



Evaluation of methods to increase the oxygen partial pressure in PEM fuel cells

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Abstract

This paper compares the performance of a hydrogen–air fuel cell system with the oxygen electrode operating under different conditions of pressure, stoichiometry and oxygen enrichment. This paper shows that the net power density can be improved using a pressurized or oxygen enrichment system when the oxygen electrode is limited by oxygen mass transfer. If the current density is determined by kinetics, then the ambient pressure system has a higher net power density at the same fuel efficiency.

List of symbols

a	surface area per volume ($\text{cm}^2 \text{cm}^{-3}$)
A	area (cm^2)
b	effective Tafel slope (mV)
c	concentration (mol cm^{-3})
D	effective diffusivity ($\text{cm}^2 \text{s}^{-1}$)
E	potential (V)
F	Faraday's number (C equiv^{-1})
G	permeability ratio, $K_{\text{O}_2}/K_{\text{N}_2}$
H	Henry's constant ($\text{atm cm}^3 \text{mol}^{-1}$)
ΔH_f	heat of formation (J mol^{-1})
i	electrode current density (A cm^{-2})
$j(z)$	local current (A cm^{-3})
k	electrokinetic rate constant ($\text{A cm}^{-2} \text{atm}^{-1}$)
K	membrane permeability
L	thickness of a layer (cm)
N	number of finite elements
p	partial pressure (atm)
P	pressure (W or W cm^{-2})
q	equivalent flow rate (A cm^{-2})
Q	molar flow rate (mol s^{-1})
r	membrane pressure ratio
R	resistance (Ωcm^2)
R	gas constant

T	temperature (K)
V	volume (cm^3)
x	molar fraction
X	dimensionless concentration
Y	dimensionless potential, E/b
z	position (cm)
Z	effectiveness factor

Greek symbols

α	diffusion mass transfer rate (A cm^{-2})
σ	migration mass transfer rate (A cm^{-2})
δ	effective agglomerate depth (cm)
φ	migration rate modulus
ϕ	diffusion rate modulus
Φ	electrode potential (V)
κ	ionic conductivity (S cm^{-1})
ν	intrinsic kinetic rate (A cm^{-2})

Subscripts

0	initial, reference, or entrance
agg	agglomerate
cath	cathode active layer
mem	membrane layer
migr	migration

1. Introduction

The power density of an acid polymer electrolyte membrane (PEM) fuel cell increases with the oxygen partial pressure at the cathode. Air is the most economical means of obtaining oxygen for use in the fuel cell. There are three means of increasing the oxygen partial pressure in the fuel cell when air is used: increasing the airflow through the cell (i.e., reducing oxygen utilization

by raising stoichiometry and mean partial pressure), increasing the air pressure and selectively separating the oxygen from the air to increase the oxygen mole fraction (i.e., oxygen enrichment). All these methods require parasitic energy. For the same increase in oxygen partial pressure at constant stoichiometry, oxygen enrichment requires a higher compression ratio than pressurization due to the irreversible separation work. However, oxygen enrichment gives a lower net gas flow rate for

the same oxygen stoichiometry through the flow fields. Low stoichiometry reduces the partial pressure of oxygen in the cell and high stoichiometry requires excessive pumping energy. Calculations are required to determine which method is more advantageous from the viewpoint of net system power and efficiency. This paper compares the performance of a hydrogen–air fuel cell system with the oxygen electrode operating under different conditions of pressurization, stoichiometry and oxygen enrichment.

2. Theory

Three levels of fuel cell system are compared here: (i) ambient pressure operation with a fan to circulate air through the cathode, (ii) pressurized cathode operation with a compressor/expander, and (iii) oxygen enrichment with a selectively permeable membrane, as shown in Figure 1. In the oxygen enrichment mode, the oxygen fraction from air is increased by passing air at ambient pressure at a high flow rate through tube bundles containing an oxygen selective membrane and allowing it to permeate through the membrane by applying a partial vacuum. This method is used in preference to compressing the large volume of air feedstock required to maintain high oxygen concentration at the incoming surface of the separation membrane. The permeate gas is re-pressurized to one atmosphere or higher and fed to the fuel cell cathode (after humidification if necessary). If the fuel cell is operating under pressure, the cathode effluent is expanded to recover as much work as possible.

A model was developed to simulate the performance of a fuel cell system which consists of three main parts: an analytical expression for the local electrochemical performance of the electrode at a location on the electrode area, a numerical finite difference solution for the variables as they change over the electrode area, and expressions for the parasitic losses due to the gas flow subsystems. Parameters for the fuel cell model were determined from experiments with different cathode loading, cathode pressure, oxygen enrichment fraction and gas flow stoichiometry. The fuel cell model was combined with models for the parasitic power requirements to evaluate system performance in terms of net power density versus fuel efficiency and to find optimum operating conditions.

