

# Numerical study of hydrogen permeation flux in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ and $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$ (II)

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## EXTENDED ABSTRACT

One of the main technical challenges presently faced in the production of hydrogen is the cost of separation from gas mixtures such as syngas. One of the major hydrogen separation processes, gas separation membranes, seems to be the most promising technology for hydrogen purification when compared to other alternative technologies. Attractive candidates for hydrogen separation membranes are dense ceramic membranes, commonly based on perovskite-type oxides such as 5%- Ytterbium (Yb)-doped strontium cerate ( $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ ), and 5%- Thulium (Tm)-doped strontium cerate ( $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$ ). Our previous study estimated the hydrogen permeation flux of  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  and  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$  and compared the model results with experimental data (Matsuka et al., 2007). It was found that the effect of the hydrogen partial pressure gradient on the hydrogen permeation in the model result was not as significant as indicated by the experimental results. It was suspected that the disagreements may possibly have arisen from one of the model assumptions where the influence of the  $\text{O}_2$  partial pressure gradient is assumed to have no influence on the hydrogen permeation flux. Therefore, the aims of this study are to 1) analyse the model with the additional terms to include the  $\text{O}_2$  partial pressure gradients; 2) analyse sensitivity properties of the modified model; and 3) tune model parameters in the modified model to predict hydrogen permeation flux in  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$ . It is noted that Song et al. (2003) listed three cases (Case 1, 2, and 3) for hydrogen permeation flux calculations. However due to the nature of the model structure where  $P_{\text{H}_2\text{O}}$  is fixed for the step-wise calculations (i.e.  $P_{\text{H}_2\text{O}}$  is constant throughout the membrane.), Case 2 in Song et al. (2003) is not analysed in this study. Therefore, this study investigated Case 1 and Case 3 in Song et al. (2003) and they are referred to as Case A and Case B in this study, respectively. The results showed that the hydrogen permeation flux, calculated with the additional term for the  $\text{O}_2$  partial pressure gradients (Case B), agrees reasonably well with the

experimental data. However the effect of hydrogen partial pressure gradients on the hydrogen permeation in the model result was still not as significant as indicated by the experimental results. This indicated that the discrepancy in the effect of hydrogen partial pressure gradients is not due to the influence of  $\text{O}_2$  potential gradients. Parametric sensitivity analysis showed that the model is generally more sensitive to the charge carrier mobilities, a result which disagrees with the previous study. This may be due to the modified method for defect concentration calculations which allows incorporation of the concentration constraints in the parametric sensitivity analysis. The effect of the thermodynamic equilibrium constants may be suppressed by the concentration constraints incorporated in the analysis, since the thermodynamic equilibrium constants greatly influence the defect concentrations, and the defect concentrations influence the conductivity of charge carriers (Eq. (8)-(12) and (15)). It was expected that the model may become more sensitive to hole mobility ( $\mu_{\text{h}}$ ) and the thermodynamic equilibrium constant for oxygen ion incorporation ( $K_{\text{OX}}$ ) in Case B, due to the incorporation of  $\text{O}_2$  partial pressure gradients.  $\text{O}_2$  partial pressures influence the hole concentration, and consequently the overall electrical conductivity of the membrane. Concentration of oxygen vacancy also depends on the value of  $K_{\text{OX}}$ . However, they remained the least sensitive parameters. Further there is no significant difference in the sensitivity of the model by comparing Case A and B. Thus, these suggest that the influence of  $\text{O}_2$  partial pressures on these types of membrane may not be significant. As a result of parameter tuning, the hydrogen permeation flux in  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$  is fairly well predicted with the tuned parameters. The tuned parameters showed a similar trend to the previous study. As expected, the tuned values for oxygen vacancy mobility ( $\mu_{\text{vo}}$ ) and thermodynamic equilibrium constant for oxygen ion incorporation ( $K_{\text{OX}}$ ) in  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$  resulted in their lower boundary values. This may further indicate a lower affinity of  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$  to oxygen even under the influence of oxygen partial pressures.

