

Comprehensive Review on High Hydrogen Permselectivity of Palladium Based Membranes: Part II

Hydrogen permeation flux under concentration polarisation influence

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This article completes the presentation of various techniques reducing concentration polarisation in palladium based membranes for supplying ultra-high purity hydrogen to a polymer electrolyte fuel cell (PEFC), such as the implementation of baffles and the use of microchannel configuration. The present paper also reviews and reports the current methods for estimating hydrogen permeation flux

under concentration polarisation influence, which will be a useful guide for academics and industrial practitioners.

1. Factors Affecting Concentration Polarisation in Palladium Based Membranes

Miguel *et al.* examined the decrease in the hydrogen concentration along the membrane length of a finger-like configuration (1–3) for the case of binary hydrogen mixtures with inhibitive carbon monoxide or carbon dioxide, by replacing the terms of feed partial pressure of inhibitive species and the difference in the square root of hydrogen partial pressure in the Sieverts' Langmuir equation (4) with the average partial pressure of inhibitive species and logarithm mean driving force (5), respectively. In this case, the authors obtained an excellent concordance between the predicted results obtained from their rearranged Sieverts' Langmuir equation with the actual hydrogen permeation flux (2), which proved the existence of concentration polarisation during the permeation.

With the apparent advantage of using sweep gas during hydrogen permeation (6), Chen *et al.* have further investigated the concentration polarisation phenomena under sweep gas and baffles implementation (7). The flows of feed gas and sweep gas were in the form of countercurrent mode. It is interesting to note that higher hydrogen flux can be obtained from the membrane when a smaller diameter of the shell (smaller distance between the shell and tubular membrane) is used. As an example, when the pressure difference, temperature, mass flow rate of feed gas and

Reynolds number of flow at the permeate side were set to 9 atm, 623 K, 267.48 mg s⁻¹ and 1000, respectively, the hydrogen flux for the cases of large, medium and small shell were 0.88 mol m⁻² s⁻¹, 0.96 mol m⁻² s⁻¹ and 1.03 mol m⁻² s⁻¹, respectively. This is due to the reduction of boundary layer thickness, as demonstrated by the numerical results (7). Besides, the introduction of baffles to the shell side causes disturbance to the boundary layer and more hydrogen is directed towards the membrane surface. Therefore, concentration polarisation is weakened and more permeated hydrogen can be obtained. Interestingly, due to the trade-off between the installation cost and slight improvement in permeation performance when more baffles are installed, one baffle installation has been recommended (7). In this case, Coroneo *et al.* also have asserted there should be an optimum number of baffles installed after observing just a slight improvement in permeated flow when the number of baffles is increased, from around 38% (two baffles configuration) to just around 46% (three baffles configuration) (8).

Further investigation by Chen *et al.* (9) then discovered the optimum baffles configuration for minimising concentration polarisation while obtaining maximum hydrogen recovery. In this case, the authors emphasised the importance of concentrating hydrogen at the membrane surface through the flow contraction mechanism. The optimum conditions for baffle installations are as follows: (a) installation of single baffle at shell wall; (b) installation at the leading edge of the membrane and (c) use of a sufficiently high ratio of baffle length to shell radius (ratio of 0.75) (9).

Faizal *et al.* (10) investigated the effect of hydrogen partial pressure and feed flow rate on the level of concentration polarisation for flat sheet palladium/silver membrane, despite widespread research interest in tubular type membranes. A third degree polynomial equation has been introduced as a tool to predict hydrogen permeation flux for such geometry. Based on the predicted profile of hydrogen mole fraction at the membrane surface, the difference between the predicted average hydrogen mole fraction at the membrane surface and hydrogen mole fraction at the inlet becomes larger at higher inlet hydrogen partial pressure. For the case of a binary mixture of H₂:N₂ (inlet hydrogen mole fraction of 0.75), when operating temperature, feed mole flux and hydrogen partial pressure at downstream (permeate) side were set to 623 K, 0.40 mol m⁻² s⁻¹ and 0.10 MPa, respectively, the aforementioned difference increased from 9%

to 20% when inlet hydrogen partial pressure was increased from 0.150 MPa to 0.225 MPa. Therefore, the concentration polarisation was strengthened. Compared to the previous studies, the changes in the concentration polarisation level concerning the inlet hydrogen partial pressure and feed flow rate are similar qualitatively (10).

