimental runs (for example, was a single membrane sample tested at progressively increasing temperatures or progressively decreasing temperatures so that the water contents suffered from a ‘memory’ of the previous water content) and the duration of each run are all possibly significant. We have, for example, observed PEM cells taking days rather than hours to reach equilibrium (as evidenced by a completely constant voltage), a feature that we attributed to slow equilibration of the water content of the membrane.

## 5. Summary and conclusions

In general, prediction of activation and concentration polarization in a PEMFC model, should pay more attention to the proper evaluation of  $p_{\text{gas}}$  and  $c_{\text{gas}}$ .

Expressions such as Eqs. (6) and (7) must be derived to provide  $i_o$ , essentially the kinetic rate equation for the rate-determining step(s). This expression will require surface concentrations that will be modelled using expressions such as Eqs. (8)–(10) and (11)–(27).

A major modelling challenge is the selection of the appropriate Henry’s Law correlation for the MEA being modelled, the form and the water content of the Nafion at the gas/Pt/Nafion interface having a large influence on the resultant concentration of the reactant gas at the catalyst surface.

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