

# Operation of Nafion<sup>®</sup>-based PEM fuel cells with no external humidification: influence of operating conditions and gas diffusion layers

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Received 4 March 2004; accepted 15 April 2004

Available online 2 July 2004

## Abstract

Polarization tests were conducted on proton exchange membrane fuel cells (PEMFCs) at cell temperatures between 60 and 80 °C with various reactant humidification levels; varied from no external humidification to fully saturated on both the anode and the cathode. Elimination of cathode external humidification, while maintaining a fully humidified anode inlet, resulted in cell performance loss of only 5% or 33 mV (from 0.674 to 0.641 V) at 400 mA/cm<sup>2</sup> at an anode stoichiometry of 3 and a cathode stoichiometry of 4. When both the anode and the cathode humidification were removed (“dry operation”), cell performance strongly depended on the cell operating temperature and the inlet gas stoichiometric flow rates. High performance of non-humidified PEMFCs was demonstrated by optimizing the operating cell temperature and the inlet gas stoichiometric flow rates, to find a balance between cell “flooding”, oxygen mole fraction, and proton conductivity. Performance of a cell with an in-house cathode gas diffusion layer (GDL) showed a loss of only 4% or 29 mV (from 0.674 to 0.645 V) compared to the near-saturated condition, at 400 mA/cm<sup>2</sup> and optimum stoichiometry. Using a commercial E-TEK\_V.2.11 carbon cloth cathode GDL showed significantly greater loss when operated with no external humidification at the same optimized condition. An overall system analysis suggested that at optimum stoichiometric flow rates and cell temperatures, with the in-house GDL, while the net power output might be reduced by at most 17% under dry operation the total required non-stack energy duty would be cut by over 46% when compared to operation with saturated inlet gases.

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*Keywords:* PEM; No external humidification; Dry inlet; Gas diffusion layer; Nafion; System

## 1. Introduction

Proton exchange membrane fuel cells (PEMFC) can be operated at varying conditions of cell temperature, total pressure, partial pressure of reactants, and relative humidity. While most PEMFC studies were performed at near-saturated operating conditions at various temperatures and pressures, several studies were performed with dry inlet reactant gases [1–9]. Removal or minimization of inlet gas humidification greatly simplifies the overall fuel cell system by alleviating water and heat balance issues. However, cell performance with dry inlet gases usually suffers from low proton conductivity and non-uniform current distribution due to cell “dry-out”.

Several modeling studies attempted to define the operating regime where PEMFC operation with no external humidification (called “dry operation”) is feasible [1–4]. Most models and experiments [1–3,5] found that cell temperature, the pressure gradient between the anode and the cathode compartments, anode stoichiometry, and cathode stoichiometry have a strong influence on the performance under “dry conditions”. Inlet and exit water calculations showed that water produced from the cathode was able to keep the anode well humidified at temperatures up to 70 °C at ambient pressure [1]. Performance curves have been generated for dry operation at temperatures up to 60 °C [1,6–9]. A few studies used self-humidifying membranes to reduce ohmic losses from low proton conductivity with no external humidification [8,9]. The results were positive, but the experiments were conducted only up to 50 °C.

This work presents polarization curves collected at various cell temperatures between 60 and 80 °C, at various humidification levels between 0 and 100% inlet relative

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humidity (RH) of both the cathode and the anode, at various values of the cathode stoichiometry between 1.5 and 4, and at two different values of the anode stoichiometry (1.3 and 3), all at atmospheric pressure. Optimum operating conditions for dry operation between 60 and 80 °C provide cell performance comparable to that at fully saturated conditions using a Nafion<sup>®</sup>-based membrane electrode assembly (MEA) prepared in-house. Influence of the type of gas diffusion layer (GDL) used on performance will also be discussed. Water and oxygen mass balance calculations provide understanding of the experimental results.

A system analysis comparing operation of “state-of-the-art” commercial MEAs at near-saturated conditions with operation of the in-house MEA with no external humidification is shown. A fuel cell system with the in-house MEA operated at an optimum dry condition provides net power output comparable to that of a much more complicated system at a near-saturated condition.

## 2. Experimental

### 2.1. Membrane electrode assembly preparation

A schematic of PEM fuel cell components and their approximate thicknesses are shown in Fig. 1. In preparing a membrane electrode assembly, cathode and anode catalyst inks were sprayed directly onto each side of an Ionomem/UConn high temperature Nafion<sup>®</sup>-Teflon<sup>®</sup>-phosphotungstic acid composite membrane [10]. The catalyst-coated membrane was then sandwiched between two gas diffusion layers to obtain a 5 cm<sup>2</sup> MEA for single cell polarization measurement. The anode catalyst was 30.1 wt.% Pt-23.3 wt.% Ru/C (Tanaka Kikinokogyo, Tokyo, Japan) and the cathode catalyst was 46 wt.% Pt/C (Tanaka Kikinokogyo, Tokyo, Japan).

The Nafion<sup>®</sup> loading in both the anode and the cathode catalyst inks was 35 wt.%. A suitable Nafion<sup>®</sup> loading in the electrode is important for high performance under low relative humidity operation. A suitable Nafion<sup>®</sup> loading provides sufficient proton conductivity at the desired relative humidity while not causing severe oxygen transport losses in the electrode. A Nafion<sup>®</sup> loading of 35% was found suitable for high temperature/low relative humidity fuel cell operation (120 °C and 35% RH), with the supported catalysts used, in previous work done at the University of Connecticut [11]. The prepared MEA is considered a “Nafion<sup>®</sup>-based” MEA because it comprises a Nafion<sup>®</sup>-based composite membrane and Nafion<sup>®</sup> is used in the electrodes as the proton conductor.

Two 5 cm<sup>2</sup> membrane electrode assemblies made from identical catalyzed membranes, but different types of cathode gas diffusion layer were prepared. The in-house GDL was used in a cell called “in-house GDL MEA” and the E-TEK\_V.2.11 carbon cloth GDL (E-TEK Inc., Somerset, NJ) was used in a cell called “E-TEK GDL MEA”. Table 1 reports the main MEA characteristics of the two cells: membrane thickness, platinum loading on the cathode, platinum-ruthenium loading on the anode, and type and thickness of the anode and cathode GDLs. The anode GDL of both cells is the dual-layer SGL\_10BB (SGL Carbon Group, Short Hills, NJ) so that the only difference between these two cells is the cathode GDL.

