

Buildup of nitrogen in direct hydrogen polymer-electrolyte fuel cell stacks

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Abstract

Hydrogen-fueled polymer-electrolyte fuel cell stacks (PEFC) operate at less than 100% fuel utilization per pass, with the anode exit gas being recycled to the anode inlet. Any inert gases present in the anode gas then increase in concentration as the hydrogen is consumed. A portion of the recirculating anode gas is purged to prevent excessive buildup of the inert gases. It has been observed that N_2 diffuses across the polymer-electrolyte membrane from the cathode side to the anode side, adding to the inert gases in the anode channels. This paper discusses the results of a study to model and analyze the buildup of N_2 in the recirculating anode gas, and the impact of this N_2 on the performance of an automotive 90 kWe PEFC stack. Results show that N_2 crossover from the cathode air to the anode gas depends on a number of parameters, including the power level, N_2 concentration in feed hydrogen (if any), purge rate, and membrane thickness. The buildup of N_2 is mainly a function of the degree of purge, defined as the average fraction of the anode exit gas that is vented. Even with pure fuel H_2 and 90% hydrogen consumption per pass, N_2 concentrations can reach 50–70% at low purge rates, and 5–20% at a 2% purge rate. As a result of this N_2 , the cell voltage decreases by 10–18 mV if the N_2 concentration in anode channels is allowed to reach 25–60%, but by <5 mV if the N_2 concentration is limited to 2–25% by purging. There is an optimum level of purge for which the overall degradation in cell performance is the smallest. The optimum purge level is about 2% with pure H_2 feed, but increases to about 9% if the fuel hydrogen contains 2% N_2 . The allowable level of N_2 impurity in the fuel gas depends on the acceptable loss in stack efficiency. For a 25 μm thick membrane, 0.08% N_2 in feed can be tolerated if the acceptable loss in efficiency is 0.1 percentage point, 0.5% N_2 in the H_2 for a 0.5 percentage point loss in efficiency, and 1.5% N_2 in the H_2 if a 1 percentage point loss in system efficiency is acceptable. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Producing fuel-cell quality hydrogen by reforming hydrocarbon fuels, commonly natural gas, necessarily involves a purification step such as pressure swing adsorption (PSA). In PSA, inerts, primarily nitrogen, argon and helium, are relatively more difficult to remove than the reactive impurities, such as ammonia, carbon monoxide, sulfur species and halogenates, that are known poisons to the Nafion membrane or the Pt based electrocatalysts commonly used in polymer-electrolyte fuel cells (PEFC). Nitrogen removal significantly affects hydrogen recovery in PSA, capital cost of the purification equipment and the process operating cost [1]. The energy efficiency and the eco-

nomics of the overall hydrocarbon reforming process improves substantially if the allowable level of inert impurities in the product hydrogen can be relaxed from the proposed specification of 100 ppm. One purpose of this study was to assess the degradation in PEFC stack performance due to the diffusion of N_2 across the fuel cell membrane from the cathode to the anode and, in view of this diffusion, the relative significance of the N_2 impurity present in the fuel H_2 at concentrations higher and lower than the 100 ppm level.

The PEFC stacks operate at substantially less than 100% H_2 utilization per pass. For reasonable energy conversion efficiency, the bulk of the spent anode gas containing unconverted H_2 must be recycled to the anode inlet. This recycling, however, enriches the inert impurities within the recirculating anode gas. It is of interest to determine the degree to which the gas in the anode channels of the stack can be enriched in inert impurities and the factors that control this enrichment.

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Nomenclature

A	membrane area
c_p	specific heat
D	diffusivity
E	potential (or activation energy)
f_p	purge fraction
f_v	volume fraction of water
F	Faraday constant
I	current density
N	molar flow rate
P	pressure
R	gas constant
T	temperature
V	cell voltage

Greek letters

α	coefficient of net water transport across membrane
δ	thickness
λ	water content of membrane
η	overpotential
Φ	utilization
σ	conductivity
ψ	permeance

Subscripts

e	electronic
g	gas
i	ionic
w	water

Superscripts

a	anode
ae	anode electrode
c	cathode
ce	cathode electrode
m	membrane
p	bipolar plate

Nitrogen in cathode air that enters the anode circuit by permeating through the membrane also gets concentrated by the recycling of the spent anode gas. Thus, N_2 can build up in the anode gas even if the fuel H_2 is completely pure. It is of interest to determine the design and operating parameters that control the N_2 permeation rate.

The buildup of N_2 in the recirculating anode gas can be controlled by periodically or continuously purging a portion of the spent gas. The amount of gas to be purged should be kept to a minimum because the H_2 in the purge gas is lost irrecoverably. Also, the purge gas may have to be treated (e.g., the hydrogen in it may have to be oxidized in a catalytic reactor or mixed with the cathode exit air) to avoid a safety hazard.

The overall purpose of this paper is to analyze buildup of N_2 in the anode channels and determine how it affects the per-

formance of the PEFC stacks for automotive applications. The following are some of the questions that were addressed in the analysis:

1. How much N_2 crosses over from the cathode to anode gas channels and what design and operating parameters affect the amount of this nitrogen?
2. How does N_2 buildup in the anode channels depend on the purge rate?
3. What is the effect of the N_2 buildup on cell voltage?
4. What are the combined effects of the purge rate and the N_2 buildup on stack efficiency?
5. What might be the allowable levels of N_2 impurity in fuel H_2 ?