Chen *et al.* performed experimental studies on a H₂:N₂ mixture permeation test using high permeance tubular palladium based membranes (palladium and palladium/copper membrane with porous stainless steel) (11). Here, the thickness applied was from 6–7 μm. Similar to the previous study on ultrathin high permeance palladium/silver membrane with ceramic support (thickness of 2.5 μm) (12), the authors revealed that concentration polarisation was most affected by the concentration of the hydrogen feed, notably when the hydrogen concentration was decreased from 75 vol% to 50 vol%. The severity of concentration polarisation becomes higher even though the hydrogen partial pressure difference has been set to the same value. In this case, it can be noticed that in order to obtain the same hydrogen partial pressure difference, when the hydrogen partial pressure at the permeated side is set constant, higher total upstream pressure is necessary for smaller feed hydrogen fraction, and this increases the levels of concentration polarisation. Within their selected operating condition, feed flow rate and hydrogen partial pressure difference cause concentration polarisation as well, but with minor influence compared to the feed hydrogen concentration factor (11). Zhao *et al.* performed a permeation test for a mixture that was almost similar to coal gasification product (<40% H₂ and <40 ppm H₂S) to simultaneously determine the effect of sulfur contamination and concentration polarisation. The authors found that the influence of concentration polarisation was dominant for the mixture with lower hydrogen composition (50% mole fraction) especially at a low feed flow rate due to the minor effect of sulfur poisoning in the specified condition (13).

As a continuation of their previous study (10), Faizal *et al.* (14) investigated the concentration polarisation phenomena for various binary hydrogen mixtures with different inlet hydrogen mole fraction (0.70–0.80) and species (nitrogen, argon, helium and carbon dioxide). It is interesting to note that a mixture of hydrogen and argon was used due to different chemical characteristics, whereas the mixture of hydrogen and helium was used due to the different binary diffusivity compared to the

hydrogen mixture that contained nitrogen (14). The authors compared the analytical results calculated by using their previously introduced theoretical equation that takes into account the effect of hydrogen permeation itself (10) with the actual hydrogen permeation flux. The study demonstrated an excellent concordance between the estimated hydrogen permeation flux and the actual flux regardless of inlet hydrogen mole fraction and species, thus elucidates the significant effect of hydrogen permeation itself on the decrease in hydrogen concentration at the membrane surface during concentration polarisation. Therefore, it is interesting to note that the severity of concentration polarisation is determined by feed flow rate and inlet hydrogen mole fraction, but not the different chemical characteristics and binary diffusivity of the mixtures (14).

Nakajima *et al.* reduced the boundary layer thickness to abate concentration polarisation by improving physical geometry of a reactor vessel containing a tubular palladium/silver membrane (15). In this case, the reduction of boundary layer thickness was performed by narrowing the path between the membrane surface and the inner surface of the vessel shell (15). For instance, by narrowing the path from 23.9 mm to 16.6 mm, the amount of produced hydrogen can be improved by around 25% even though there is only a 2% increment in methane conversion during hydrogen production from natural gas (for feed flow rate of $9 \text{ Nml min}^{-1} \text{ cm}^{-2}$) (15). Such improvement is due to the reduction in distance between the inner surface of the vessel and the membrane surface, which has also been observed through the previous numerical simulation performed by Chen *et al.* (7).

As an alternative to the numerical simulation technique performed by Chen *et al.* (6, 16), the profiles of average axial concentration and concentration at the membrane surface can also be obtained by determining an analytical solution of the governed ordinary differential equation (ODE) (17). Further discussion on the analytical solution is presented in the following section.