## 1 INTRODUCTION

The greenhouse gas emissions from the stationary energy, transport energy and fugitive emissions sectors, which are the largest sources in Australia, may be reduced by introducing cleaner energy sources such as hydrogen. There is an increasing worldwide interest in the hydrogen economy and technologies (Phair and Badwal, 2006). One of the main technical challenges presently faced in the production of hydrogen is the cost of separation of hydrogen from gas mixtures such as syngas. One of the major hydrogen separation processes, gas separation membranes, seems to be the most promising technology for hydrogen purification when compared to other alternative technologies. It requires low cost and simple operation, if practical hydrogen separation rates and stabilities can be achieved (Adhikari and Fernando, 2006).

Attractive candidates for hydrogen separation membranes are dense ceramic membranes, commonly based on perovskite-type oxides. Some of the highest hydrogen permeation fluxes through perovskite oxides with mixed protonic and electronic conduction, have been reported as  $2.0 \times 10^{-7}$  mol/cm<sup>2</sup>/s through a 2 μm dense 5%- Ytterbium (Yb)-doped strontium cerate (SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-α</sub>), in 10% H<sub>2</sub>/He at 950K, and  $1.5 \times 10^{-7}$  mol/cm<sup>2</sup>/s through a 150 μm dense 5%- Thulium (Tm)-doped strontium cerate (SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3-α</sub>) in 20% H<sub>2</sub>/He at 1173K (Hamakawa et al., 2002, Cheng et al., 2005).

Although, hydrogen permeation properties of the perovskite oxides have been studied extensively, few studies have been undertaken on theoretical modelling of hydrogen permeation. The accurate prediction of the hydrogen permeation flux through a mixed protonic and electronic conducting membrane requires a detailed knowledge of the transport properties of the oxides, the charge carrier mobility and the concentrations of each charge carrier (Song et al., 2003, Li and Iglesia, 2003). Our previous study estimated the hydrogen permeation flux of SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-α</sub> and SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3-α</sub> by using the method described by Song et al. (2003), and compared the model results with experimental data obtained by Hamakawa et al. (2002) and Cheng et al. (2005) (Matsuka et al., 2007). It was found that the effect of hydrogen partial pressure gradient on the hydrogen permeation in the model result was not as significant as indicated by the experimental results. It was suspected that the disagreements may possibly have arisen from one of the model assumptions where the influence of the oxygen

partial pressure gradient is assumed to have no influence on the hydrogen permeation flux.

Therefore, the aims of this study are to 1) analyse the model with the additional terms to include the oxygen partial pressure gradients; 2) analyse sensitivity properties of the modified model; and 3) tune model parameters in the modified model to predict hydrogen permeation flux in SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3-α</sub>.

## 2 MODELLING METHODS

The hydrogen permeation experiments by Hamakawa et al. (2002) and Cheng et al. (2005) were conducted in a dry hydrogen atmosphere (H<sub>2</sub>/He or H<sub>2</sub>/N<sub>2</sub>) at the upstream side of the membrane system. The permeate at the downstream side of the membrane was swept with O<sub>2</sub>/N<sub>2</sub> or O<sub>2</sub>/He. The downstream hydrogen partial pressure, upstream oxygen partial pressure and both upstream and downstream water vapour partial pressures were not reported in either of the experiments, and there was not enough experimental information reported in the papers to calculate the actual partial pressures. Therefore the following assumptions are utilised in this study:

- I. The water vapour partial pressure is  $10^{-4}$  atm (dry) for both upstream and downstream sides of the membrane (Qi and Lin, 2000).
- II. Relationship between partial pressures of water, hydrogen and oxygen are described by:
$$\text{H}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{H}_2\text{O} \rightarrow K_w' = P_{\text{H}_2\text{O}}/P_{\text{H}_2}/P_{\text{O}_2}^{1/2} \quad (1)$$
where  $K_w' = \exp(29809/T - 6.64)$ , and T is temperature in Kelvin (Schober et al., 1996), so that unknown partial pressures can be calculated.
- III. The system is in local thermodynamic equilibria (Song et al., 2003)
- IV. The system is under open circuit condition (Song et al., 2003, Li and Iglesia, 2003)
- V. The bulk diffusion of hydrogen is the rate-limiting process in hydrogen permeation (i.e. high surface exchange kinetics) (Hamakawa et al., 2002, Cheng et al., 2005).
- VI. There is no leakage though the membrane system, and the membrane is gas tight (Hamakawa et al., 2002, Cheng et al., 2005).