To maintain intimate contact between different components of an MEA, seal gaskets used in assembling the MEA in the cell hardware had a total thickness 0.31 mm less than the total MEA thickness (catalyst + electrodes + two GDLs). This difference in thicknesses permitted enough compressive force to neglect contact resistance for the MEAs.

Flow field design is critical for PEM fuel cell operated under dry conditions to avoid localized cell “dry-out”,

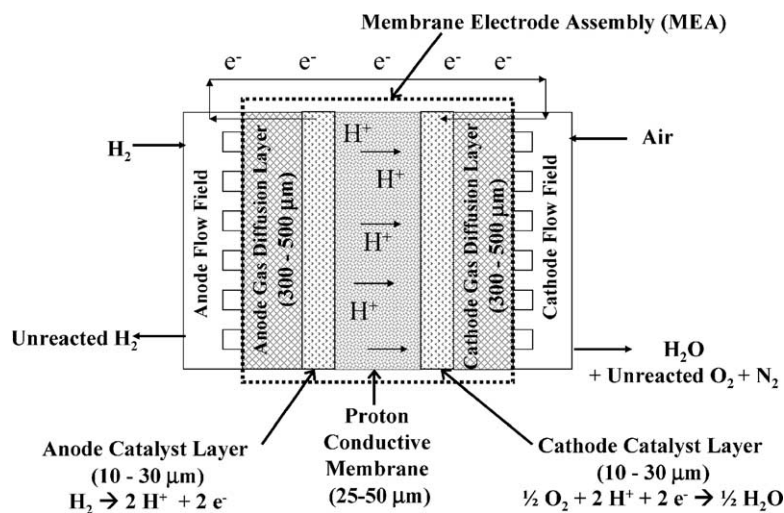


Fig. 1. Schematic diagram of PEM fuel cell components showing membrane, catalyst layers, gas diffusion layers, membrane electrode assembly, and flow fields, with their approximate thicknesses.

Table 1

Comparison of primary characteristics of the two cells with different cathode gas diffusion layers called “in-house GDL MEA” and “E-TEK GDL MEA”

Cell	Membrane thickness (mm)	Cathode Pt loading (mg/cm <sup>2</sup> )	Anode Pt-Ru loading (mg/cm <sup>2</sup> )	Anode GDL type	Anode GDL thickness (μm)	Cathode GDL type	Cathode GDL thickness (μm)	Cathode GDL fraction of hydrophobic pores (%)
In-house GDL MEA	26	0.57	0.53	SGL_10BB	429	In-house	373	81
E-TEK GDL MEA	26	0.56	0.55	SGL_10BB	417	E-TEK_V.2.11	366	100

especially at the flow field inlet (more details of the cell “dry-out” is in the Section 3). The graphite flow field used was a single-serpentine flow pattern with a rectangular channel of 0.84 mm in width and 0.81 mm in depth, and 14 180°-turns (15 passages total). The total length of the single channel was 38.1 cm and the total active area was 6.25 cm<sup>2</sup>. The anode and cathode flow fields are in counter-flow orientation, which is suitable for dry operation in best utilizing the accumulated product water in the cathode exit for humidifying the anode inlet. However, a single-serpentine flow pattern is not expected to be the best design for a large active area fuel cell (such as a full-size 300 cm<sup>2</sup> active area) not only due to the excess pressure drop, but also that the much larger dry inlet flow rate in one single channel will cause cell “dry-out”. For small elemental cells like described here, a single-serpentine flow field provides good performance even under dry operation (as will be shown in this paper).

The in-house GDL MEA was used to study the influence of inlet relative humidity, operating temperature, and cathode stoichiometry. The E-TEK GDL MEA was compared to the in-house GDL MEA to investigate the influence of cathode GDL on PEM fuel cell performance under near-saturated operation and dry operation.

## 2.2. Two cathode GDLs for comparison

The in-house GDL and the commercial E-TEK\_V.2.11 carbon cloth GDL consisted of two layers; the micro-porous layer that is in contact with the cathode catalyst layer and the macro-porous substrate that is in contact with the graphite flow field.

The commercial E-TEK\_V.2.11 GDL is made of electrically conductive carbon cloth. Both the E-TEK GDL and the in-house GDL were thoroughly characterized previously for several parameters including gas permeability, porosity, fraction of hydrophobic pores, pore size distribution, and in-plane electronic conductivity [12]. The E-TEK\_V.2.11 carbon cloth was more hydrophobic than the in-house GDL (100% fraction of hydrophobic pores compared to 81%). Commercial GDLs, including the E-TEK\_V.2.11 carbon cloth, are typically designed to avoid a condition where liquid water blocks oxygen access to reaction sites. The condition is a common and serious problem in PEMFC operation at near-saturated conditions (inlet gases close to 100%RH). The E-TEK\_V.2.11 carbon cloth was selected for comparison with the in-house GDL because Williams et al.

[12] showed that the E-TEK carbon cloth outperformed four other commercial gas diffusion layers.

The in-house GDL consisted of TGPH-120 carbon paper (Toray Corporation, Japan) as the macro-porous substrate. The hydrophobic micro-porous layer of the in-house GDL containing Vulcan XC-72R (Cabot Corporation, Billerica, MA) and polytetrafluoroethylene (Aldrich, St. Louis, MO) was applied onto the macro-porous substrate using a silk-screen technique. The polytetrafluoroethylene content of the in-house micro-porous layer was 14 wt.%. Details of the fabrication method of the in-house GDL were described previously [13,14].

The in-house GDL has been designed for elevated temperature and/or low relative humidity thus it has less hydrophobicity. The in-house GDL had an overall 81% fraction of hydrophobic pores, with its macro-porous substrate having an 85% fraction of hydrophobic pores [12].

## 2.3. Measurement of polarization curves

Several operating conditions were tested for the in-house GDL MEA to study the influence of inlet humidification, cell temperature, and cathode stoichiometry on membrane resistance and cell performance. Significant parameters that define partial pressures of hydrogen, oxygen, and water are cell temperature, cell pressure, humidifier temperatures, and reactant stoichiometry.