In 2018, Kian *et al.* investigated the concentration polarisation phenomenon for the case of various ternary mixtures (18). They found the hydrogen permeation behaviour for ternary mixtures is similar to the case of binary mixtures, in which competitive adsorption becomes dominant when strong inhibitive carbon monoxide is used in the ternary hydrogen mixture ($\text{H}_2:\text{CO}_2:\text{CO}$) while concentration polarisation starts to play a

significant role when methane is used instead of carbon monoxide. In the same year, Helmi *et al.* also proved the concentration polarisation phenomenon for the case of a fluidised membrane reactor (19). The good agreement between the developed model that considers concentration polarisation (so called ' $1D/k_d$ ') with experimental results elucidates that this phenomenon becomes more significant when lower inlet hydrogen mole fraction and higher inlet velocity are used (19). Based on the comprehensive review of the research scenarios in the previous paragraphs, it is evident that concentration polarisation is an undesirable phenomenon. This is because the ability of the membrane to permeate a very high amount of hydrogen cannot be fully utilised. However, it is unavoidable due to the advances in membrane technology that cause the fabrication of very thin membranes. Consequently, the external mass transfer becomes the permeation controlling step instead of diffusion in the metallic lattice. Although the development of compact devices with sufficiently high hydrogen recovery is possible, the concentration polarisation level becomes high due to the significant effect of permeation itself during the permeation.

In brief, several techniques have been introduced to address such disadvantages and effectively reduce the severity of concentration polarisation. For example, baffles may be implemented (7, 8) in the membrane reactor and the path between membrane surface and inner vessel wall may be narrowed (7, 15) to reduce the boundary layer at the membrane surface (15). The implementation of a spherical particles bed between tubular membranes in a membrane reactor has been confirmed to reduce the effect of concentration polarisation, due to the increase in the interparticle velocity and the increase in the Reynolds number between the particles and membrane surfaces (20). Helmi *et al.* have used fluidising particles inside a fluidised membrane reactor to significantly reduce the concentration polarisation effect due to better mixing of gases (21). The permeation system with microchannel configuration (22, 23) also has been suggested as a technique for concentration polarisation abatement due to the ability to decrease boundary layer thickness near to the membrane surface (22, 24). The combined usage of baffles and perforated pipe to reduce concentration polarisation effect has been demonstrated by Peters *et al.* (25) due to the creation of turbulence. Recently, an integrated compact system that consists of combustor, prereformer, reformer and

hydrogen separator (palladium membrane) in a single module was developed by Wunsch *et al.* for small hydrogen demand applications (26). Since the height of the integrated system was relatively very small (12.4 mm) with eleven plates arranged in a stack, the concentration polarisation effect could be minimised, thus improving hydrogen yield as well as hydrogen productivity (26).

2. Estimation Methods for Hydrogen Permeation under Concentration Polarisation Influence

In 2008, Chen *et al.* introduced a constant concentration method with the aim to characterise the membrane by eliminating the effect of concentration polarisation (27). Based on this method, the tubular membrane reactor was filled with non-H₂ species first and followed by H₂ to obtain the desired hydrogen partial pressure without allowing any permeation. Once permeation began, the hydrogen that permeated out of the membrane was made up or replaced by the fresh hydrogen from the pressurised tank to maintain the hydrogen partial pressure at the retentate side. Therefore, the variation of hydrogen concentration at the membrane surface could be eliminated (27). However, this technique is not practical for industrial application since the flow stream at the upstream side of industrial membrane reactor is usually in plug flow, and not perfectly mixed flow, in which concentration polarisation usually could be triggered.

Extensive studies on concentration polarisation phenomena have been performed by Caravella *et al.* (28) and Catalano *et al.* (12). Caravella *et al.* (28) have created concentration polarisation maps which are very useful for hydrogen purification system design. Here, the maps are a two-dimensional graph of concentration polarisation coefficient versus hydrogen retentate molar fraction that was derived based on Equation (i):

$$H_2flux \text{ (elementary steps)} = \frac{1}{(1 - CPC) \pi^{membrane} DF^{bulk}} \quad (i)$$

where H_2flux (elementary steps) is the hydrogen permeation flux that is calculated by considering all the permeation elementary steps (external mass transfer, superficial adsorption, diffusion through the palladium-based bulk and superficial desorption) (29), in which in this case, involved complex procedures. Meanwhile, the concentration polarisation coefficient (CPC) is a concentration