## 2.1 Defect concentrations

The concentrations of defects in SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-α</sub> and SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3-α</sub> are calculated with the 10 defect 'species', [Sr<sub>Sr</sub><sup>x</sup>], [V<sub>Sr</sub><sup>''</sup>], [Ce<sub>Ce</sub><sup>x</sup>], [Yb'<sub>Ce</sub>] ([Tm'<sub>Ce</sub>]), [V<sub>Ce</sub><sup>'''</sup>], [O<sub>o</sub><sup>x</sup>], [OH<sub>o</sub><sup>•</sup>], [V<sub>o</sub><sup>''</sup>], [e'] and [h<sup>•</sup>] and shown Table 1.

**Table 1.** 10 defect 'species' in SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-α</sub> and SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3-α</sub>

Sr site	Normal cation, Sr <sub>Sr</sub> <sup>x</sup>	Cation vacancy, V <sub>Sr</sub> <sup>''</sup>	
Ce site	Normal cation, Ce <sub>Ce</sub> <sup>x</sup>	Substitutional cation, Yb' <sub>Ce</sub> (Tm' <sub>Ce</sub> )*	Cation vacancy, V <sub>Ce</sub> <sup>'''</sup>
O site	Normal oxygen, O <sub>o</sub> <sup>x</sup>	Proton, OH <sub>o</sub> <sup>•</sup>	Oxygen Vacancy, V <sub>o</sub> <sup>''</sup>
	Electron, e'	Electron hole, h <sup>•</sup>	

\*N.B. for SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3-α</sub>.

The independent equations for describing the oxide SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-α</sub>, are as follows (Song et al., 2003, Poulsen, 1999, Matsuka et al., 2007)

Site Balances where [i] specifies a mole fraction of species *i*:

$$\text{Sr site: } [\text{Sr}_{\text{Sr}}^x] + [\text{V}_{\text{Sr}}''] = 1, \quad (2)$$

$$\text{Ce site: } [\text{Ce}_{\text{Ce}}^x] + [\text{Yb}'_{\text{Ce}}] + [\text{V}_{\text{Ce}}'''] = 1, \quad (3)$$

$$\text{Oxide site: } [\text{O}_{\text{o}}^x] + [\text{OH}_{\text{o}}^{\bullet}] + [\text{V}_{\text{o}}''] = 3. \quad (4)$$

Mass balances relating the mole fraction to molar quantities:

$$[\text{Ce}_{\text{Ce}}^x] / [\text{Yb}'_{\text{Ce}}] = (1-x)/x, \quad (5)$$

$$\text{A/B site ratio: } [\text{Sr}_{\text{Sr}}^x] / ([\text{Ce}_{\text{Ce}}^x] + [\text{Yb}'_{\text{Ce}}]) = z, \quad (6)$$

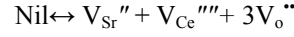
where *x* is the dopant level on the Ce site and *z* is the A/B stoichiometric ratio that relates the concentration of occupied Sr sites to occupied Ce sites.

Electroneutrality condition:

$$2[\text{V}_{\text{Sr}}''] + [\text{Yb}'_{\text{Ce}}] + 4[\text{V}_{\text{Ce}}'''] + [e'] = [\text{OH}_{\text{o}}^{\bullet}] + 2[\text{V}_{\text{o}}''] + [h^{\bullet}]. \quad (7)$$

Mass action laws:

Schottky reaction for vacancy generation (Schottky-Wagner disorder):

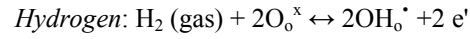


$$\rightarrow K_s = [\text{V}_{\text{Sr}}''] [\text{V}_{\text{Ce}}'''] [\text{V}_{\text{o}}'']^3. \quad (8)$$

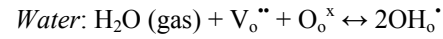
Internal electronic equilibrium:

$$K_i = [e'][h^{\bullet}]. \quad (9)$$

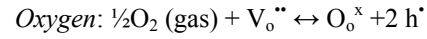
External equilibria (equilibria between the oxide and the gas atmosphere):



$$\rightarrow K_H = [\text{OH}_{\text{o}}^{\bullet}]^2 [e']^2 / (P_{\text{H}_2} [\text{O}_{\text{o}}^x]^2), \quad (10)$$



$$\rightarrow K_w = [\text{OH}_{\text{o}}^{\bullet}]^2 / (P_{\text{H}_2\text{O}} [\text{V}_{\text{o}}''] [\text{O}_{\text{o}}^x]), \quad (11)$$