The tested operating conditions ranging between cell temperatures of 60 and 80 °C, anode and cathode inlet RH of 0 and 100%, and anode and cathode stoichiometry of 1.3 and 4 are summarized in Table 2. All operating conditions throughout this study were at atmospheric pressure. Fuel was pure hydrogen and the oxidant gas was air. The operating conditions shown in Table 2 are divided into three sections: different inlet humidification levels at constant stoichiometry, different cell temperature at constant stoichiometry with no external humidification, and different cathode stoichiometry at constant cell temperature and constant anode stoichiometry with no external humidification. The nomenclature to be used in referring to each operating condition throughout this paper is  $T_{\text{cell}}/T_{\text{anode humidifier}}/T_{\text{cathode humidifier}}$  (sixth column, Table 2). The word “Dry” used with the nomenclature refers to no external humidification where the inlet gas bypasses the humidifier.

Current was stepped up from zero (open circuit voltage) in increments of 10 mA/cm<sup>2</sup> until a current density of 100 mA/cm<sup>2</sup> was set and then the current was incremented

Table 2  
Summary of all operating conditions tested, all at atmospheric pressure

Comparison	$T_{\text{cell}}$ (°C)	Anode $T_{\text{humidifier}}$ (°C)	Cathode $T_{\text{humidifier}}$ (°C)	Nomenclature $T_{\text{cell}}/T_{\text{A, Hum}}/T_{\text{C, Hum}}$	Cathode stoichiometry	Anode stoichiometry	Anode inlet RH (RH <sub>an</sub> ) (%)	Cathode inlet RH (RH <sub>cat</sub> ) (%)
Humidification	70	70	70	70/70/70	4	3	100	100
	70	70	62	70/70/62	4	3	100	75
	70	70	–	70/70/Dry	4	3	100	0
	70	–	–	70/Dry/Dry	4	3	0	0
Cell temperature	60	–	–	60/Dry/Dry	1.5	1.3	0	0
	65	–	–	65/Dry/Dry	1.5	1.3	0	0
	70	–	–	70/Dry/Dry	1.5	1.3	0	0
	75	–	–	75/Dry/Dry	1.5	1.3	0	0
	80	–	–	80/Dry/Dry	1.5	1.3	0	0
Cathode stoichiometry	$T_{\text{cell}}^{\text{a}}$	–	–	$T_{\text{cell}}^{\text{a}}/\text{Dry}/\text{Dry}$	1.5	1.3	0	0
	$T_{\text{cell}}^{\text{a}}$	–	–	$T_{\text{cell}}^{\text{a}}/\text{Dry}/\text{Dry}$	2	1.3	0	0
	$T_{\text{cell}}^{\text{a}}$	–	–	$T_{\text{cell}}^{\text{a}}/\text{Dry}/\text{Dry}$	2.5	1.3	0	0
	$T_{\text{cell}}^{\text{a}}$	–	–	$T_{\text{cell}}^{\text{a}}/\text{Dry}/\text{Dry}$	3	1.3	0	0

<sup>a</sup>  $T_{\text{cell}}$  is either 60, 65, 70, 75, or 80 °C.

at 100 mA/cm<sup>2</sup>. The maximum current density tested was the last current before the cell voltage went below the minimum set point of 0.05 V. Five minutes were spent at each current density with cell voltage collected every 20 s. The last three values of cell voltage at each current density were averaged and the average values were used in all polarization curve plots and the data analysis to be shown in later sections. A 10-amps Model 890B Scribner load box (Scribner Associates, Southern Pines, NC), which has built-in current interrupt resistance measurement was used for the polarization measurement.

The anode and the cathode gas line temperatures were always set 10 °C above the cell temperature to ensure no water condensation in the gas lines. Constant stoichiometry was used instead of constant flow rate because it is more representative of fuel cell operation. Since gas flow rates should not be zero at open circuit voltage, minimum gas flow rates were set at 25 cm<sup>3</sup>/min for the anode and 50 cm<sup>3</sup>/min for the cathode, resulting in different onset current densities for the constant stoichiometry region of the polarization curve at different stoichiometric flow rates. The onset current densities at cathode stoichiometry of 1.5, 2.0, 2.5, 3.0, and 4.0 are at test current densities of 400, 300, 300, 200, and 200 mA/cm<sup>2</sup>, respectively.

Cell internal resistance was measured and recorded at current densities higher than 100 mA/cm<sup>2</sup> using a current-interrupt technique through the Scribner V.3.1b Software (Scribner Associates Inc., Southern Pines, NC) included with the loadbox. The cell internal resistance comprises mostly ionic resistance of the conductive membrane and all pure electrical (bulk and contact) resistances. However, the cell internal resistance equals the membrane ionic resistance when other pure and contact resistances are made negligible by sufficiently compressing the gas diffusion layers of the MEA. The difference in the total thickness of the seal gaskets and the total thickness of the

MEA was 0.31 mm, which was shown to be sufficient to neglect contact resistances [15].

### 3. Results and discussion

#### 3.1. Influence of inlet humidification levels

The in-house GDL MEA was used to study the influence of reducing inlet gas humidification of both the anode and the cathode on cell voltage and the membrane ionic resistance (refer to conditions in the top four rows of Table 2). Fig. 2 shows cell voltage and cell internal resistance at different humidification levels at 70 °C cell temperature. The in-house cathode GDL, which is not completely hydrophobic on the surface, results in severe “flooding” at the fully saturated condition of 70/70/70 ( $T_{\text{cell}}/T_{\text{anode humidifier}}/T_{\text{cathode humidifier}}$ ) above 500 mA/cm<sup>2</sup>. Flooding is a cell condition where liquid water blocks oxygen access in the cathode and causes a sharp drop in cell performance as current density increases (as seen for the saturated 70/70/70 condition at above 500 mA/cm<sup>2</sup>).

As the cathode relative humidity is reduced to 75% at the 70/70/62 condition, the cell voltage increases as flooding is eliminated and the cell internal resistance is still minimal. There is a moderate decrease in cell voltage when the cathode humidification is completely removed at the 70/70/Dry condition compared to the near-saturated condition of 70/70/62: 33 mV at 400 mA/cm<sup>2</sup> and 59 mV at 1000 mA/cm<sup>2</sup>. When the cathode humidification is also removed at the 70/Dry/Dry condition, there is a significant drop in cell performance compared to the 70/70/Dry condition: 159 mV at 400 mA/cm<sup>2</sup> and the cell “stops performing” at a current density of only 900 mA/cm<sup>2</sup>. (The current density where a cell stops performing is the highest tested current density before cell performance goes below the minimum limit of 0.05 V.)