polarisation coefficient that becomes as an indicator for concentration polarisation level. The values of CPC were obtained by solving Equation (i) for various operating conditions and the values were plotted with respect to hydrogen retentate molar fraction. Here, when the value of CPC is 0, it means no concentration polarisation occurs while the CPC value of 1 indicates maximum level of concentration polarisation that has been defined as 'total polarisation' in their study. $\pi^{Membrane}$ is the membrane permeance that can be obtained from permeation test for pure hydrogen. Meanwhile, DF^{Bulk} is bulk driving force that can be obtained from the difference in square root of hydrogen partial pressure between the feed side and permeate side when the effect of concentration polarisation is negligible. For those who want to evaluate the concentration polarisation level by using these maps, only knowledge of the operating condition of the membrane reactor is required. The CPC can be determined manually from the maps. Finally, hydrogen permeation flux can be predicted by substitution of the CPC value into Equation (i) and followed by solving the equation. Despite the simplicity of this prediction method, the determined CPC actually does not account for the remaining length (and remaining area) of the tubular membrane where no permeation occurs anymore due to very fast decay of driving force at the region around the inlet. This situation occurs when concentration polarisation becomes significant (16), thus hydrogen concentration is overestimated when the aforementioned CPC value is used. This weakness was then solved through the introduction of the powerful parameter so called effective average CPC (EAC) (30). The determination of EAC is stated as follows, Equation (ii):

$$EAC = 1 - \frac{[Permeation \text{ rate with polarisation}]}{[Permeation \text{ rate without polarisation}]} \quad (ii)$$

$$= 1 - \frac{\int_0^L Flux(z) dz}{\int_0^L \frac{Flux(z)}{1 - CPC(z)} dz}$$

where L , z and CPC are the membrane length, membrane axial abscissa and concentration polarisation coefficient, respectively. Here, the local value of CPC for each position on the membrane in z -direction is determined analogously as was introduced previously (28). Meanwhile, the hydrogen concentration profile and the respective profile of hydrogen permeation flux can be obtained

by simultaneously solving the external mass transfer and hydrogen permeation equations (30). Here, the calculation of mass transfer coefficient is as reported by Caravella *et al.* (29). Finally, Equation (ii) can be solved to obtain the value of EAC. Based on the previous individual elaboration on the prediction techniques using CPC (28) and EAC (30), it can be said that the use of EAC is more desirable, since it has the ability to represent the real behaviour of a hydrogen permeation device. It is interesting to note that once the EAC maps have been prepared, similar to the previous technique of using the CPC maps (28), the hydrogen permeation flux can be estimated by simply substituting the value of the EAC obtained from the maps into Equation (ii).

Similarly, Catalano *et al.* (12) concluded the existence of non-negligible resistance to hydrogen transport in the gaseous phase itself, in addition to resistance caused by the membrane. For the case of a hydrogen mixture, the authors demonstrated a significant deviation from Sieverts' Equation (Equation (iii)) when the hydrogen partial pressure of the bulk gas is substituted into the equation. To compensate for this situation, semi-empirical equations were developed for a tubular type membrane (membrane thickness of 2.5 μm) as follows (12), Equations (iv) and (v):

$$f = \frac{q}{d}(\sqrt{P_{H_2,1}} - \sqrt{P_{H_2,2}}) \quad (iii)$$

$$N_{H_2,int} = k_G \ln \left(\frac{p_{ret} - p_{H_2,int}}{p_{ret} - p_{H_2,ret}} \right) \quad (iv)$$

$$N_{H_2,int} = \bar{K}_{H_2} (p_{H_2,int}^{0.5} - p_{H_2,per}^{0.5}) \quad (v)$$

where $N_{H_2,int}$ is the hydrogen flux crossing the membrane interface and is defined as the hydrogen flux within the gas-metal interface, k_G is the mass transport coefficient, p_{ret} is the pressure at the retentate side, $p_{H_2,int}$ is the hydrogen partial pressure at gas-metal interface, $p_{H_2,ret}$ is the hydrogen partial pressure at retentate side, $p_{H_2,per}$ is the hydrogen partial pressure at permeate side and \bar{K}_{H_2} is the hydrogen permeance obtained from pure hydrogen experiment. It is interesting to note that once the value of k_G is obtained by solving Equations (iv) and (v) simultaneously and by using experimental data of $N_{H_2,int}$, the same value of k_G can then be used to estimate hydrogen permeation flux for the cases with different hydrogen partial pressure difference.