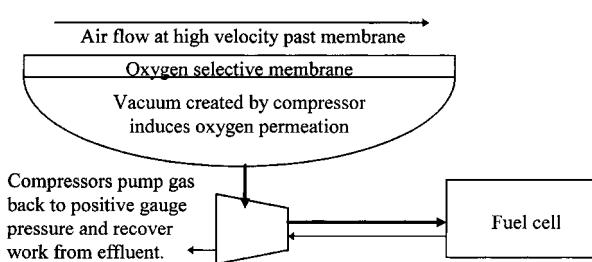


Fig. 1. Diagram of fuel cell with the oxygen enrichment membrane and compressor subsystems.

2.1. Model for local electrode performance

This investigation selected a simple model that meaningfully describes the local electrochemical behaviour as a function of the electrode design properties and operating conditions. The model neglects mass transfer and activation losses at the hydrogen electrode and assumes isotropic mass transfer and kinetic properties through each layer of the oxygen electrode (Figure 2). It also assumes the cell is working with negligible problems due to gas crossover, shorting, flooding or drying.

The potential change of the essentially reversible hydrogen electrode as a function of pressure was assumed to follow the Nernst relationship. The oxygen electrode reaction is a function of the potential, the oxygen concentration at the catalyst surface and the surface area of platinum per area of electrode. The Tafel equation was used to describe the intrinsic kinetic rate:

$$v = a_v L_{\text{cath}} k p_{\text{O}_2} \exp[(E_{\text{ref}} + \Phi_{\text{anode}} - E_{\text{cell}})/b] \quad (1)$$

where $\Phi_{\text{anode}} = (RT/2F) \ln(p_{\text{H}_2}/p_{\text{reference}})$.

Mass transfer restricts the current produced by an electrode. The significant mass transfer losses in the membrane electrode assembly (MEA) include: oxygen diffusion through the substrate layer (also called backing or diffusion layer), proton migration through the electrolyte in the membrane and active layer, and localized or microscopic oxygen diffusion through polymer electrolyte to the catalyst in the active layer. This approach differs from some other PEM fuel cell models in the literature, which consider macroscopic oxygen diffusion through the active layer to be important and neglect microscopic localized diffusion [1, 2]. Recent measurements in this laboratory of oxygen diffusivity through the active layer show values that are much higher than those reported in the literature, which were acquired by fitting to macroscopic diffusion models. Also, these models do not correctly predict electrode performance versus electrode thickness (i.e., catalyst loading). An agglomerate model incorporating microscopic diffusion has a better fit.

Useful expressions derived from the model incorporate an 'effectiveness factor' which quantifies the degree to which a mass transfer process will reduce the intrinsic

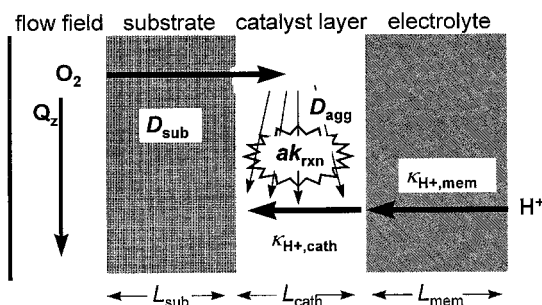


Fig. 2. Physical picture of the electrode model.

kinetic current [3]. The effectiveness factor arises from solutions to the differential material balances in each layer. A combination of the effectiveness factors for each mass transfer process yields the overall effectiveness of the electrode (the fraction of the maximum kinetic current actually produced).

Oxygen diffuses through the substrate layer from the flow fields to the active layer according to Fick's law. Substrate layers consisting of carbon cloth impregnated with acetylene black/PTFE have a pore size from 1 mm to 0.02 mm. At low pressure (1 to 3 atm) the diffusion mechanism is mixed Knudsen and molecular diffusion [1, 4]. This is shown in Figure 3 which demonstrates that the limiting current increases as a function of pressure via a Knudsen mechanism at low pressure, and then it becomes constant at higher pressure as molecular diffusion takes over. The effectiveness factor for the substrate is given by

$$Z_{\text{sub}} = 1 - j/\alpha_{\text{sub}} \quad (2)$$

where

$$\alpha_{\text{sub}} = \frac{4F x_{\text{O}_2} p_{\text{tot}}}{L_{\text{sub}} RT} \left\{ \frac{1}{D_{\text{kn}}} + \frac{p_{\text{tot}}}{p_0 D_{\text{molec}}} \right\}^{-1}$$

is the substrate diffusion rate in A cm^{-2} . Since the reactant gases are humidified, the oxygen concentration in the flow field is corrected for the saturation pressure of water vapour. Thus,

$$x_{\text{O}_2, \text{humid}} = x_{\text{O}_2, \text{dry}} (1 - p^{\text{sat}}/p_{\text{tot}}).$$