2. Model formulation

As briefly outlined in Ref. [2], we solve a set of equations for

- (1) the ionic potential and electronic potential distribution,
- (2) current generation in catalyst layers [3],
- (3) ionic and electronic current distribution,
- (4) water transport across the polymer-electrolyte membrane [4],
- (5) H_2 , O_2 , N_2 and H_2O concentrations across the porous catalyst and gas diffusion media layers,
- (6) species concentration in the gas channels, and
- (7) capillary transport of liquid water across the porous media [5].

From these solutions, we determine the Nernst potential, E_N , and the overpotentials, η in terms of which the cell voltage V can be written as

$$V = E_N - \eta_e^{ae} - \eta_g^{ae} - \eta_e^a - \eta_i^a - \eta_g^a - \eta_s^a - \eta_i^m - \eta_e^c - \eta_i^c - \eta_g^c + \eta_s^c - \eta_e^{ce} - \eta_g^{ce} - \eta_e^p \quad (1)$$

In Eq. (1), the subscripts 'e', 'i', 'g', and 's' denote the electronic, ionic, gas phase, and activation components of the overpotentials, and the superscripts 'ae', 'a', 'm', 'c', 'ce', and 'p' represent the anode electrode (gas diffusion layer), anode catalyst, membrane, cathode catalyst, cathode electrode (gas diffusion layer), and the bipolar plate. With reference to Fig. 1, the various terms in Eq. (1) can be calculated from the following equations:

$$E_N = E_0 + \frac{RT}{2F} \ln(P_{H_2}^{(0)}) + \frac{RT}{4F} \ln(P_{O_2}^{(5)}) - \frac{RT}{2F} \ln(P_w^{(5)}),$$

$$\eta_e^{ae} = \frac{I}{\sigma_e^{ae}} \delta_{ae}, \quad \eta_g^{ae} = \frac{RT}{2F} \ln \left(\frac{X_{H_2}^{(0)}}{X_{H_2}^{(1)}} \right),$$

$$\eta_e^a = \beta_e^a \left(\frac{I}{\sigma_e^a} \right) \delta_a, \quad \eta_i^a = \beta_i^a \left(\frac{I}{\sigma_i^a} \right) \delta_a,$$

$$\eta_g^a = \frac{RT}{2F} \ln \left(\frac{X_{H_2}^{(1)}}{X_{H_2}^{(2)}} \right), \quad \eta_i^m = \frac{I}{\sigma_i^m} \delta_m,$$

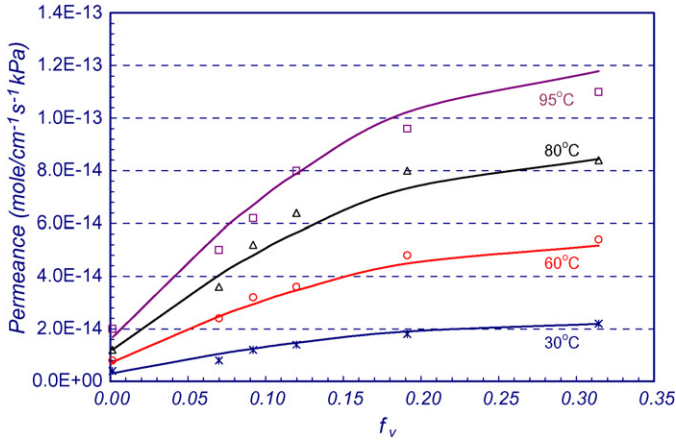


Fig. 2. Correlation for N_2 permeance as a function of temperature and water content.

anode inlet boundary conditions (in) to the gas composition at the anode outlet (out). With reference to Fig. 3, it was found that the iteration procedure could be expedited by first writing the following equations for molar balance of H_2 at the boundaries i and in as

$$N_{H_2}^{out} = (1 - \Phi_{H_2})N_{H_2}^{in} - N_{H_2}^c - 2N_{O_2}^c,$$

$$N_{H_2}^i = \Phi_{H_2}N_{H_2}^{in} + N_{H_2}^c + 2N_{O_2}^c + f_p N_{H_2}^{out}$$

and then combining them into one equation

$$N_{H_2}^{in} = \frac{N_{H_2}^i - (1 - f_p)(N_{H_2}^c + 2N_{O_2}^c)}{1 - (1 - f_p)(1 - \Phi_{H_2})} \quad (7)$$

Similarly, the following equation can be developed for the molar flow rate of N_2

$$N_{N_2}^{in} = \frac{1}{f_p} N_{N_2}^i + \frac{1 - f_p}{f_p} N_{N_2}^c \quad (8)$$

Eqs. (7) and (8) express the inlet boundary conditions for H_2 and N_2 in terms of $N_{H_2}^i$ and $N_{N_2}^i$ which are known, f_p and Φ_{H_2} , which are specified parameters, and $N_{H_2}^c$, $N_{O_2}^c$ and $N_{N_2}^c$ that are the unknowns. It was found that $N_{H_2}^c$ and $N_{O_2}^c$ could be estimated a priori and changed only slowly between iterations.