As a continuity of the previous study (28), Caravella *et al.* (31) considered simultaneously both concentration polarisation and inhibition by carbon monoxide species in their model, by introducing the permeation reduction coefficient. Similar to the prediction technique introduced previously (28), the permeation reduction coefficients were plotted for different operating conditions, or so called 'permeation reduction maps'. The simple relation for the permeation reduction coefficient as shown by Equation (vi) was derived from definitions of CPC and inhibitive coefficient (IC), that were obtained from previous studies by Caravella *et al.* (28) and Barbieri *et al.* (4), respectively through complex calculation steps, Equation (vi):

$$PRC = 1 - (1 - CPC)(1 - IC) \quad (vi)$$

where PRC is the permeation reduction coefficient, CPC is the concentration polarisation coefficient and IC is the inhibition coefficient. To predict the hydrogen permeation flux for certain operating conditions, the value of PRC is determined manually from the 'permeation reduction maps' and then the value is substituted into Equation (vii) as follows:

$$J_{H_2} = (1 - PRC) \pi^{Sieverts} \left(\sqrt{P_{H_2}^{retentate}} - \sqrt{P_{H_2}^{permeate}} \right) \quad (vii)$$

where J_{H_2} is the hydrogen permeation flux, PRC is the permeation reduction coefficient, $\pi^{Sieverts}$ is the permeance which is similar to the hydrogen permeance coefficient, obtained from pure-hydrogen test. Meanwhile, $\sqrt{P_{H_2}^{retentate}} - \sqrt{P_{H_2}^{permeate}}$ is the bulk driving force for hydrogen permeation, that is bulk difference in square root of hydrogen partial pressures between the retentate and permeate side.

As one of the solutions for the difficulty in obtaining a general relation that consists of several interdependent parameters as has been mentioned by Morgues *et al.* (32), Faizal *et al.* (10, 14, 33) have introduced a theoretical approach for hydrogen permeation through a flat sheet palladium based membrane after observing a significant deviation between the actual permeation flux and the estimated flux by Sieverts' equation (Equation (iii)) when inlet hydrogen concentration was used (33). As asserted by previous researchers on the significant effect of permeation flux during concentration polarisation phenomena (6, 12, 16), the term of hydrogen partial pressure at membrane surface of upstream side in the Sieverts' equation (Equation (iii)) has been modified to consider the effect of hydrogen permeation flux during

permeation. The modification of Equation (iii) leads to the formation of Equation (viii) as follows (14):

$$f_p = \frac{q}{d} \left(\sqrt{\frac{f_{H_2,in} - f_p}{f_{in} - f_p} P_{in}} - \sqrt{P_{H_2,2}} \right) \quad \text{(viii)}$$

where f_p is the estimated hydrogen permeation mole flux, q is the hydrogen permeance coefficient, d is the membrane thickness, $f_{H_2,in}$ is the mole flux of hydrogen from inlet (feed flow rate of hydrogen divided by effective membrane surface area), f_{in} is the mole flux of the mixture from inlet (feed flow rate of mixture divided by effective membrane surface area), P_{in} is the total pressure at inlet (total upstream pressure) and $P_{H_2,2}$ is the hydrogen partial pressure at membrane surface of the downstream side. In order to predict f_p , the values of operating parameters are substituted into Equation (viii) and followed by solving the equation for f_p . Surprisingly, the modified equation as shown by Equation (viii) can estimate accurately hydrogen permeation flux for any noninhibitive binary hydrogen mixture with different chemical characteristics and binary diffusivity, along with any hydrogen concentration and with any mole flux of mixture from the inlet. For instance, when the mole flux of mixture from the inlet is increased, the effect of concentration polarisation is weakened. Therefore, the estimated flux obtained from Equation (viii) approaches the flux obtained from Equation (iii) due to the weaker effect of f_p . The introduced method is supposed to be very useful for reactors with similar type of membrane used (34–36).