Water content and transport through the membrane effects the ionic resistance. In thin membranes, the gradient in the chemical potential of water through the electrolyte layer is approximately linear as a function of current density, so the effective membrane resistance is constant at all current densities [5, 6]. The effectiveness factor for the membrane is

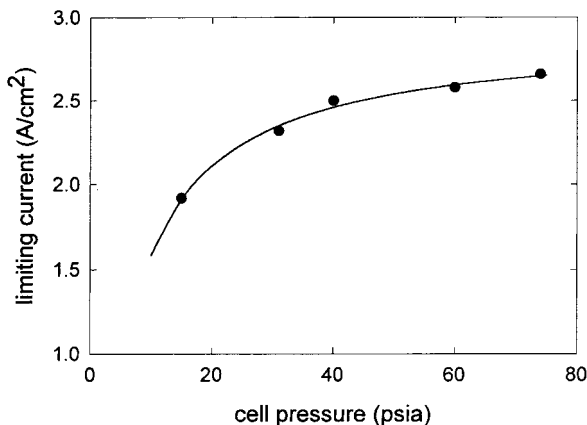


Fig. 3. The oxygen mass transfer limiting current increases with pressure due to Knudsen diffusion at low pressure and becomes constant at high pressure as molecular diffusion dominates. Key: (●) experimental data; (—) model simulation.

$$Z_{\text{mem}} = \exp[-j/\sigma_{\text{mem}}] \quad (3)$$

where $\sigma_{\text{mem}} = b/R_{\text{mem}}$ is the membrane migration rate in A cm^{-2} .

Oxygen diffusion and proton migration combine to determine the effectiveness factor of the active layer. The dominant oxygen mass transfer resistance in the cathode active layer is localized diffusion through pores filled with water and polymer. These pores can be modeled as agglomerates within a microscopic volume of the active layer [7]. Assuming a constant potential through a particular agglomerate, the dimensionless oxygen material balance is

$$\frac{d^2 X(z_2)}{dz_2^2} = \frac{\nu Z_{\text{mem}} Z_{\text{migr}}(z_1)}{\alpha_{\text{agg}}} X(z_2) \quad (4a)$$

$$X(0) = 1 \quad (4b)$$

$$\frac{dX}{dz}(1) = 0 \quad (4c)$$

where

$$\alpha_{\text{agg}} = \frac{a_{\text{agg}} L_{\text{cath}} 4F x_{\text{O}_2} p_{\text{tot}} D_{\text{agg}}}{\delta_{\text{agg}} H_{\text{O}_2 - \text{agg}}}$$

is the agglomerate diffusion rate and Z_{mem} and Z_{migr} account for migration losses to the agglomerate. The resulting effectiveness factor for oxygen transport in the agglomerates is

$$Z_{\text{agg}}(z_1) = \tanh\left[\frac{\sqrt{\phi_{\text{agg}}}}{\sqrt{\phi_{\text{agg}}}}\right] \quad (5)$$

where $\phi_{\text{agg}} = Z_{\text{mem}} Z_{\text{migr}}(z_1) \nu / \alpha_{\text{agg}}$.

Assuming a constant oxygen concentration in the gas pores of the active layer, the dimensionless proton material balance may be written as

$$\frac{d^2 Y(z_1)}{dz_1^2} = \frac{\nu Z_{\text{agg}}(z_1) Z_{\text{mem}} Z_{\text{sub}}}{\sigma_{\text{cath}}} \exp[-Y(z_1)] \quad (6a)$$

$$Y(1) = 0, \quad \frac{dY}{dz}(0) = 0 \quad (6b)$$

where $\sigma_{\text{cat}} = \kappa_{\text{H}^+, \text{cath}}^{\text{eff}} b / L_{\text{cath}}$ is the cathode migration rate. An approximate analytical solution exists if $Z_{\text{agg}}(z_1)$ is replaced by a constant, $Z_{\text{agg}}^{\text{avg}}$. Then, the effectiveness factor for proton transport in the active layer is given by [8]

$$Z_{\text{migr}} = \sin[\bar{\omega}] / \sqrt{\phi_{\text{migr}}/2} \quad (7)$$

where $\bar{\omega}$ is a dummy variable satisfying $\bar{\omega} = \sqrt{\phi_{\text{migr}}/2} \cos[\bar{\omega}]$ and $\phi_{\text{migr}} = Z_{\text{agg}}^{\text{avg}} Z_{\text{mem}} Z_{\text{sub}} \nu / \sigma_{\text{cath}}$. The analytical solution emulates the numerical solution when the average agglomerate effectiveness is estimated empirically by $Z_{\text{agg}}^{\text{avg}} \approx Z_{\text{agg}}^{1.25}(z=L)$.