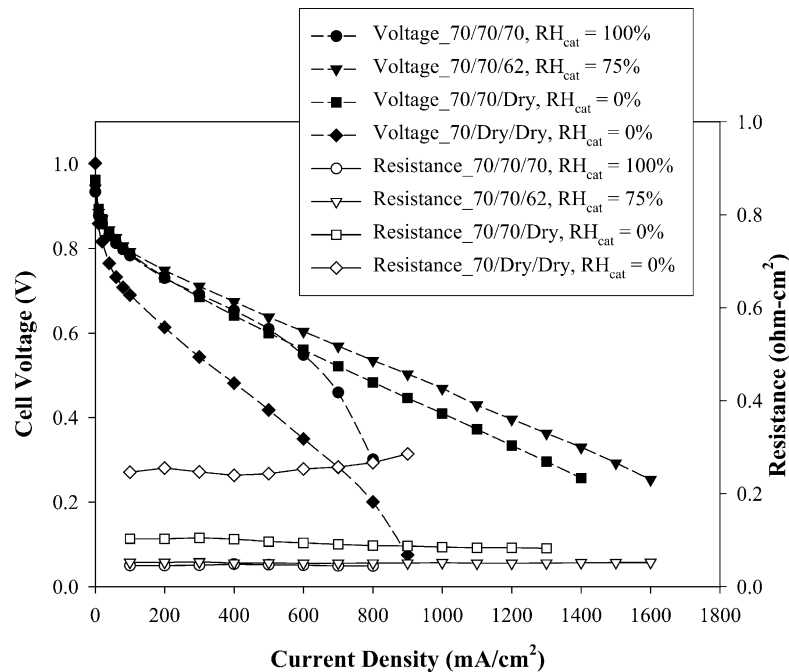


Fig. 2. Cell voltage and cell internal resistance at various humidification levels: the in-house GDL MEA (cathode GDL is in-house GDL), 70 °C, hydrogen/air, 1 atm, high stoichiometry, anode stoichiometry of 3 and cathode stoichiometry of 4, the temperatures listed in the legend are in degree Celcius. ( $T_{\text{cell}}/T_{\text{anode humidifier}}/T_{\text{cathode humidifier}}$ , “Dry” refers to no external humidification of the inlet gas,  $\text{RH}_{\text{cat}}$  refers to cathode inlet relative humidity).

Membrane ionic resistance increases as the inlet relative humidity is reduced from the 70/70/70 condition to the 70/70/62, to the 70/70/Dry, and to the 70/Dry/Dry conditions, respectively. Please note that membrane ionic resistance to be reported throughout the paper is determined at a reference current density of 400 mA/cm<sup>2</sup> unless noted otherwise. The reduction of cathode inlet relative humidity from 100% (at 70/70/70) to 75% (at 70/70/62) increases ionic resistance by a very minimal amount from 0.048 to 0.051  $\Omega \text{ cm}^2$ , which equates to only 1 mV loss at 400 mA/cm<sup>2</sup>. The removal of the cathode humidification doubles the ionic resistance from 0.051  $\Omega \text{ cm}^2$  (at 70/70/62) to 0.102  $\Omega \text{ cm}^2$  (at 70/70/Dry), but the loss in cell voltage is still moderate at 21 mV at 400 mA/cm<sup>2</sup>. However, as the anode humidification is also removed, cell resistance increases dramatically from 0.102 (at 70/70/Dry) to 0.239 (at 70/Dry/Dry), which equates to an additional 55 mV loss at 400 mA/cm<sup>2</sup>.

Both cell voltage and membrane resistance shown in Fig. 2 show that removing the inlet cathode humidification alone while maintaining saturated inlet anode causes a very moderate performance loss of only 5% at 400 mA/cm<sup>2</sup> (33 mV). However, removing both the anode and cathode humidification causes a more significant loss in cell performance of 29%, at 400 mA/cm<sup>2</sup> (193 mV). The open circuit voltage at the 70/Dry/Dry condition (about 1 V) is higher than other conditions because of the high hydrogen and oxygen partial pressure with no water in the inlet gases.

All the operating conditions reported in Fig. 2 are at an anode stoichiometry of 3 and a cathode stoichiometry of 4,

which are relatively high for fuel cell applications. The high stoichiometric flow rates have been used because they are the standard condition used and reported in previous publications by the Fenton/Kunz Fuel Cell Research Group at the University of Connecticut [11,12,16]. The standard stoichiometric flow rates were chosen so that there is no significant reactant partial pressure differences between the inlet and the exit. Results that follow are at a lower stoichiometric flow rate which is more appropriate for fuel cell applications: 1.3 for the anode and between 1.5 and 3 for the cathode.

### 3.2. Influence of cell temperature under dry operation

Fig. 3 shows cell voltage and cell internal resistance of the in-house GDL MEA at different cell temperatures between 60 and 80 °C with no external humidification at fixed anode and cathode stoichiometric flow rates of 1.3 and 1.5, respectively, which are reasonable for fuel cell applications (refer to conditions in the middle five rows of Table 2) [3,6].

Cell voltage will be compared only at the current density of 400 mA/cm<sup>2</sup> and higher, because 400 mA/cm<sup>2</sup> is the onset current density of the constant stoichiometry region of the polarization curve at 1.5 cathode stoichiometry. Differences in cell performance between different operating temperatures are greater at higher current density. The cell performance increases as cell temperature increases from 60 °C to 65 °C, to 70 °C, and to 75 °C, respectively. Cell performance reaches the maximum at 75 °C (0.629 V at 400 mA/cm<sup>2</sup>) then decreases as cell temperature increases further to 80 °C.