To prevent membrane damage due to mechanical stress, the palladium/silver tubular membrane was created in the form of a ‘finger-like’ configuration, thus allowing the free elongation and contraction of the membrane (2). For this kind of configuration, the way to predict hydrogen permeation flux is supposed to be similar to that for the tubular type membrane with common configurations (Figures 2(a) and 2(b) in Part I (37)) because the hydrogen mixture similarly flows horizontally along the membrane length for both cases. In the research performed by Miguel *et al.* (2), a model to simultaneously consider both concentration polarisation and inhibition by carbon monoxide or carbon dioxide has been introduced based on the logarithm-mean driving force (for considering concentration polarisation effect) and correction factor due to inhibitive effect (4). Compared to the approach by Barbieri *et al.* (4), the model introduced by Miguel *et al.* could provide more accurate results for the simultaneous occurrence

of both phenomena. This is because the previous approach by Barbieri *et al.* (4) only considers the feed hydrogen partial pressure for prediction. However, the model introduced by Miguel *et al.* is semi-empirical and therefore, experimental data is necessary in order to determine certain parameters in the correction factor. The combination of correction factor and rearranged Sieverts’ equation forms the rearranged Sieverts’-Langmuir equation as shown below (2), Equation (ix):

$$J_{H_2}^{SL} = \left(1 - \alpha \frac{K_i \bar{p}_i}{1 + K_i \bar{p}_i} \right) \frac{L_{H_2}}{\delta} \Delta P_{in} \quad \text{(ix)}$$

where the term $\alpha \frac{K_i \bar{p}_i}{1 + K_i \bar{p}_i}$ is the correction factor due to adsorption of inhibitive species on the membrane surface and the term $\frac{L_{H_2}}{\delta} \Delta P_{in}$ is the rearranged Sieverts’ equation.

Here, $J_{H_2}^{SL}$ is the hydrogen permeation flux, α is the Sieverts’-Langmuir reduction factor, K_i is the Langmuir’s adsorption constant for species (CO or CO₂), \bar{p}_i is the average partial pressure of species (CO or CO₂) between the feed and retentate sides, L_{H_2} is the hydrogen permeance or hydrogen permeation coefficient, δ is the membrane thickness and ΔP_{in} is the logarithm mean driving force that is determined based on theory of heat exchanger for parallel flow case (2, 5). It is important to note that the values of α and K_i for carbon monoxide and carbon dioxide are dependent on operating temperature, thus these values need to be fitted with experimental data first before using Equation (ix) to estimate hydrogen permeation flux.

A prediction method for hydrogen permeation capacity (length of membrane for hydrogen permeation) has been introduced by Xie *et al.* (38) through computer programming. The investigation was performed analytically for seven important scenarios with a different flow pattern on both sides (upstream and downstream side). In this case, the concept is similar to that performed by Faizal *et al.* (10, 14, 33), in which the effect of hydrogen permeation rate is taken into account when determining hydrogen partial pressure at the membrane surface of the upstream side, as shown by the following Equation (x) (example for the scenario with plug flow at upstream side, and no sweep gas):

$$P_H(x) = \frac{M_1 - M_x}{M_1 + M_2 - M_x} P_1 \quad \text{(x)}$$

where $P_H(x)$ is the hydrogen partial pressure of an infinitesimal permeation capacity (infinitesimal membrane length for permeation), dx in the high pressure (upstream) side, M_1 is the feed flow rate of hydrogen at upstream side, M_2 is the feed flow rate of nonpermeable gas at upstream side, P_1 is the total pressure of upstream side and M_x is the hydrogen permeation rate through a membrane for length from 0 to x . Then, the local hydrogen permeation rate through the infinitesimal permeation capacity dx can be predicted by substituting Equation (x) into the Sieverts' equation as follows, Equation (xi):

$$dM_x = C \left(\left(\frac{M_1 - M_x}{M_1 + M_2 - M_x} P_1 \right)^{0.5} - P_2^{0.5} \right) dx \quad (xi)$$

where C is the constant for membrane and P_2 is the total pressure of downstream side. In their study, Equation (xi) is rearranged and then followed by integration of x with respect to M_x in order to predict the permeation capacity (membrane length for separation) x as shown by Equation (xii):

$$x = \int_0^{M_x} \left[C \left(\frac{M_1 - M_x}{M_1 + M_2 - M_x} \right) P_1^{0.5} - CP_2^{0.5} \right]^{-1} dM_x \quad (xii)$$

Differently to other techniques, the technique introduced by Xie *et al.* (38) is used to estimate the value of x instead of M_x .