Current as a function of cell potential can be calculated from the product of the effectiveness factors for each mass transport process:

$$j = \nu Z_{\text{mem}} Z_{\text{sub}} Z_{\text{agg}} Z_{\text{migr}} = \text{fn}(x_{\text{oxy}}, P, E_{\text{cell}}, j) \quad (8)$$

The use of this analytical expression saves the extensive computational time required to obtain a numerical solution for the catalyst layer. This becomes rather important in optimization studies which may require several thousand evaluations of local electrode performance per case.

2.2. Model describing average current for electrode area

The current density varies over the surface of the electrode due to local changes in the oxygen concentration. The effect of gas stoichiometry appears in the model for the flow field, which describes the degree of oxygen depletion over the electrode area. Neglecting dispersion, the oxygen mass balance in a perfectly distributed flow field is

$$\frac{dQ_{\text{O}_2}}{dV} = -r_{\text{O}_2} \quad (9)$$

where Q_{O_2} is the oxygen molar flow rate, V is the volume of flow field space and r_{O_2} is the consumption of oxygen by the electrode surface contained in a volume element of the flow field. Neglecting flow changes due to changes in water vapour pressure, a simple finite difference solution can be written in dimensionless form. Thus,

$$X_{n+1} = X_n - \frac{j_n(1 - x_0 X_n)^2}{Nq(1 - x_0)}, \quad X(0) = 1 \quad (10)$$

where $q = 4Fx_0Q_0/A$ is the gas flow rate in A cm^{-2} , and stoichiometry is defined as q/i .

The local current density, j_n , is solved using the model in Section 2.1 at each step, and then the average electrode current density is calculated by averaging the local currents of all steps. That is,

$$i_{\text{ave}} = \frac{1}{N} \sum_1^N j_n \quad (11)$$

The product of the voltage and average current density gives the output power density of the fuel cell:

$$P_{\text{cell}} (\text{W cm}^{-2}) = E_{\text{cell}} (V) \times i_{\text{ave}} (\text{A cm}^{-2}) \quad (12)$$

2.3. Expressions for parasitic power requirements

Air is oxygen enriched by drawing it through a membrane which selectively transports oxygen faster than nitrogen. The degree of oxygen enrichment depends on the pressure ratio between the air and permeate sides. Table 1 shows the experimental performance of a fluorinated hydrocarbon, oxygen selective membrane developed by compact membrane systems (CMS), designated as CMS-X (information provided

Table 1. Performance of CMS-X (Data Provided by CMS)

Oxygen fraction /mol %	Membrane pressure ratio /(atm atm ⁻¹)	Energy consumed /(W SLM ⁻¹) 60% comp. eff.
31.3	2.25	3.07
35.6	3.5	4.72
39.1	6.0	7.45

by CMS). A simple permeability model ($N_A = K_A(p_{A,\text{air}} - p_{A,\text{perm}})$) predicts the enriched oxygen fraction to be

$$x_{\text{O}_2,\text{permeate}} = \frac{1}{2} (1 - ar - \sqrt{1 - 2br + a^2r^2}) \quad (13)$$

where $a = [1 - x_{\text{O}_2,\text{air}}(1 - G)]/(1 - G)$ and $b = [1 - x_{\text{O}_2,\text{air}}(1 + G)]/(1 - G)$ are constants, r is the ratio of air pressure to permeate pressure and G is the ratio of oxygen permeability to nitrogen permeability. For the CMS-X membrane, the effective permeability ratio is 3.07. Permeability ratios have been achieved as high as 6.92 with a TPX/siloxane blend membrane [9], however the gas flux is too low for practical fuel cell use. The advantage of the CMS membrane is its high gas flux, which allows a relatively small device to produce the high flow rates required for a fuel cell stack.

The oxygen enrichment membrane will have a pressure ratio across it which depends on the gas flow drawn through it. From the simple permeability model, this function is

$$\frac{p_{\text{permeate}}}{p_{\text{air}}} = \frac{1}{r} = \frac{1}{2} \left(1 - \alpha Q + \sqrt{1 + 2(2x_{\text{O}_2,\text{air}} - 1)\beta Q + \beta^2 Q^2} \right) \quad (14)$$

where $\alpha = (G + 1)/AK_{\text{O}_2}p_{\text{air}}$ and $\beta = (G - 1)/AK_{\text{O}_2}p_{\text{air}}$ are constants, Q is the total molar flow rate of the permeate and K_{O_2} is the oxygen permeability of the membrane. These equations consider x_{air} as a constant which is approximate for high air feedstock flow rates through the tube bundles. If low feedstock flow rates are used, then an air utilization factor must be added to the model.