$$\rightarrow K_{\text{ox}} = [\text{O}_{\text{o}}^x] [h^{\bullet}]^2 / (P_{\text{O}_2}^{1/2} [\text{V}_{\text{o}}'']), \quad (12)$$

where  $K_s$ ,  $K_i$ ,  $K_H$ ,  $K_w$ , and  $K_{\text{ox}}$  are the thermodynamic equilibrium constants. The equations (10), (11) and (12) are interrelated by Eq. (1) and  $K_w' = K_H K_{\text{ox}} / K_w / K_i^2$  (Schober et al., 1996).

A series of defect concentrations and hydrogen and oxygen partial pressures is calculated from Eq. (1) to (12) above, with fixed values of the thermodynamic equilibrium constants ( $K_w$ ,  $K_i$ ,  $K_{\text{ox}}$ ,  $K_s$ ), the dopant level ( $x=0.05$ ), A/B ratio ( $z=1$ ), and the water vapour partial pressure ( $P_{\text{H}_2\text{O}}$ ), and by varying [Yb'<sub>Ce</sub>] within its concentration interval,  $0 < [i] < x$ . The step-wise calculation continues while defect concentrations are within their concentration intervals;  $0 < [i] < 1$  for [Sr<sub>Sr</sub><sup>x</sup>], [V<sub>Sr</sub><sup>''</sup>], [Ce<sub>Ce</sub><sup>x</sup>], [V<sub>Ce</sub><sup>'''</sup>], [e] and [h] and  $0 < [i] < 3$  for [O<sub>o</sub><sup>x</sup>], [OH<sub>o</sub><sup>•</sup>] and [V<sub>o</sub><sup>''</sup>]. It is noted that in this study, [Yb'<sub>Ce</sub>] is utilised as an independent variable for the step-wise calculation instead of [V<sub>o</sub><sup>''</sup>], for the reasons that 1) the concentration interval of [Yb'<sub>Ce</sub>] is narrower than [V<sub>o</sub><sup>''</sup>], 2) the modified method allows a shorter model simulation run time, 3) which consequently allows incorporation of the concentration constraints in the parametric sensitivity analysis, and 4) it still produces the same set of defect concentrations as calculated in the previous methods. Table 2 summarises the parameter values for SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-α</sub> that are utilised in this study.

## 2.2 Hydrogen permeation flux

The hydrogen permeation flux is computed with the defect concentrations calculated in section 2.1,

based on the method developed by Song et al. (2003). Song et al. (2003) listed three cases (Case 1, 2, and 3) for hydrogen permeation flux calculations. Our previous study analysed Case 1 where the hydrogen permeation flux is assumed to be a function of hydrogen partial pressures only. This study aims to analyse the model in terms of the other cases. Due to the nature of the model structure where  $P_{H_2O}$  is fixed for the step-wise calculations (i.e.  $P_{H_2O}$  is constant throughout the membrane.), Case 2 in Song et al. (2003) is not analysed in this study. Therefore, this study is to investigate Case 1 and Case 3 in Song et al. (2003) and they are referred to as Case A and Case B in this study, respectively:

Case A: under  $P_{H_2}$  gradient only

$$j_{H_2} = \frac{1}{L} \frac{RT}{4F^2} \left\{ \int_{P_{H_2}''}^{P_{H_2}' } \sigma_i t_{OH} (t_{VO} + t_e) d \ln P_{H_2} \right\}, \quad (13)$$

Case B: under  $P_{H_2}$  and  $P_{O_2}$  gradients

$$j_{H_2} = \frac{1}{L} \frac{RT}{4F^2} \left\{ \int_{P_{H_2}''}^{P_{H_2}' } \sigma_i t_{OH} (t_{VO} + t_e) d \ln P_{H_2} + \frac{1}{2} \int_{P_{O_2}''}^{P_{O_2}' } \sigma_i t_{OH} t_{VO} d \ln P_{O_2} \right\} \quad (14)$$