Recently, algebraic functions that can be used to predict the profiles of hydrogen permeation flux under the influence of the concentration polarisation phenomenon have been introduced (17). Concentration polarisation is accounted through the use of an effectiveness factor which was derived in the previous study (39). The effectiveness factor is the ratio of actual permeation flux over the calculated flux based on the average concentration, and it is a function of separation parameter that represents the ratio of diffusive to permeation flux. The effectiveness factor and separation parameter that obeys Sieverts' Law can be expressed as Equation (xiii) and Equation (xiv), respectively (2):

$$\eta = \frac{\sqrt{P_{H_2w}^{ret}} - \sqrt{P_{H_2w}^{per}}}{\sqrt{\langle P_{H_2}^{ret} \rangle} - \sqrt{P_{H_2w}^{per}}} \quad (xiii)$$

$$\Gamma = \frac{DSh}{dk \sqrt{P^{ret}}} \quad (xiv)$$

where (Equation (xv)):

$$K = \frac{K_{H_2}}{c_{tot}} \quad (xv)$$

Here, η is the effectiveness factor, $P_{H_2w}^{ret}$ is the hydrogen partial pressure at membrane surface

of retentate side, $P_{H_2w}^{per}$ is the hydrogen partial pressure at membrane surface of permeate side, $\langle P_{H_2}^{ret} \rangle$ is the average hydrogen partial pressure at retentate side, Γ is the separation parameter, D is the diffusion coefficient of hydrogen in the gaseous phase, Sh is the Sherwood number, d is the characteristic length, P^{ret} is the pressure at retentate side, K_{H_2} is the hydrogen permeability and c_{tot} is the total molar density. To predict the profile of hydrogen permeation flux, the algebraic functions presented by Nekhamkina *et al.* (17) need to be solved.

3. Conclusions

The background of the scenarios related to palladium based membranes has been elaborated. It was found that concentration polarisation becomes unavoidable in parallel with advances in membrane technology. The scenario of parametric studies on the concentration polarisation phenomenon specifically for palladium based membranes was reviewed comprehensively. Based on the present review, it is evident that an increase in total upstream pressure, membrane temperature and permeance promotes concentration polarisation. The same trend is also achieved when the feed flow rate, inlet hydrogen concentration, total downstream pressure and membrane thickness are reduced. When the ratio of hydrogen permeation rate to hydrogen feed rate at the inlet becomes sufficiently high, the effect of hydrogen permeation flux on the hydrogen concentration decrease at the membrane surface becomes significant, thus concentration polarisation becomes strong. Therefore, it can be said that an increase in hydrogen recovery percentage leads to a stronger tendency for concentration polarisation to occur, and as a consequence, larger deviation from the hydrogen permeation flux estimated by Sieverts' equation could be observed. For both tubular type and flat sheet type membranes, when concentration polarisation is triggered, the hydrogen concentration decreases in the horizontal direction (from the leading edge to the tailing edge) and radial direction, respectively. Furthermore, the existence of inhibitive species such as carbon monoxide in the hydrogen mixture somehow causes the membrane performance in terms of hydrogen permeation flux to become worse due to the simultaneous occurrence of concentration polarisation and inhibition by carbon monoxide. Meanwhile, the concentration polarisation level does not depend on the number of noninhibitive species, chemical characteristics of noninhibitive

species or binary diffusivity in the hydrogen mixture (binary or ternary mixture).

Several techniques have been identified to effectively abate concentration polarisation such as coupling of upstream flow with sweep flow in countercurrent mode, installation of baffles in the appropriate number, size and position, and by narrowing the space for upstream flow, that is reduction of the distance between the shell and membrane. Basically, the aforementioned techniques were implemented to increase the hydrogen concentration at the membrane surface of upstream side, thus concentration polarisation could be reduced.

Finally, several estimation methods for hydrogen permeation flux have been reported for different membrane configurations. Several methods are empirical, in which experimental data is necessary to obtain certain coefficients while some of the methods can be used by just substituting the operating parameters into the introduced equation.

For future work, it is suggested that the methods to estimate hydrogen permeation flux for the application of steam reforming should be intensively developed for various operating conditions. In this case, the detailed chemical kinetics must be considered to obtain the accurate mixture composition near the membrane surface. The competitive adsorption by excessive steam and excessive vaporised alcohols (methanol for instance) in addition to carbon monoxide during the occurrence of steam reforming reaction should also be taken into account in the future development of estimation methods.

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