The energy required to make the separation is the energy to produce the partial vacuum on the permeate side of the membrane. This can be described by the adiabatic compression of an ideal gas, Equation 15:

$$P[W] = Q[\text{mol s}^{-1}]RT[\text{J mol}^{-1}] \frac{K}{K - 1} \times \left(\left(\frac{p_{\text{out}}}{p_{\text{in}}} \right)^{(K-1)/K} - 1 \right) \xi_{\text{efficiency}}^{-1} \quad (15)$$

The energy requirements reported by CMS in Table 1 correspond to a compressor efficiency of 60%. Higher efficiencies (70–80%) at the design point can be obtained

Table 2. Parameters used in the fuel cell model

Parameter	Low loaded MEA /A cm ⁻²	High loaded MEA /A cm ⁻²
α_{sub}	$\frac{486 x_0 P}{(1/0.0832) + (P/0.0252)}$	$\frac{486 x_0 P}{(1/0.0832) + (P/0.0252)}$
α_{agg}	$x_0 P 3.0$	$x_0 P 7.0$
σ_{cat}	0.25	0.6
σ_{mem}	0.13	0.25
ν^*	$x_0 P^{1.5} (4 \times 10^{-8}) \exp\left(\frac{1.23 - Ec}{0.03}\right)$	$x_0 P^{1.5} (1.05 \times 10^{-6}) \exp\left(\frac{1.23 - Ec}{0.03}\right)$

* Pressure is multiplied by 1.5 to account for oxygen and hydrogen electrodes

with more state-of-the-art compressors. Compressor efficiency goes down rapidly away from the designed operating point, but this was not considered in the calculations.

When the cell operates under pressure, some of the compression work can be recovered by expanding the cathode effluent. The gas flow rate of the effluent when water vapour pressure effects are neglected is

$$Q_{\text{out}} = Q_{\text{in}} \left(\frac{1 - x_{\text{O}_2, \text{inlet}}}{1 - x_{\text{O}_2, \text{outlet}}} \right) \quad (16)$$

Due to system inefficiencies, the pressure drop through the flow field, and the loss of the oxygen fraction consumed in the cell, expansion work recovered is less than 40% of the compression work.

The net power generated by the system is the power generated by the fuel cell minus the power required for gas separation and/or pressurization. For oxygen enrichment or direct pressurization to have a clear advantage over a atmospheric pressure air system, the power increase in the fuel cell at constant efficiency must be greater than the power required to increase the oxygen partial pressure. The total power density of the system is

$$P_{\text{net}} = P_{\text{cell}} - P_{\text{enrich, vac}} - P_{\text{comp}} - P_{\text{expan}} \quad (17)$$

Efficiency is defined as the net output power divided by the theoretical power of the fuel. That is,

$$\text{Efficiency} = \frac{P_{\text{net}}}{i \times \Delta H_{\text{f, water}}} \quad (18)$$

where $\Delta H_{\text{f, water}} = 1.25 \text{ V}$. In general, the efficiency decreases with increasing power output until a peak power is reached, where mass transfer effects limit the cell from producing more current.

3. Results and discussion

3.1. Model fit to experiment

The parameters used in the model were determined by fitting the model to experimental measurements of the

potential against current in single cells with varying oxygen fraction, cell pressure and stoichiometry. The calculations were performed using the software 'Mathematica' (Wolfram Research Inc., Champaign, IL). Two types of MEAs were fabricated in this laboratory [10] to compare with the model. One had a low catalyst loading cathode (0.2 mgPt cm^{-2}), whereas the other had a high loading (1.0 mgPt cm^{-2}). In all MEAs studied, the hydrogen electrode contained $0.05 \text{ mgPt cm}^{-2}$. Cells with an electrode area of 5 cm^2 were tested with high gas stoichiometry to compare with the model for local performance and cells with an electrode area of 50 cm^2 were tested to compare affects of stoichiometry. The cells were tested using humidified gases at $50 \text{ }^\circ\text{C}$. The parameters used in the model are shown in Table 2.

Figure 4 shows experimental and calculated potential against current performance with different oxygen partial pressures in the cathode feed gas for a 5 cm^2 MEA with a low loading cathode. As expected, increasing the oxygen fraction generated more current at the same cell potential. Figure 5 shows the same performance with an MEA containing a high loading cathode.

The gas stoichiometry through the flow field also plays a large role in fuel cell power output. Figure 6

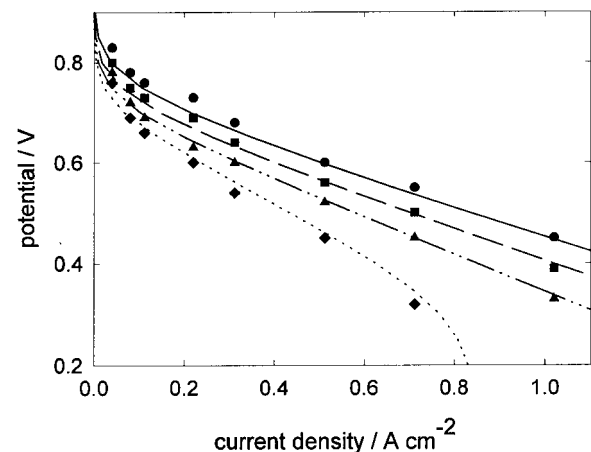


Fig. 4. Calculated and experimental current–potential performance for low catalyst loaded 5 cm^2 cell at different oxygen fractions. Key for experimental and model: (●, —) 100%; (■, - -) 40%; (▲, ···) 20%; (◆, - · -) 10%.