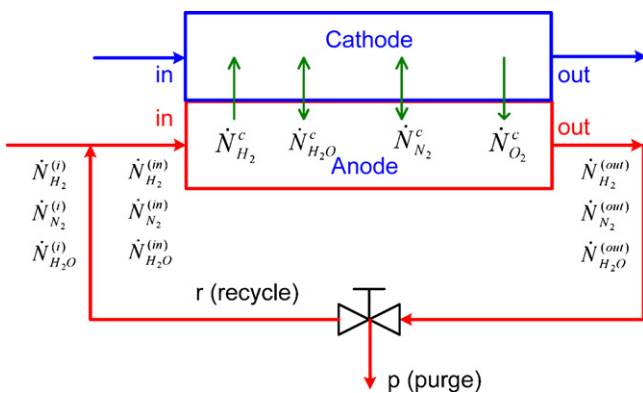


Fig. 3. Anode gas recycle with partial purge.

Thus, the main task was reduced to determining a single variable $N_{N_2}^c$, and this was accomplished with the help of a simple Newton–Raphson scheme.

3. Reference systems

Our approach for studying the behavior of N_2 in anode gas channels is first to define reference PEFC stacks that, in the absence of a N_2 crossover, generate 90 kWe gross (80 kWe net) in a pressurized fuel cell system using pure H_2 as fuel. We then allow N_2 to enter the anode channels separately via N_2 crossover and as impurity in fuel H_2 , and quantify the resulting N_2 buildup and degradation in performance of the reference stack. In order to characterize N_2 behavior as a function of H_2 utilization per pass (Φ_{H_2}) and membrane thickness (t_m), we consider stacks with three combinations of Φ_{H_2} and t_m : $\Phi_{H_2} = 90\%$, $t_m = 50 \mu\text{m}$; $\Phi_{H_2} = 70\%$, $t_m = 50 \mu\text{m}$; and $\Phi_{H_2} = 70\%$, $t_m = 25 \mu\text{m}$. Other important parameters that are common to the three stacks are listed below

- The stack voltage is 0.7 V at 90 kWe rated power.
- The cell is isothermal. The cell temperature is 80 °C at all operating points.
- The stack operates at constant oxygen utilization (50%).
- The stack pressure is constant but floats with flow rate: 2.5 bar at rated flow, 2.0 bar at 75% flow, 1.5 bar at 50% flow, 1.3 bar at 25% flow and 1.1 bar at 10% flow [8].
- Both anode and cathode inlet gas streams are humidified to 60% relative humidity (RH) at 80 °C stack temperature, i.e., the dew point temperature is 68 °C.
- The anode and cathode catalyst layers have identical electrode structures: 0.4 mg cm^{-2} Pt loading, Pt/C=0.47, ionomer/C=0.8, 54 $\text{m}^2 \text{g}_{\text{pt}}^{-1}$ electrochemical surface area, and 40% porosity. It is assumed that the electrochemical performance of the catalyst layers can be adequately described using the parameters (exchange current density, transfer coefficients, etc.) derived by Gasteiger et al. [9].

Neglecting N_2 crossover, Table 1 summarizes some indices of performance for the three stacks with pure fuel H_2 . Listed in Table 1 are the current density at 0.7 V cell voltage, active membrane area, and the stack efficiency, which is defined as the ratio of dc power generated to the lower heating value (LHV) of H_2 consumed, inclusive of losses due to H_2 and O_2 crossover. Table 1 indicates that fuel utilization has a small effect on power density. However, reducing the membrane thickness from 50 to

Table 1
Reference PEFC stacks

	I	II	III
Hydrogen utilization (%)	90	70	70
Membrane thickness (μm)	50	50	25
Active membrane area (m^2)	18.1	18.1	13.3
Current density (mA cm^{-2})	705	705	955
Power density (W cm^{-2})	0.50	0.50	0.67
Stack efficiency (%)	55.6	55.6	55.5

25 μm results in 34% enhancement in power density but the stack efficiency degrades slightly due to larger crossovers of H_2 and O_2 .

4. Results

A number of simulations were run using the model described in Section 2 to characterize N_2 buildup in Stacks I–III. Results from these simulations are discussed in Sections 4.1–4.3.

4.1. Nitrogen buildup

Fig. 4 displays the buildup of N_2 in the anode channels due to N_2 crossover from the cathode air in Stack I ($\Phi_{\text{H}_2} = 90\%$, $t_m = 50 \mu\text{m}$) with pure fuel H_2 . It indicates that with a low 0.1% purge, the steady-state N_2 concentration can reach 20% at the anode inlet and 60% at the anode outlet (all concentrations on a wet basis). With a moderate 2% purge, N_2 concentrations can be limited to 6% at the inlet and 27% at the outlet. The effect of power level on N_2 buildup is seen to be a function of the purge level and is related to the decrease in the compressor discharge pressure as the air flow rate is turned down. In our simulations, the pressure in the anode channels is regulated to follow the pressure in the cathode channels. Under these conditions, N_2 crossover is directly proportional to the operating stack pressure and, therefore, is smaller at part load. On a percentage basis, however, N_2 crossover increases as the power is decreased because of the fixed membrane area. Also, the concentration of water vapor in the humidified gas is higher at lower pressure (temperature is fixed at 80°C) so that the N_2 concentration gets diluted as the power is reduced. Thus, the trend of decreasing N_2 buildup with decrease in power at 0.1% purge is due to the dilution by water vapor as the pressure is lowered. On the other hand, the trend of a slight increase in N_2 buildup with decrease in power at 2% purge is due to the higher percentage crossover of N_2 from the cathode channel.

Fig. 5 shows N_2 buildup in Stack I ($\Phi_{\text{H}_2} = 90\%$, $t_m = 50 \mu\text{m}$) as a function of N_2 impurity in fuel H_2 with 2% purge. The steady-state N_2 concentration is seen to reach 30% at stack inlet and 70% at stack outlet if the fuel H_2 contains 1% N_2 impurity.