where  $j_{H_2}$  is the hydrogen permeation flux (mol/cm<sup>2</sup>s);  $L$  is the thickness of the membrane (cm);  $R$  is the universal gas constant (m<sup>3</sup>Pa/K/mol);  $F$  is Faraday's constant (coulomb/mol);  $P_{H_2}'$  and  $P_{O_2}'$  are the hydrogen and oxygen partial pressure (atm) at the upstream side of the membrane, respectively;  $P_{H_2}''$  and  $P_{O_2}''$  are the hydrogen and oxygen partial pressure (atm) at the downstream side of the membrane, respectively ( $P_{H_2}'' = 4.8e^{-15}$ atm and  $P_{O_2}'' = 0.14$ atm);  $t_i$  represents the transference number of defect species  $i$ ; and  $\sigma_i$  is the total conductivity (S/cm) (Qi and Lin, 2000). The partial conductivity  $\sigma_i$  of species  $i$  ( $OH_o^{\cdot}$ ,  $V_o^{\cdot\cdot}$ ,  $e'$ ,  $h'$ ) is defined as:

$$\sigma_i = z_i F \mu_i [i] / V_m, \quad (15)$$

where  $z_i$  is the charge,  $\mu_i$  is charge carrier mobilities of defect  $i$  (cm<sup>2</sup>/V s);  $[i]$  is the defect concentration of species  $i$  (mol/mol); and  $V_m$  is molar volume of the system (cm<sup>3</sup>/mol) (Song et al., 2003). The calculated hydrogen permeation fluxes are compared with the experimental data from Hamakawa et al. (2002) for SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3- $\alpha$</sub> .

**Table 2.** Parameter values for SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3- $\alpha$</sub>  and their upper and lower boundaries (Matsuka et al., 2007)

	Original	Lower bounds	Upper Bounds
$K_w$ (atm <sup>-1</sup> )	3.29	1	30
$K_i$	1e <sup>-11</sup>	1e <sup>-12</sup>	1e <sup>-10</sup>
$K_s$	1e <sup>-14</sup>	1e <sup>-15</sup>	1e <sup>-13</sup>
$K_{ox}$ (atm <sup>-1/2</sup> )	5e <sup>-6</sup>	5e <sup>-7</sup>	5e <sup>-5</sup>
$\mu_{OH}$ (cm <sup>2</sup> /V s)	1.45 e <sup>-5</sup>	1.45e <sup>-6</sup>	1.45e <sup>-4</sup>
$\mu_{V_o}$ (cm <sup>2</sup> /V s)	6.48 e <sup>-6</sup>	6.48e <sup>-7</sup>	6.48e <sup>-5</sup>
$\mu_h$ (cm <sup>2</sup> /V s)	4.11e <sup>-4</sup>	4.11e <sup>-5</sup>	4.11e <sup>-3</sup>
$\mu_e$ (cm <sup>2</sup> /V s)	4.11e <sup>-4</sup>	4.11e <sup>-5</sup>	4.11e <sup>-3</sup>

### 2.3 Parametric Sensitivity Analysis

Sensitivity analysis is applied to investigate the first order effects of the K values ( $K_w$ ,  $K_i$ ,  $K_{ox}$ ,  $K_s$ ) and  $\mu$  values ( $\mu_{OH}$ ,  $\mu_{V_o}$ ,  $\mu_h$ ,  $\mu_e$ ) on the hydrogen permeation flux in Case B by using the New Morris Method (Cropp and Braddock, 2002). It is performed by setting an upper and lower boundaries for each of the parameters, the number of runs to be undertaken and the resolution (the number of intervals that the factor ranges are to be split). The sensitivity analysis model generates 'test values' for each of the K and  $\mu$  values which are fed into the hydrogen permeation model. Then the effect on the hydrogen permeation flux caused by the changes in the parameter test value is studied (Cropp and Braddock, 2002). The upper and lower boundaries for the K and  $\mu$  values are set as one order of magnitude higher and lower to the original values, and are shown in Table 2. Results are analysed in terms of Euclidean ranks, grading the Euclidean distance of a vector which consists of the mean effect value and the standard deviation for each of the parameters.

### 2.4 Parameter tuning

The parameter tuning of the hydrogen permeation flux model to predict the hydrogen permeation flux in SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3- $\alpha$</sub>  is achieved by least-squares analysis. The error function (objective function),  $f$ , is defined as:

$$f = f(K, \mu) = \sum_{i=L_1}^L \sum_{j=p_1}^p (E_{ij} - M_{ij})^2, \quad (16)$$

where  $L$  is the thickness of the membrane,  $p$  is the upstream partial pressure of hydrogen,  $E_{ij}$  is the hydrogen permeation flux from the experiment, and  $M_{ij}$  is the hydrogen permeation flux modelled in this study. (For a more detailed explanation, see

Matsuka et al., 2007). The original values and the upper and lower boundaries are shown in Table 2.