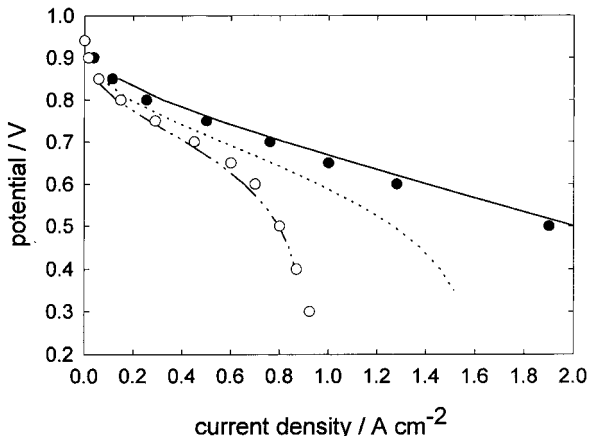


Fig. 5. Calculated and experimental current-potential performance for high catalyst loaded 5 cm^2 cell at different oxygen fractions. Key: (●) experiment, 100% oxy; (—) model, 100% oxy; (- - -) model, 35% oxy; (○) experiment, air; (---) model, air.

shows experimental data and a model simulation of the increase in current at constant potential as the gas flow stoichiometry is increased. In this cell, the differential pressure in the flow field increased with increasing stoichiometry, which was taken into account by the model. At low stoichiometry, the experimental performance fell below the calculated performance due to a nonideal distribution of gas between channels in the flow field.

3.2. Simulations

Operating with high stoichiometry uses a large amount of energy to feed gas to the cell. Figure 7 demonstrates how the net output power was affected by stoichiometry for a high cathode loading MEA. The Figure compares a pressurized cell at 0.75 V to an ambient cell at 0.7 V, because the fuel efficiency is comparable under these conditions. Under ambient pressure conditions, the optimum stoichiometry was about 2.5, whereas

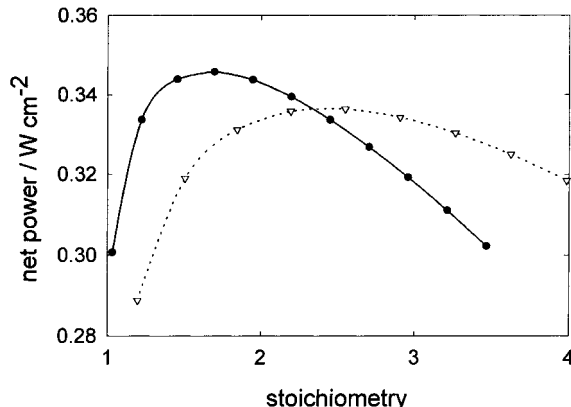


Fig. 7. Net power as a function of stoichiometry for a high catalyst loaded MEA in an ambient air system and a pressurized system with a compressor efficiency of 70%. Key: (—●—) $P = 4 \text{ atm}$ at 0.75 V; (- - ▽ - -) ambient air at 0.7 V.

under pressure, the optimum stoichiometry fell to 1.75. All systems will follow this trend, although the optima will vary with flow field design (pressure drop and flow distribution), operating pressure, and operating efficiency.

Operating with pressurized air will enhance fuel cell performance, but parasitic power requirements restrict the maximum beneficial pressure for the system. Figure 8 simulates net power output against cell pressure at constant efficiency with a compressor efficiency of 70%, an optimum stoichiometry, and a high loading cathode. The cell voltage must increase as pressure increases to operate at the same efficiency. At constant high efficiency (60% at about 0.75 V), pressurizing the cell caused a loss in net power. At constant low efficiency (40% at about 0.55 V), pressurizing the cell improved performance. Since pressurization improves oxygen mass transfer and kinetics, but not ionic transport, the cell performance will increase with pressure until proton transport in the catalyst layer becomes rate-determining.

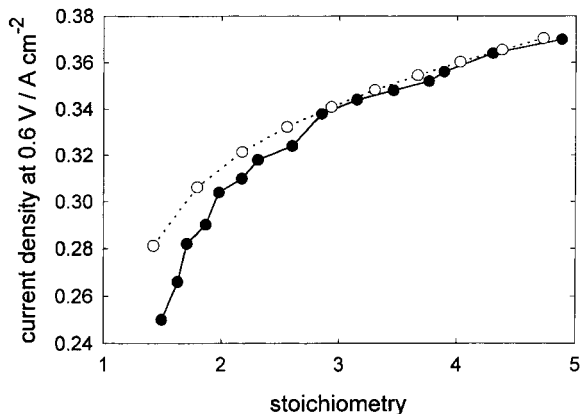


Fig. 6. Experimental data and model simulation for current density as a function of stoichiometry at constant voltage (0.6 V) for a low catalyst loaded MEA. The model accounted for pressure drop in the flow field. Key: (—●—) experiment; (- - ○ - -) model.