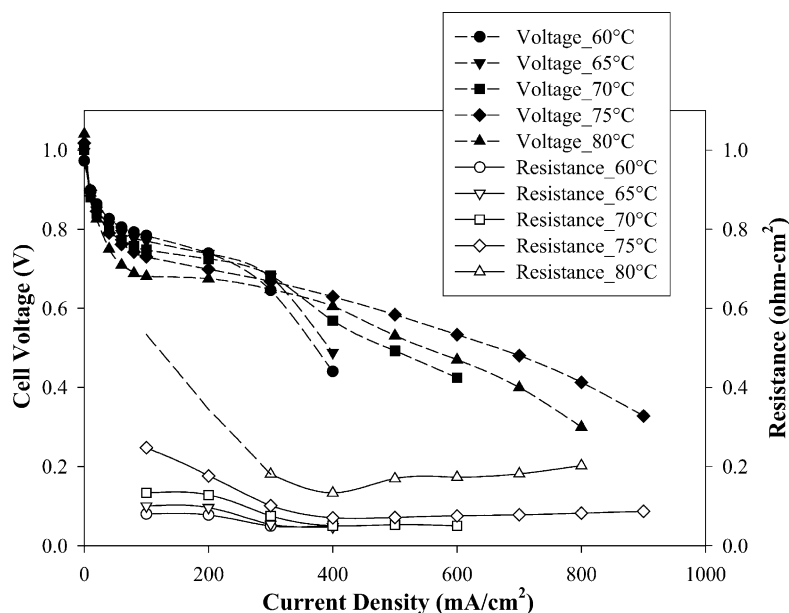


Fig. 3. Cell voltage and cell internal resistance under “dry operation” (no external humidification) at various cell temperatures: the in-house GDL MEA, hydrogen/air, 1 atm, low stoichiometry, anode stoichiometry of 1.3 and cathode stoichiometry of 1.5. Membrane resistance shown as a “dashed” line at below 300 mA/cm<sup>2</sup> for the 80 °C condition is where the cell is very dry and the measured membrane resistance is not accurate.

Membrane resistance increases with increasing cell temperature consistently throughout the whole temperature range, with the biggest increase from 75 to 80 °C (from 0.079 to 0.133 Ω cm<sup>2</sup>, at 400 mA/cm<sup>2</sup>). The decrease in performance at 80 °C compared to 75 °C is attributed to the increased membrane resistance.

At all temperatures membrane resistance reduces with increasing current density up to 400 mA/cm<sup>2</sup> where the constant stoichiometry region of the polarization curve starts. Below 400 mA/cm<sup>2</sup> the cathode stoichiometry increases with current density (due to constant 50 cm<sup>3</sup>/min flow rate) resulting in higher cell RH from more product water. For the 80 °C condition, the membrane resistance at 100 and 200 mA/cm<sup>2</sup> is very high and is shown as a “dashed” line in Fig. 3 because the measured membrane resistance is not accurate. Due to the sharp decrease in membrane resistance with increasing current density below 300 mA/cm<sup>2</sup>, cell performance at 80 °C is nearly constant at current densities between 100 and 300 mA/cm<sup>2</sup>. The increasing membrane resistance with current density at higher than 500 mA/cm<sup>2</sup> at 80 °C indicates cell “dry-out” (more discussion in a later section).

To understand the influence of cell temperature on performance under dry conditions, inlet and exit water and oxygen mass balance calculations were done for each operating condition. For easier understanding, the calculations are based on a mass balance of the cathode side alone. The simplification is reasonable because the anode flow rate was always kept constant independent of the cathode flow rate and operating conditions [1]. Results of the water and oxygen mass balance calculations are shown in Fig. 4a and b as plots of the cathode exit RH and the average oxygen partial pressure, re-

spectively. Since the cell is operated at constant stoichiometry, the calculated relative humidity and oxygen partial pressure are not a function of current density. When there is no water in the inlet gases, cell cathode relative humidity decreases with increasing temperature due to the exponential increase in saturated water vapor pressure with temperature (Fig. 4a). Results at a cathode stoichiometry of 1.5, shown as a thick “dashed” line, are used for the following discussion.

Fig. 4a shows that the cathode exit relative humidity is as high as 118% at 60 °C resulting in severe flooding that causes a sharp drop in performance at higher than 200 mA/cm<sup>2</sup> in Fig. 3. Cathode relative humidity reduces with increasing cell temperature, which alleviates the loss due to flooding and gives higher cell performance. This is true even though the membrane ionic resistance increases with higher temperature, because the membrane resistance at dry conditions between 60 and 75 °C remains fairly constant: 0.051, 0.051, 0.052, and 0.079 Ω cm<sup>2</sup> (at 400 mA/cm<sup>2</sup>), at the 60, 65, 70, and 75 °C conditions, respectively. These resistance values equate to at most 12 mV additional loss at 400 mA/cm<sup>2</sup> (comparing the 75 °C condition, exit cathode RH of 61%, with the 60 °C condition, exit cathode RH of 118%). The small additional loss due to membrane resistance at higher temperature shows that the MEA which comprises the 26-μm in-house composite membrane and the in-house GDL has membrane ionic resistance that is not a strong function of exit relative humidity until 60% showing promise for high performance at dry operation.

The average oxygen partial pressure is not a function of cell temperature, but it is a function of stoichiometry, thus it has no influence in this discussion (results in Fig. 3 are all at the same stoichiometry). Fig. 4b will be used in a later