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Hydrogen permeation flux - $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$

Figure 1 illustrates the modelled hydrogen permeation flux for  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  at 950K, plotted against the experimental data obtained from Hamakawa et al (2002), for Case A and B. It is noted that the model results in this study slightly differ from the previous study, due to the modified assumptions on gas partial pressures.

The calculated hydrogen permeation flux in Case B agrees reasonably well with the experimental data. However the effect of hydrogen partial pressure gradient on the hydrogen permeation in the model result is still not as significant as indicated by the experimental results. This indicates that the discrepancy between the model and experimental results (in terms of the effect of hydrogen partial pressure gradients) is not due to the influence of oxygen potential gradients.

#### 3.2 Parametric sensitivity analysis - $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$

The average Euclidean ranks for each of the parameters are shown in Table 3. It is observed that the model is generally more sensitive to the charge carrier mobilities,  $\mu$  values, which disagrees with the previous study.

This may be due to the modified method for defect concentration calculations which allows incorporation of the concentration constraints in the parametric sensitivity analysis. The effect of K values may be suppressed by the concentration constraints incorporated in the analysis, since the K values greatly influence the defect concentrations, and the defect concentrations influence the conductivity of charge carriers (Eq. (8)-(12) and (15)). It was expected that the model may become more sensitive to hole mobility ( $\mu_h$ ) and thermodynamic equilibrium constant for oxygen ion incorporation ( $K_{OX}$ ) in Case B, due to the incorporation of  $\text{O}_2$  partial pressure gradients in the model.  $\text{O}_2$  partial pressures influence the hole concentration, and consequently the overall electrical conductivity of the membrane. Concentration of oxygen vacancy,  $[V_o^{\bullet\bullet}]$  also depends on the value of  $K_{OX}$ . However, they remained the least sensitive parameters. Further there is no significant difference in the sensitivity of the model by comparing Case A and B. Thus,

these suggest that the influence of  $\text{O}_2$  partial pressures on these types of membrane may not be significant.

These results from the sensitivity analysis are useful to determine which parameters require more detailed investigation. For example, mobility of protons ( $\mu_{OH}$ ) should be carefully investigated as it would depend on a number of factors, such as proton jump distance, fraction of vacant jump destinations, and activation energy for proton migration (Norby, 1990). This may aid this research field where a shortage of experimental data has been a significant barrier to the improvement and validation of permeation models.

**Table 3.** Average Euclidean ranks

	EUCLIDEAN RANK	
	CASE A	CASE B
$K_w$	2	3
$K_i$	6	6
$K_s$	5	5
$K_{ox}$	7	8
$\mu_{OH}$	1	1
$\mu_{Vo}$	3	4
$\mu_h$	8	7
$\mu_c$	4	2

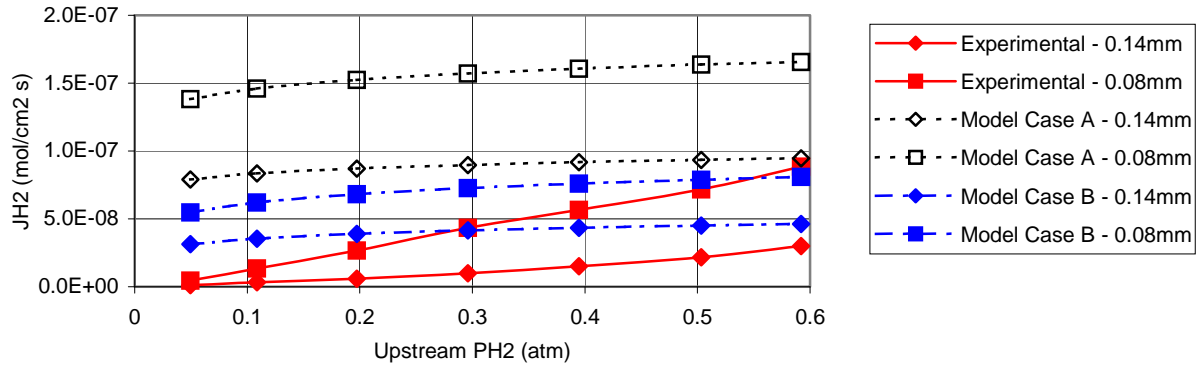
#### 3.3 Parameter tuning - $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$