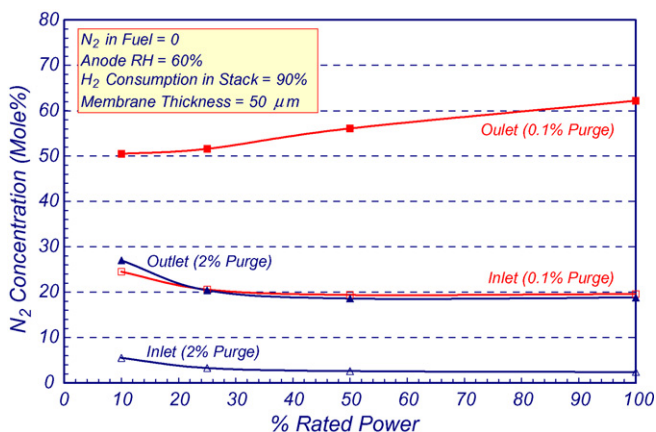


Fig. 4. Buildup of N_2 in anode channels with pure fuel H_2 ($\Phi_{\text{H}_2} = 90\%$, $t_m = 50 \mu\text{m}$).

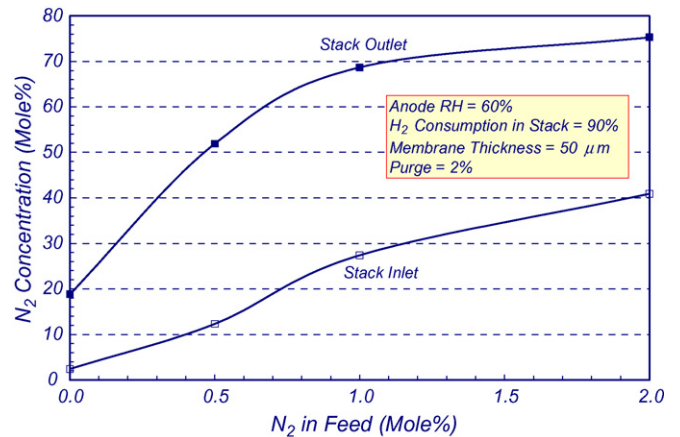


Fig. 5. Effect of N_2 content of fuel H_2 on N_2 buildup in anode channels ($\Phi_{\text{H}_2} = 90\%$, $t_m = 50 \mu\text{m}$).

Raising the N_2 content of fuel H_2 to 2% further increases the steady-state N_2 concentration in the anode channel to 40% at stack inlet and 75% at stack outlet.

Fig. 6 depicts the effect of N_2 buildup on cell voltage with pure fuel H_2 and operating conditions as in Fig. 4 (Stack I). Compared to the hypothetical case of zero N_2 crossover, the cell voltage decreases by 11–18 mV if the N_2 concentration in the anode channels is allowed to reach 20–60% as happens with 0.1% purge. The decrease in cell voltage can be reduced to 1–5 mV by increasing the purge to 2%, which limits the N_2 concentration in the anode channels to 6–27%.

Fig. 7 presents the effect of N_2 buildup on the cell voltage with up to 2% N_2 in fuel H_2 and operating conditions as in Fig. 5 (Stack I with 2% purge). Compared to the case of pure fuel H_2 with no N_2 crossover, the cell voltage decreases by 14–16 mV if fuel H_2 has 1% N_2 (30–70% N_2 concentration in the anode channels) and by 22–24 mV if there is 2% N_2 in fuel H_2 (40–75% N_2 concentration in the anode channels).

The results shown in Figs. 8–12 include nitrogen crossover from the cathode to the anode. Fig. 8 points to the existence of an optimum purge, at which the stack efficiency is highest. Here the stack efficiency is defined as the ratio of dc power generated

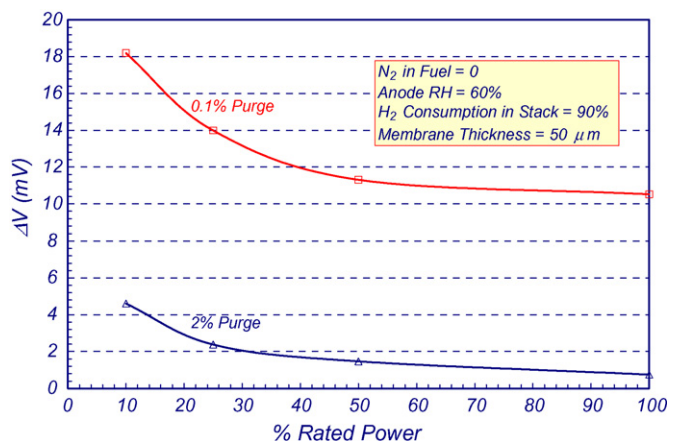


Fig. 6. Effect of N_2 buildup on cell voltage with pure fuel H_2 ($\Phi_{\text{H}_2} = 90\%$, $t_m = 50 \mu\text{m}$).