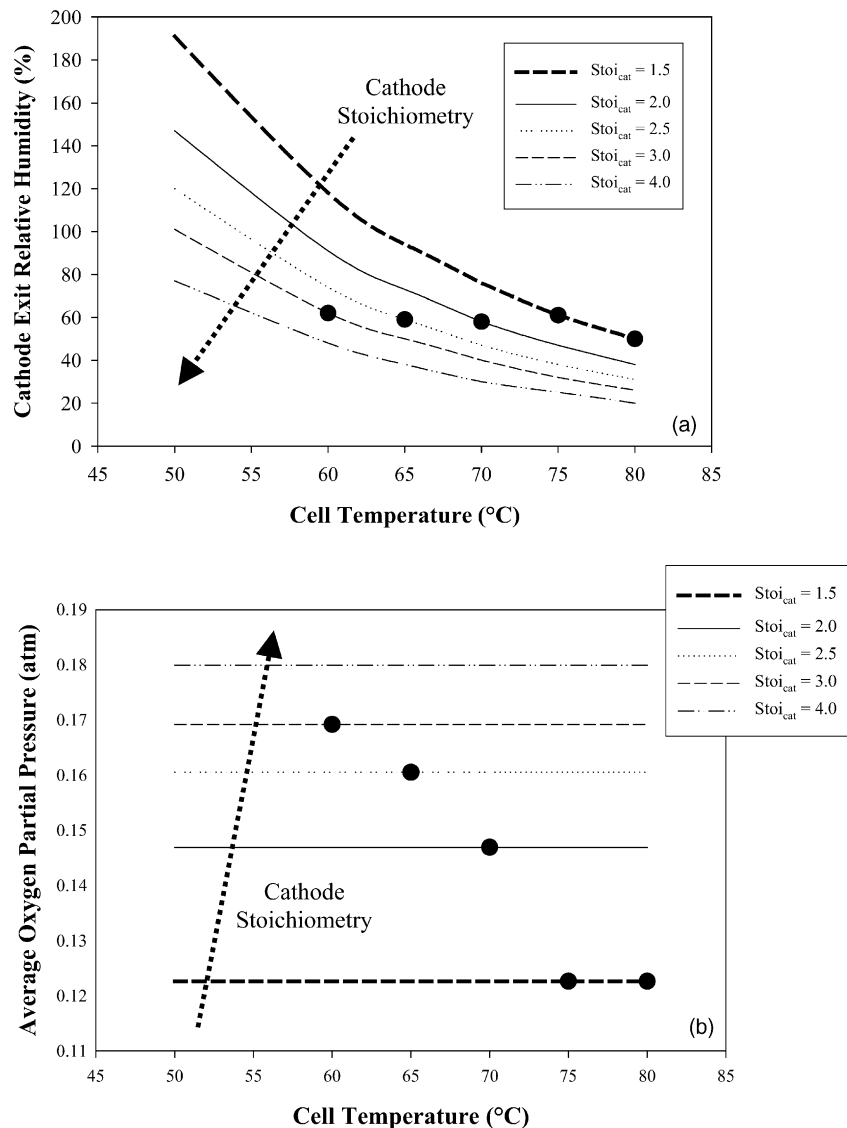


Fig. 4. Results from water and oxygen mass balance calculations under “dry operation” (no external humidification) as a function of cell temperature at several values of cathode stoichiometry ( $Stoi_{cat}$ ), 1 atm, all at anode stoichiometry of 1.3: (a) cathode exit relative humidity and (b) log-mean average oxygen partial pressure. “Solid circles” are the optimum cathode stoichiometry for maximum cell performance at each temperature (associated with results shown in Fig. 5 and Table 3).

discussion. Dry operation at a cell temperature of 75 °C, at an anode stoichiometry of 1.3, at a cathode stoichiometry of 1.5, and at exit cathode RH of 61% provides the best performance (0.629 V at 400 mA/cm<sup>2</sup>) of all temperatures tested.

### 3.3. Optimization of cathode stoichiometry for dry operation

It can be seen from Fig. 4a and b that as the cathode stoichiometry increases, the average oxygen mole fraction increases, but the exit cathode relative humidity unfavorably decreases. This suggests that there will be an optimum cathode stoichiometry for each temperature where the average oxygen partial pressure is high enough to have effective

oxygen transport and uniform current distribution, while the relative humidity is still high enough to maintain good ionic conductivity in the membrane and the electrodes.

At each of the cell temperatures of 60, 65, 70, 75, and 80 °C, polarization curves were collected at different values of cathode stoichiometry ranging from 1.5 to 3 (refer to conditions in the last four rows of Table 2) to determine an optimum stoichiometry for maximum cell performance at each temperature. The optimum cathode stoichiometry was found to be different at most temperatures: 3, 2.5, 2, 1.5, and 1.5 at 60, 65, 70, 75, and 80 °C, respectively. To remain concise, only the polarization curves at the optimum stoichiometry for maximum cell performance at different temperatures are shown in Fig. 5. The reduced membrane

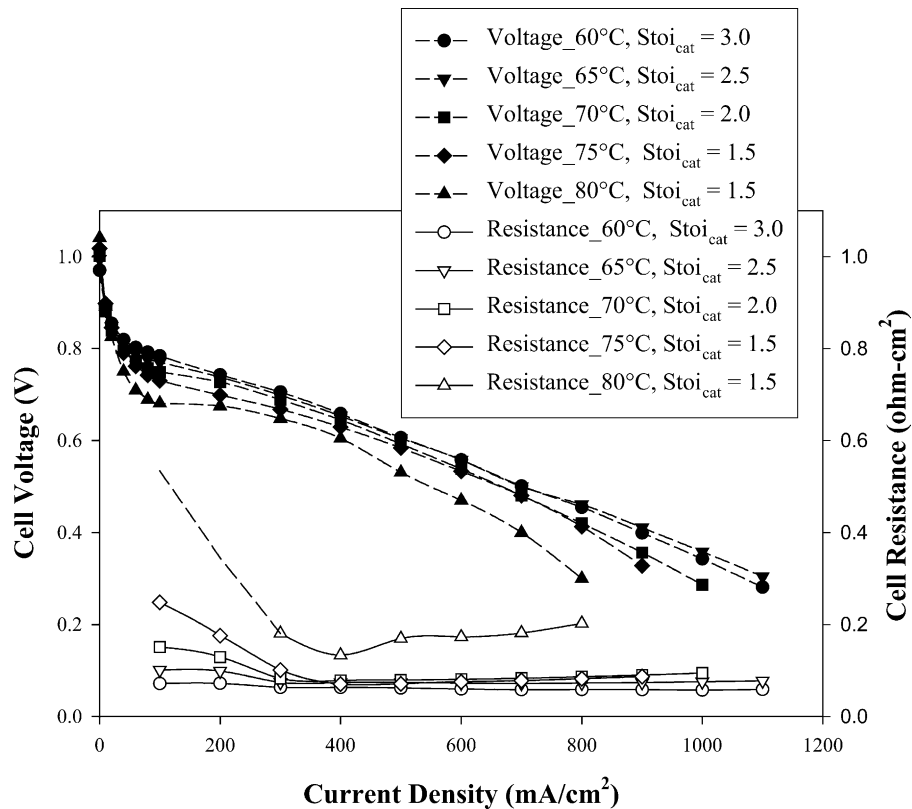


Fig. 5. Cell voltage and cell internal resistance at the optimum cathode stoichiometry for maximum performance under “dry operation” (no external humidification) at each cell temperature: the in-house GDL MEA, hydrogen/air, 1 atm, at anode stoichiometry of 1.3. ( $\text{Stoi}_{\text{cat}}$  refers to cathode stoichiometry.) Membrane resistance shown as a “dashed” line at below  $300 \text{ mA/cm}^2$  for the  $80^\circ\text{C}$  condition is where the cell is very dry and the measured membrane resistance is not accurate.

resistance with increasing current density up to  $400 \text{ mA/cm}^2$  is for the same reason mentioned in discussing Fig. 3.