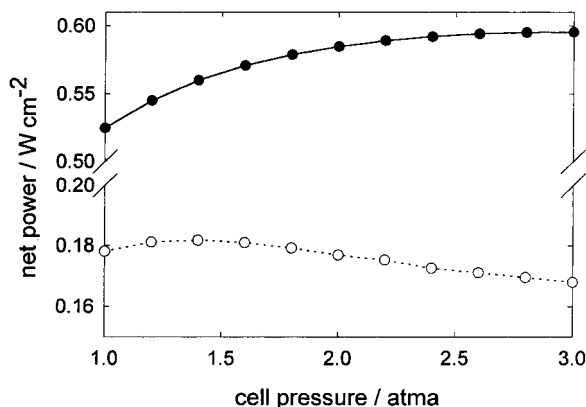


Fig. 8. Net power as a function of operating pressure for a high catalyst loaded MEA at constant efficiency (40 and 60%), a compressor efficiency of 70% and an optimum stoichiometry. Key: (—●—) 40% efficiency; (- - ○ - -) 60% efficiency.

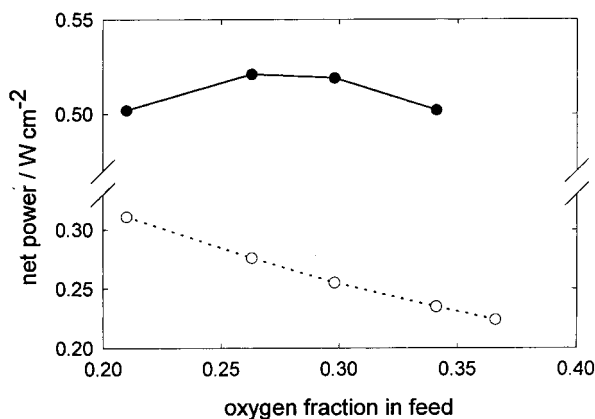


Fig. 9. Net power at constant fuel efficiency as a function of oxygen fraction fed to the cell from a CMS oxygen enrichment membrane. Key: (—●—) 43% efficiency; (- - ○ - -) 55% efficiency.

Operating with oxygen enrichment is similar to pressurized operation. Figure 9 models the net output power at constant fuel efficiency for a fuel cell operated under different conditions of oxygen enrichment via the CMS-X membrane. Again, at constant high efficiency, oxygen enrichment was not effective; whereas at constant low efficiency, net power was improved.

The parasitic losses for oxygen enrichment and air pressurization were compared by examining the power requirements to obtain gas at the same oxygen partial pressure and same oxygen gas flow rate. Table 3 presents this comparison, using the adiabatic gas compression equation with a compressor efficiency of 100%. Pressurizing air requires a lower pressure ratio than oxygen enrichment, but requires a higher total gas flow rate. The CMS membrane technology requires almost twice the amount of energy to increase the oxygen partial pressure compared with pressurizing air. The siloxane membrane, though not practical, demonstrates that it is possible for oxygen enrichment to require less energy than pressurizing air at constant oxygen partial pressure and oxygen flow rate.

During the operation of the oxygen enrichment system, the pressure ratio across the permeable membrane (and thus the oxygen concentration fed to the cathode) depends on the flow of gas passing through the membrane. At low fuel cell currents, low gas flow rates are drawn through the membrane at low pressure ratios, and the system operates like an ambient air system. At high fuel cell currents, high gas flow rates increase the pressure ratio, and thus, increase the oxygen fraction of

the permeate. If properly designed, the oxygen enrichment system can provide the efficiency advantages of the ambient air system and the power advantages of air pressurization without having to change the operating pressure of the fuel cell. This simplifies water management and the construction of a fuel cell stack.

The net performance for the different systems under investigation are compared for low and high loading cathodes in Figures 10 and 11. For the oxygen enrichment case, the area of the CMS membrane in Equation 14 was adjusted so that the oxygen concentration was the same as that in ambient air at low power, and increased to 36% at maximum power. The performance of the MEA with low catalyst loading did not markedly change with mode of operation because the cell was primarily kinetically limited. Pressurizing the system did not improve the net power density, except at very low efficiency. The best system for the ideal case of an oxygen electrode which is only limited by kinetics is ambient pressure operation.