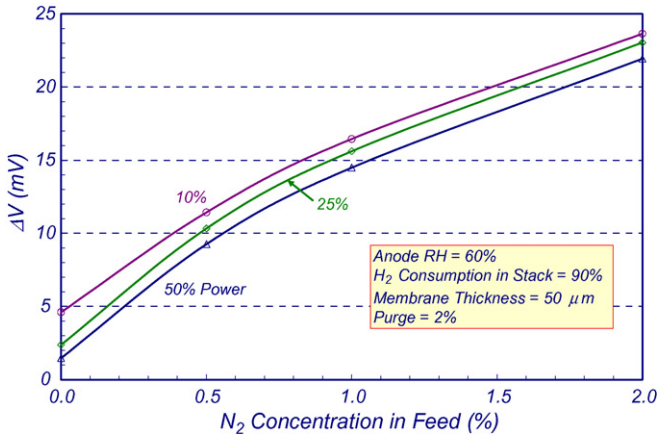


Fig. 7. Effect of N_2 content of fuel H_2 on cell voltage ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu m$).

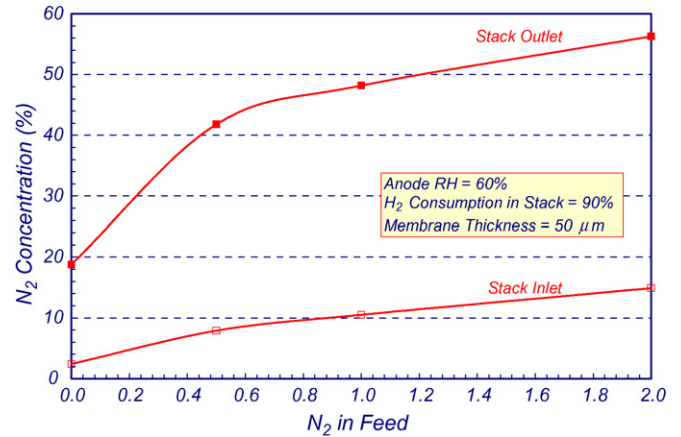


Fig. 10. N_2 buildup as a function of N_2 content of fuel H_2 with optimum purge ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu m$).

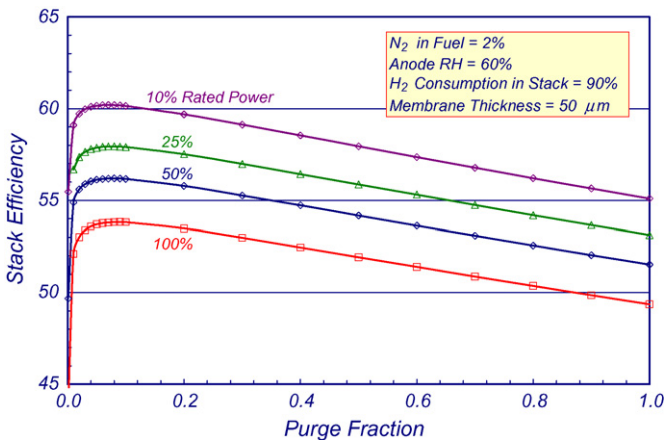


Fig. 8. Optimum purge with pure fuel H_2 ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu m$).

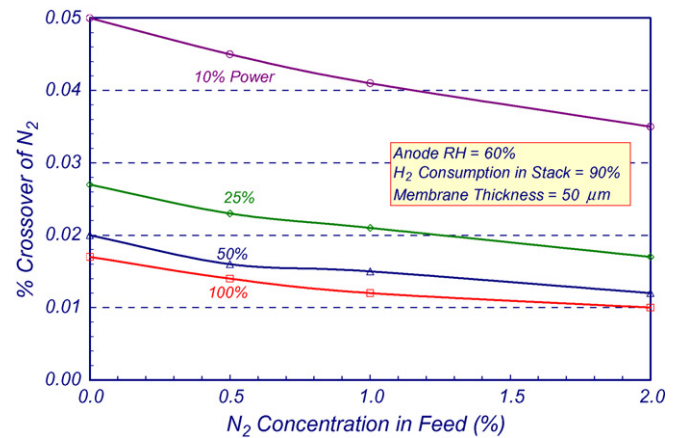


Fig. 11. N_2 crossover as function of N_2 content of fuel H_2 and power at optimum purge ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu m$).

to the LHV of the total H_2 that is fed to the fuel cell system; this includes the H_2 that is consumed in the electrochemical reaction, chemically reacted at the cathode due to H_2 crossover from anode, chemically reacted at anode due to O_2 crossover over from cathode, and purged from the recirculating anode gas to the ambient. At a purge levels lower than the optimum, the stack efficiency decreases due to the excessive buildup of N_2

in the anode gas channel and the resultant drop in cell voltage. At purge levels higher than the optimum, the stack efficiency is lower because of the excessive loss of H_2 with the purge gas. For 2% N_2 in fuel H_2 , 90% H_2 utilization per pass and 50 μm thick membrane, the optimum purge level is $\sim 9\%$ at rated power

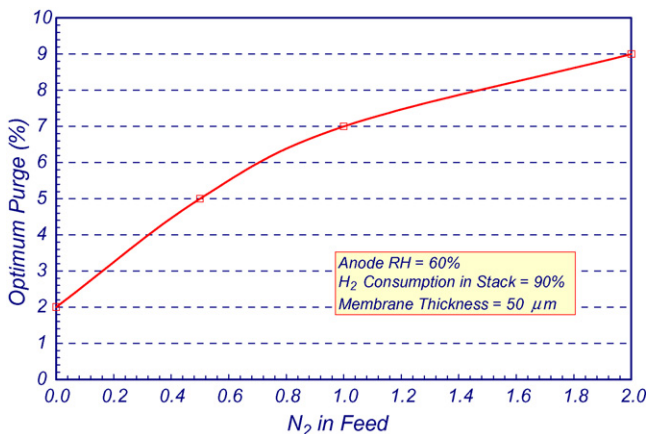


Fig. 9. Effect of N_2 content of fuel H_2 on optimum purge ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu m$).