Table 3 summarizes cell voltage at  $400 \text{ mA/cm}^2$ , cell internal resistance, cathode stoichiometry, cathode exit relative humidity, and average oxygen partial pressure at the optimum conditions. The optimum conditions are also shown as “solid circles” on the calculation results of Fig. 4a and b. The maximum cell performance at different temperatures (each was operated at its own optimum cathode stoichiometry) is similar to each other at temperatures between  $60$  and  $75^\circ\text{C}$ . Membrane ionic resistance among those temperatures is also close to each other: between  $0.0634$  and  $0.0794 \Omega \text{ cm}^2$  at be-

tween  $60$  and  $75^\circ\text{C}$ , respectively, which equates to at most a  $6 \text{ mV}$  difference at  $400 \text{ mA/cm}^2$ . All optimum performances were experimentally found to be at the cathode stoichiometry which gives an exit RH of about  $60\%$ . The slightly lower maximum cell performance at higher temperature is attributed to the decreasing average oxygen partial pressure (when the relative humidity remains fairly constant).

However, there is a significant drop in cell performance when the cell temperature increases further to  $80^\circ\text{C}$ . At this temperature, the exit cell relative humidity cannot reach  $60\%$  (does reach  $50\%$ ) even at the minimum cathode stoichiometry of  $1.5$ .

Table 3

Summary of optimum cathode stoichiometry and performance in dry operation (with no external humidification on both anode and cathode) at different temperatures using the in-house GDL MEA

$T_{\text{cell}}$ ( $^\circ\text{C}$ )	Nomenclature $T_{\text{cell}}/T_A, \text{Hum}/T_C, \text{Hum}$	Cell voltage @ $400 \text{ mA/cm}^2$ (V)	Cell internal resistance ( $\Omega \text{ cm}^2$ )	Optimum cathode stoichiometry	Optimum anode stoichiometry	Cathode exit RH (%)	Average oxygen partial pressure (atm)
60	60/Dry/Dry	0.658	0.0634	3	1.3	62	0.169
65	65/Dry/Dry	0.654	0.074	2.5	1.3	59	0.161
70	70/Dry/Dry	0.645	0.0784	2	1.3	58	0.147
75	75/Dry/Dry	0.629	0.0794	1.5	1.3	61	0.123
80	80/Dry/Dry	0.605	0.1334	1.5	1.3	50	0.123



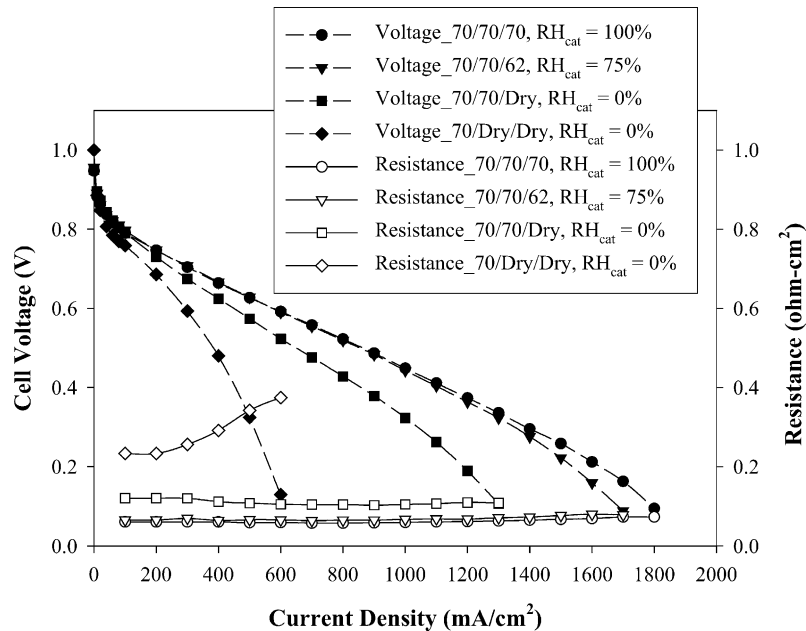


Fig. 6. Cell voltage and cell internal resistance at various humidification levels: the E-TEK GDL MEA (cathode GDL is E-TEK.V.2.11 carbon cloth), 70 °C, hydrogen/air, 1 atm, high stoichiometry, anode stoichiometry of 3 and cathode stoichiometry of 4, the temperatures listed in the legend are in °C. ( $T_{\text{cell}}/T_{\text{anode humidifier}}/T_{\text{cathode humidifier}}$ , “Dry” refers to no external humidification of the inlet gas, RH<sub>cat</sub> refers to cathode inlet relative humidity).

Optimum cathode stoichiometry at each temperature was that which gives cathode relative humidity of about 60%. When the relative humidity gets lower than 60%, there is a sharp drop in cell performance because the ionic resistance both in the membrane and in the electrodes of the Nafion<sup>®</sup>-based MEA becomes so predominant that high cell performance cannot be obtained. It is important to mention that the optimum relative humidity depends on the flow field design, single-serpentine in this case.

### 3.4. Comparison of MEA performance with different cathode GDLs

Fig. 6 shows cell voltage and cell internal resistance at different humidification levels at 70 °C cell temperature; similar to Fig. 2, but with the E-TEK GDL MEA. The E-TEK GDL MEA was prepared in a similar manner as the in-house GDL MEA with the only difference being the E-TEK.V.2.11 carbon cloth cathode GDL (see Table 1).

Unlike the in-house GDL MEA, the E-TEK GDL MEA performs best at saturated conditions (70/70/70) because the ionic conductivity is at the highest with water saturation while the E-TEK GDL helps avoid flooding and prevents oxygen mass transport losses. The high hydrophobicity of the E-TEK GDL avoids flooding better than the in-house GDL. As the cathode inlet relative humidity decreases to 75% at the 70/70/62 condition, there is hardly any difference in performance until very high current densities (more than 1000 mA/cm<sup>2</sup>).

However, the performance of the E-TEK GDL MEA is lower than the in-house GDL MEA at conditions with less in-

let humidification. At the 70/70/Dry condition, the cell voltage is 37 mV lower at 400 mA/cm<sup>2</sup>. At the 70/Dry/Dry condition, the cell voltage is only 14 mV lower at 400 mA/cm<sup>2</sup>, but the difference grows significantly larger at a higher current density of 600 mA/cm<sup>2</sup> (220 mV) where the cell stops performing. (The in-house GDL MEA can operate up to 900 mA/cm<sup>2</sup>, refer to Fig. 2).

The membrane resistance is similar at the two near-saturated conditions of 70/70/70 and 70/70/62 (0.05 Ω cm<sup>2</sup>).