The K and  $\mu$  values for  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  are tuned to predict the hydrogen permeation flux in  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$  for Case B with the concentration constraints listed in Table 2. Table 4 summarises the tuned K and  $\mu$  values for  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$ . Figure 2 and Figure 3 illustrate the hydrogen permeation flux calculated with the original and tuned K and  $\mu$  values for  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$ , plotted against the experimental data, respectively (Cheng et al., 2005).

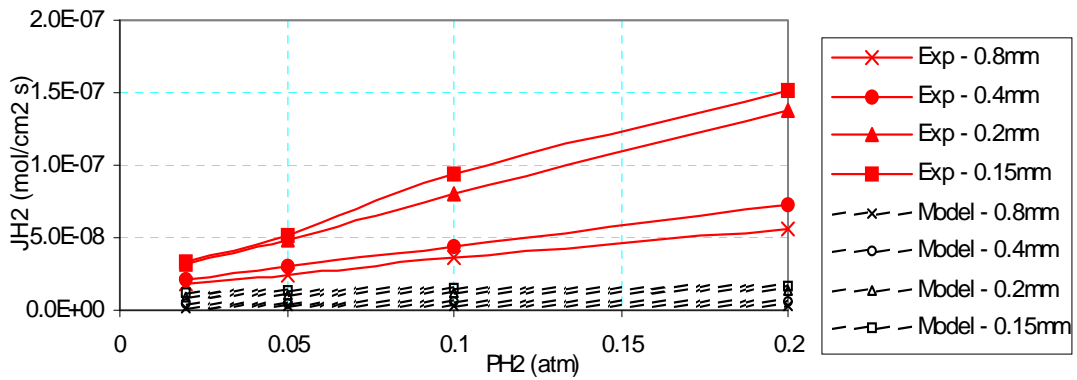
The hydrogen permeation flux for  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$  at 1173K is fairly well predicted with the tuned parameters. The tuned parameters showed a similar trend to the previous study. For instance, the tuned mobilities of proton ( $\mu_{OH}$ ) are higher than those in  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ , possibly contributing to the higher hydrogen flux in  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$ . The resulting value of the thermodynamic equilibrium constant for proton incorporation from hydrogen gas ( $K_H$ ) is again predicted higher for  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$ , which may indicate a higher affinity of  $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\alpha}$  to hydrogen (Li and Iglesia, 2003). Further, the tuned value of the thermodynamic equilibrium constant for proton incorporation from water vapour ( $K_w$ )

for  $\text{SrCe}_{0.95}\text{TM}_{0.05}\text{O}_{3-\alpha}$  is higher than that for  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ . A higher  $K_w$  indicates more proton incorporation or that more protons are kept in the system (Krug, 1996), which may possibly contribute to the higher hydrogen flux in  $\text{SrCe}_{0.95}\text{TM}_{0.05}\text{O}_{3-\alpha}$ .

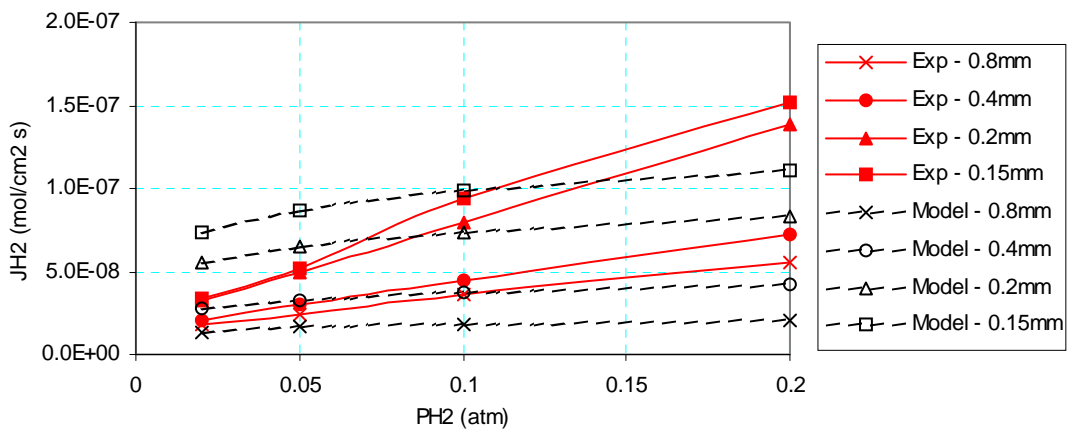
As expected, the tuned values for oxygen vacancy mobility ( $\mu_{\text{vo}}$ ) and thermodynamic equilibrium constant for oxygen ion incorporation ( $K_{\text{OX}}$ ) in  $\text{SrCe}_{0.95}\text{TM}_{0.05}\text{O}_{3-\alpha}$  resulted in their lower boundary values (Table 2 and Table 4). This may further indicate a lower affinity of  $\text{SrCe}_{0.95}\text{TM}_{0.05}\text{O}_{3-\alpha}$  to oxygen even under the influence of oxygen partial pressures.