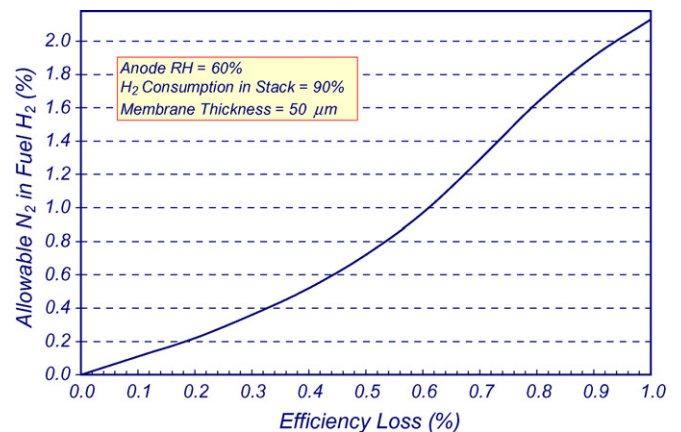


Fig. 12. Allowable N_2 content of fuel H_2 as function of acceptable loss of stack efficiency ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu m$).

and only slightly smaller at 10% of rated power. Compared to pure fuel H_2 for which the optimum purge is $\sim 2\%$, the stack efficiency at rated power is ~ 0.9 percentage points smaller if fuel H_2 contains 2% N_2 .

Fig. 9 shows the dependence of the optimum purge in Stack I ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu\text{m}$) on the N_2 content of fuel H_2 . The optimum purge is seen to increase with the N_2 content from 2% with pure fuel H_2 to 9% with 2% N_2 in fuel H_2 .

Fig. 10 shows the buildup of N_2 in the anode channels of Stack I at the optimum purge conditions identified in Fig. 9. With pure fuel H_2 at 2% optimum purge, N_2 crossover from the cathode air causes N_2 concentration in anode channels to reach 2% at the stack inlet and 19% at the stack outlet. With 2% N_2 in fuel H_2 and the 9% optimum purge, the steady-state N_2 concentration in anode channels reaches 15% at stack inlet and 56% at stack outlet.

Fig. 11 quantifies N_2 crossover in Stack I as a function of the N_2 content of fuel H_2 and the stack power level. The results are for optimum purge levels as given in Fig. 9 for different N_2 contents of fuel H_2 . Here, crossover is defined as the fraction of N_2 in cathode air feed that permeates to the anode channels. Fig. 11 indicates that N_2 crossover decreases with increasing N_2 content in the anode gas, and that it is higher at partial loads than at rated power. The crossover fraction varies from 0.017% to 0.05% for pure fuel H_2 (2% purge) and 0.01% to 0.035% for 2% N_2 in fuel H_2 (9% purge).

The results in Fig. 11 may be used to determine the N_2 concentration in fuel H_2 (X_{N_2}) for which the amounts of N_2 entering the stack with fuel and by crossover are equal. For the conditions of Fig. 11 ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu\text{m}$), (X_{N_2}) is calculated to be 260 ppm at 100% power, 300 ppm at 50% power, 430 ppm at 25% power and 840 ppm at 10% power. N_2 crossover can be ignored if N_2 concentration in fuel H_2 is much larger than X_{N_2} . On the other hand, an attempt to reduce N_2 concentration in fuel H_2 to levels much smaller than X_{N_2} may not be justifiable.

Fig. 12 presents the allowable concentration of N_2 in fuel H_2 for different specified losses in stack efficiency. The results are for Stack I ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu\text{m}$) at rated power with optimum purge conditions as given in Fig. 9. The datum is 54% stack efficiency that is obtained with pure fuel H_2 at 2% optimum purge. The current ISO draft specifies 100 ppm N_2 (total inerts) concentration in fuel-cell quality H_2 [10]. We estimate that this level of N_2 impurity in fuel H_2 causes only 0.01 percentage point loss in stack efficiency. Fig. 12 further indicates that if the specification is relaxed to 1000 ppm N_2 in the fuel H_2 , the corresponding stack efficiency loss would be 0.1 percentage point; with a further relaxation to 1% N_2 in the fuel H_2 , the stack efficiency loss increases only to 0.6 percentage points.

4.2. Effect of hydrogen utilization on N_2 buildup

Fig. 13 compares the optimum purge levels calculated for Stack I ($\Phi_{H_2} = 90\%$, $t_m = 50 \mu\text{m}$) and Stack II ($\Phi_{H_2} = 70\%$, $t_m = 50 \mu\text{m}$). It indicates that the smaller the hydrogen utilization per pass (i.e., the higher the anode stoichiometry) the lower the

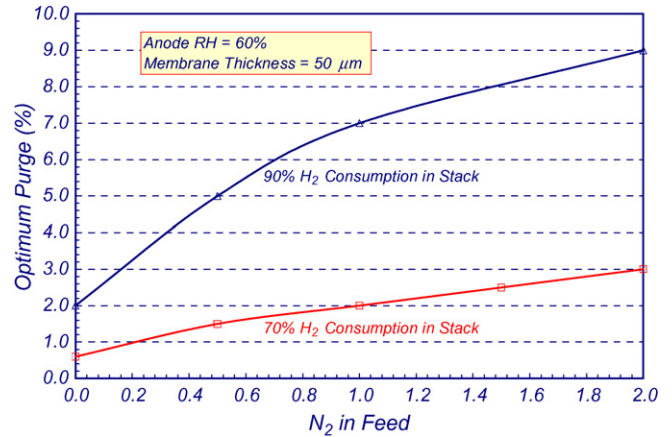


Fig. 13. Effect of H_2 utilization per pass on optimum purge ($t_m = 50 \mu\text{m}$).

optimum purge. This can be explained on the basis of increase in H_2 concentration at stack outlet with decrease Φ_{H_2} so that the optimum purge has to be smaller to limit loss of H_2 in the purge stream.