Differences in system performance becomes more evident using a high loading cathode because of oxygen mass transfer limitations at high current densities. At high efficiency (low current density), the ambient air system has the highest net power density. At low efficiency (high current density), pressurized air shows the highest net power density. The oxygen enrichment system operates like an ambient air system at high

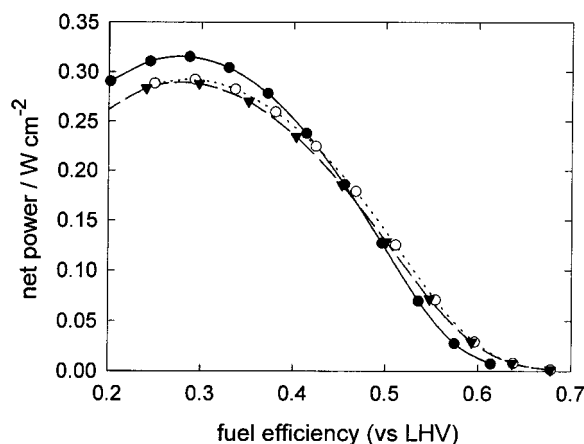


Fig. 10. Comparison of net power as a function of fuel efficiency for the different systems with a LOW catalyst loaded MEA. Comparing ambient air, oxygen enrichment with CMS the membrane and pressurization of air to 3 atm. Key: (—●—) pressurized at 3 atm; (- - ○ - -) oxygen enrichment; (- - ◆ - -) ambient system.

Table 3. Comparison of power requirements to produce one standard liter per minute of oxygen for oxygen enrichment at atmospheric pressure and for direct pressurization of air

Oxygen partial pressure / (atm)	Enrichment energy CMS, $G = 3.07$ / (W SLM ⁻¹ O ₂)	Enrichment energy Siloxane, $G = 6.92$ / (W SLM ⁻¹ O ₂)	Pressurization energy / (W SLM ⁻¹ O ₂)
0.3	4.82	3.06	3.30
0.35	7.52	4.04	4.83
0.4	12.07	4.97	6.22

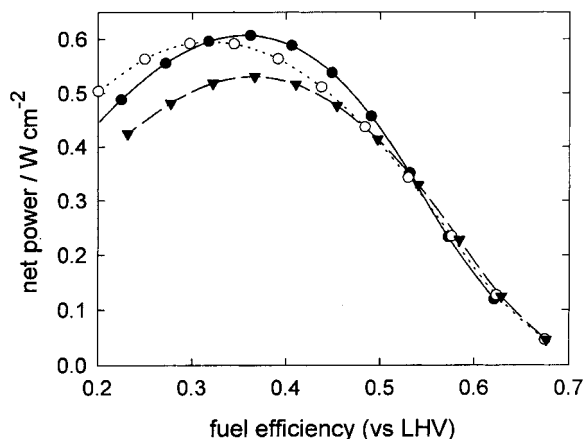


Fig. 11. Comparison of net power as a function of fuel efficiency for the different systems with a HIGH catalyst loaded MEA. Comparing ambient air, oxygen enrichment with CMS the membrane and pressurization of air to 3 atm. Key: (—●—) pressurized at 3 atm; (- - ○ - -) oxygen enrichment; (- ◆ - -) ambient air system.

efficiency (low power density) and like a pressurized system at low efficiency (high power density). Thus, for applications with high performance MEAs, where the power load (and operating efficiency) will vary with time, oxygen enrichment may provide a means of improving the peak power density of a fuel cell without compromising efficiency at low power.

4. Conclusions

It may seem advantageous to operate fuel cells under pressure because this approach produces a higher peak power density with present MEA technology. Operating the cell pressurized helps to overcome oxygen mass transfer limitations into the electrode, and may improve the distribution of reactant gas through the flow fields. However, operating with pressurized air lowers the fuel efficiency and increases the complexity and cost of the system.

An oxygen enrichment system could allow a fuel cell to operate at atmospheric pressure at high power densities without loss of efficiency. However, practical oxygen enrichment membranes available today have insufficient performance to attain as high a peak power as air pressurization at constant efficiency. The enrich-

ment system is also complex and expensive. If more oxygen selective membranes can be developed which can operate at higher gas fluxes, then oxygen enrichment will permit a higher net power density than pressurization.

Ambient air operation is the most efficient and simplest system with the lowest cost. When the cell current is not restricted by oxygen mass transfer, ambient air operation will have a higher power density than that of a pressurized air system at constant efficiency. The power densities of ambient air systems will improve as electrode design removes oxygen mass transfer limitations. This suggests that effort should be directed toward improving cathode design, rather than in developing pressurized systems with inferior cathodes.

Fuel cell electrodes are under constant development, and their kinetic and mass transfer properties will change as the technology progresses. The model developed in this paper can be used to determine whether air pressurization or oxygen enrichment will improve the net power output of the system at constant efficiency. It can also be used to find an optimum operating stoichiometry at constant efficiency for any system.

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