**Figure 1.** Hydrogen permeation for  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  at 950K, with  $L=0.14$  &  $0.08\text{mm}$  – Case A and B.



**Figure 2.** Hydrogen permeation flux calculated with the original  $K$  and  $\mu$  values for  $\text{SrCe}_{0.95}\text{TM}_{0.05}\text{O}_{3-\alpha}$  at 1173K, with  $L=0.8, 0.4, 0.2$  &  $0.15\text{mm}$  – Case B



**Figure 3.** Hydrogen permeation flux calculated with the tuned  $K$  and  $\mu$  values for  $\text{SrCe}_{0.95}\text{TM}_{0.05}\text{O}_{3-\alpha}$  at 1173K, with  $L=0.8, 0.4, 0.2$  &  $0.15\text{mm}$  – Case B

**Table 4.** Original and tuned K and  $\mu$  values for SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3- $\alpha$</sub>  at 1173K

CONSTANTS	ORIGINAL VALUES	TUNED VALUES
K <sub>w</sub> (atm <sup>-1</sup> )	3.29	6.72
K <sub>i</sub>	1.00e <sup>-11</sup>	2.11 e <sup>-11</sup>
K <sub>s</sub>	1.00e <sup>-14</sup>	1.27 e <sup>-15</sup>
K <sub>ox</sub> (atm <sup>-1/2</sup> )	5.00e <sup>-6</sup>	5.01e <sup>-7</sup>
$\mu_{OH}$ (cm <sup>2</sup> /V s)	1.45e <sup>-5</sup>	4.84e <sup>-5</sup>
$\mu_{vo}$ (cm <sup>2</sup> /V s)	6.48e <sup>-6</sup>	6.48e <sup>-7</sup>
$\mu_h$ (cm <sup>2</sup> /V s)	4.11e <sup>-4</sup>	7.56e <sup>-5</sup>
$\mu_e$ (cm <sup>2</sup> /V s)	4.11e <sup>-4</sup>	1.14e <sup>-4</sup>
Resulting K <sub>H</sub> (atm <sup>-1</sup> )	5.26e <sup>-6</sup>	1.57 e <sup>-4</sup>
Objective function, f(K, $\mu$ )	5.75e <sup>-14</sup>	1.09 e <sup>-14</sup>

#### 4 CONCLUSION

This study analysed the hydrogen permeation flux model with (1) modifications in the defect concentration calculations where [Yb'<sub>ce</sub>] was utilised as an independent variable for the step-wise calculation instead of [V<sub>o</sub>''], and (2) the additional terms to include the oxygen partial pressure gradients for calculation of hydrogen permeation flux. The modification (1) allowed a short model simulation run time, which consequently allowed incorporation of the concentration constraints in the parametric sensitivity analysis, and it still produced the same set of defect concentrations as calculated in the previous methods. It was also found in this study that the discrepancy between the model and experimental results (in terms of the effect of hydrogen partial pressure gradients) is not due to the influence of oxygen potential gradients. Parametric sensitivity analysis showed that there is no significant difference in the sensitivity of the model by comparing Case A and B, suggesting that the influence of oxygen partial pressures on these types of membrane may not be significant. As a result of parameter tuning, the hydrogen permeation flux for SrCe<sub>0.95</sub>Tm<sub>0.05</sub>O<sub>3- $\alpha$</sub>  at 1173K is fairly well predicted with the tuned parameters.

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