Fig. 14 illustrates the influence of H_2 utilization per pass on N_2 buildup in the anode channels for the optimum purge levels identified in Fig. 13. For a given N_2 content in the fuel H_2 , the N_2 concentration at stack inlet is higher for $\Phi_{H_2} = 70\%$ than for $\Phi_{H_2} = 90\%$, but the N_2 concentrations at stack outlet are similar.

Fig. 15 presents the effect of H_2 utilization per pass on the N_2 impurity specifications. It indicates that, because of the relationship between optimum purge and Φ_{H_2} seen in Fig. 13, the specifications need to be tighter for $\Phi_{H_2} = 70\%$ than for $\Phi_{H_2} = 90\%$, i.e., for a given loss in stack efficiency, the allowable level of N_2 in fuel H_2 decreases as Φ_{H_2} is made smaller. Whereas, from the standpoint of efficiency degradation due to N_2 buildup, it is preferable to maintain as high fuel utilization per pass as possible, there are other mitigating factors that limit operation at very high Φ_{H_2} . For example, the problem of anode channel flooding is exacerbated at low anode stoichiometry (high Φ_{H_2}), particularly at low loads.

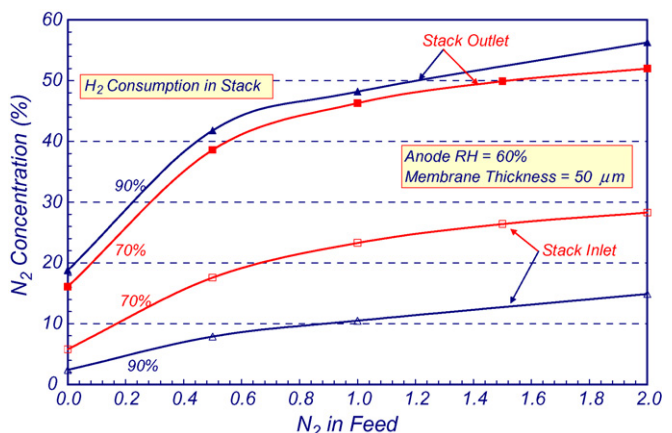


Fig. 14. Effect of H_2 utilization on N_2 buildup in anode channels ($t_m = 50 \mu\text{m}$).

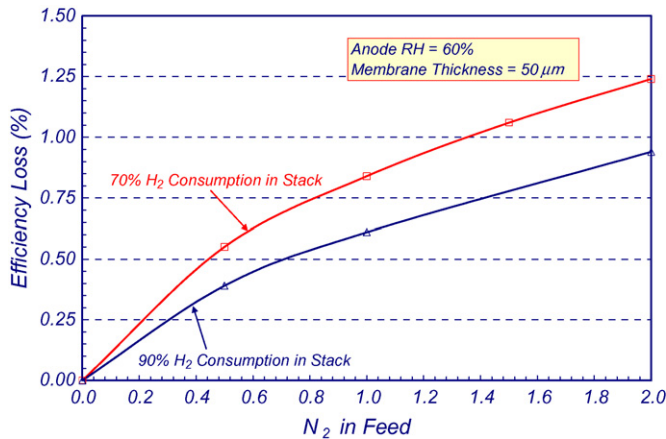


Fig. 15. Effect of H₂ utilization on acceptable levels of N₂ in fuel H₂ ($t_m = 50 \mu\text{m}$).

4.3. Effect of membrane thickness on N₂ buildup

Fig. 16 compares the N₂ impurity specifications for Stack 2 ($\Phi_{\text{H}_2} = 70\%$, $t_m = 50 \mu\text{m}$) and Stack III ($\Phi_{\text{H}_2} = 70\%$, $t_m = 25 \mu\text{m}$). It indicates that for a specified stack efficiency loss at rated power, the allowable levels of N₂ impurity in fuel H₂ are quite similar for 25 and 50 μm thick membranes. The following caveats apply to the results in Fig. 16, however:

- The results are for optimum purge levels which are functions of N₂ content of fuel H₂ and are similar for the 25 and 50 μm thick membranes. Nitrogen crossover for the two membrane thicknesses is nearly the same as the effect of higher N₂ crossover per unit area across the thinner membrane cancels the effect of the smaller membrane (18.1 m² versus 13.3 m²) area because of the higher power density.
- In calculating the stack efficiency loss, the efficiency for pure fuel H₂ at optimum purge is taken as the reference datum. This datum for the 25 μm thick membrane is 54.5%, corresponding to an optimum purge of 0.6%. For the 50 μm thick membrane, the datum is 54.8% stack efficiency, corresponding to an optimum purge of 0.6%.

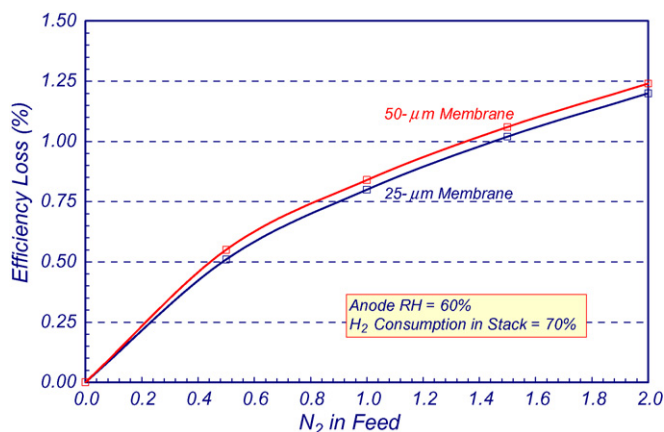


Fig. 16. Effect of membrane thickness on acceptable levels of N₂ in fuel H₂ ($\Phi_{\text{H}_2} = 90\%$).

- At optimum purge levels, the N₂ concentration in the anode channels for the 25 and 50 μm thick membranes are similar.
- It is interesting to compare N₂ buildup as a function of H₂ utilization per pass and membrane thickness. For a given membrane thickness, the optimum level of purge is such that the N₂ concentration at stack outlet is a function of N₂ content of fuel H₂ but only weakly depends on Φ_{H_2} , although N₂ concentration at stack inlet remains a function of Φ_{H_2} . On the other hand, for a given H₂ utilization per pass, the optimum purge level is such that the N₂ concentration at stack outlet is only a function of N₂ content of fuel H₂ and only weakly depends on Φ_{H_2} .

5. Conclusions

We have conducted a comprehensive study on buildup of N₂ in the anode channels of a pressurized PEFC stack for automotive applications. The major conclusions from the analysis in response to the questions posed in Section 1 are briefly summarized below.

- N₂ crossover from the cathode to anode gas channels depends on a number of factors that include the power level, N₂ content in the fuel H₂, purge rate from the recirculating anode gas, and the fuel cell membrane thickness. As one example, at optimal purge, 0.008–0.024% of N₂ in cathode inlet air permeates to the anode channels of a 90 kWe PEFC stack (50 μm membrane thickness, 0.7 V cell voltage at rated power) operating at 50% O₂ utilization and 90% H₂ utilization per pass.
- With pure fuel H₂, the steady-state N₂ concentration in anode channels can reach 50–70% at a low purge ($\Phi_{\text{H}_2} = 90\%$, $t_m = 50 \mu\text{m}$) due to the N₂ crossover from the cathode to the anode. This N₂ buildup can be reduced to 5–20% with a moderate purge of 2% of the anode exit gas.
- With pure fuel H₂, there is a voltage decrease of 10–18 mV if the N₂ concentration is allowed to reach 25–60%. This voltage decrease can be reduced to <5 mV by increasing the purge rate to limit the N₂ concentration to 2–25%.
- Both the buildup of N₂ and purging a portion of the recirculating anode gas degrade stack efficiency, but the purge also limits N₂ buildup. There is an optimum purge that minimizes degradation in the net stack efficiency due to N₂ buildup. This optimum purge is a function of the N₂ content in the fuel H₂, fuel cell membrane thickness, and H₂ utilization per pass, among other operating parameters. In a stack with 90% H₂ utilization per pass and a 50 μm thick membrane, the optimum purge is ~2% with pure fuel H₂ and ~9% if there is 2% N₂ in fuel H₂.
- Just from the point of view of the detrimental effect of a N₂ impurity in the fuel H₂ on stack efficiency, there is little incentive to remove inert impurities in fuel H₂ to stringent levels as N₂ can build up in anode channels by crossing over from cathode air even if no N₂ is present in the fuel H₂. Table 2 shows the relationship between the level of N₂ impurity in the fuel H₂ and the resulting decrease in stack efficiency at the

Table 2
Allowable N₂ content of fuel H₂ ($\Phi_{H_2} = 70\%$, $t_m = 25 \mu\text{m}$)

Acceptable efficiency loss (% point)	Allowable N ₂ in fuel H ₂ (%)
0.1	0.08
0.2	0.17
0.3	0.27
0.4	0.38
0.5	0.50
0.6	0.63
0.7	0.79
0.8	0.98
0.9	1.20
1.0	1.47

rated power point for a stack (Stack III) with a 25 μm thick membrane operating at 70% H₂ utilization per pass.

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Appendix A

There are different ways of defining the purge rate. In this work, we chose to define f_p as

$$f_p = \frac{N^P}{N^{\text{out}}}$$

Another way is to define a recycle ratio (R) as

$$R = \frac{N^r}{N^P}$$

which is related to f_p as

$$R = \frac{1 - f_p}{f_p}$$

Yet another way is to define H₂ purge loss as a fraction of the H₂ feed rate

$$f_{H_2} = \frac{N_{H_2}^P}{N_{H_2}^i}$$

It can be shown that f_{H_2} is related to f_p as

$$f_{H_2} = \frac{f_p(1 - \Phi_{H_2})}{1 - (1 - f_p)(1 - \Phi_{H_2})} \left[\frac{1 - (1 - f_p)(N_{H_2}^c + 2N_{O_2}^c)}{N_{H_2}^i} \right]$$

A particularly useful expression for f_{H_2} is obtained if H₂ and O₂ crossovers are neglected.

$$f_{H_2} = \frac{f_p(1 - \Phi_{H_2})}{1 - (1 - f_p)(1 - \Phi_{H_2})}$$

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