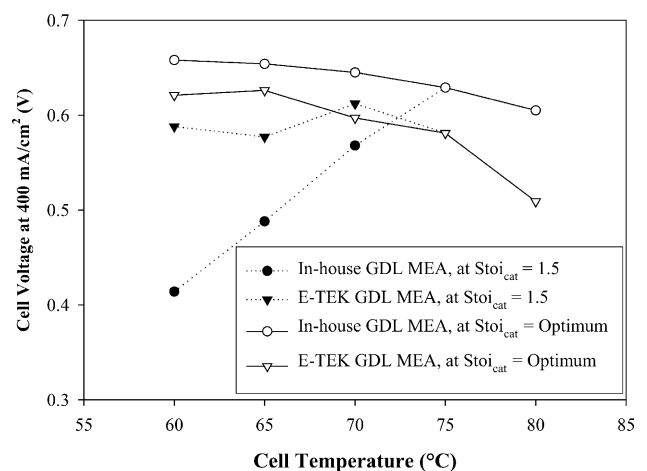


Fig. 7. Comparison of cell voltage at 400 mA/cm<sup>2</sup> between the in-house GDL MEA and the E-TEK GDL MEA under “dry operation” (no external humidification) as a function of operating temperature, anode stoichiometry of 1.3; “solid” symbols are at cathode stoichiometry of 1.5 and “empty” symbols are at optimum cathode stoichiometry for maximum cell performance under dry operation (from Table 3).

At the 70/Dry/Dry condition, the membrane resistance increases more significantly with current density causing the cell to stop performing at 600 mA/cm<sup>2</sup>. The sharp increase in cell resistance with current density indicates cell “dry-out”.

Similar sets of experiments that were conducted with the in-house GDL MEA (Figs. 3 and 5) were also conducted for the E-TEK GDL MEA to evaluate the influence of cell temperature and stoichiometric flow rates to cell performance in dry operation with the E-TEK GDL.

Fig. 7 is a plot of cell voltage at 400 mA/cm<sup>2</sup> of the in-house GDL MEA compared to the E-TEK GDL MEA at different temperatures, all with no external humidification and at the anode stoichiometry of 1.3. The “solid” symbols are from the two cells at constant cathode stoichiometry of 1.5. The “empty” symbols are from the two cells at various

cathode stoichiometry optima at different cell temperatures: 3, 2.5, 2, 1.5, and 1.5 for the 60, 65, 70, 75, and 80 °C, respectively. The performance of the in-house GDL MEA and the E-TEK GDL MEA at the near-saturated condition of 70/70/62 is very similar to each other at 0.674 and 0.662 V, respectively, at 400 mA/cm<sup>2</sup> (from Figs. 2 and 6). However, at dry conditions the performance of the two cells differs significantly.

At a fixed cathode stoichiometry of 1.5 (Fig. 7, “solid” symbols), the E-TEK GDL MEA outperforms the in-house GDL MEA at lower temperatures (60–70 °C), while the in-house GDL MEA outperforms the E-TEK GDL MEA at higher temperatures (75–80 °C). The E-TEK\_V.2.11 carbon cloth prevents “flooding” better than the in-house GDL at higher relative humidity (or low temperature), while the

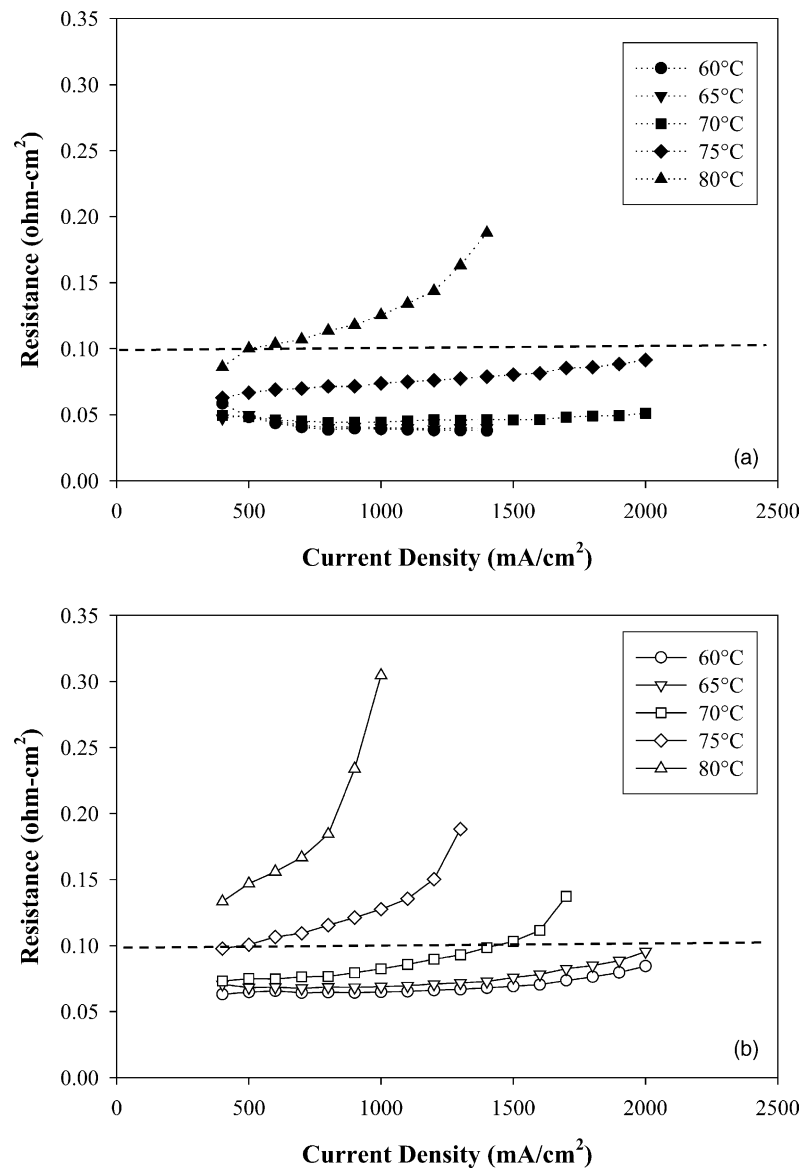


Fig. 8. Cell internal resistance under “dry operation” (no external humidification) at different cell temperatures, low stoichiometry, anode stoichiometry of 1.3 and cathode stoichiometry of 1.5: (a) the in-house GDL MEA (b) the E-TEK GDL MEA.

in-house GDL prevents cell “dry-out” better at lower relative humidity (or high temperature).

At the optimum cathode stoichiometry (Fig. 7, “empty” symbols) where there is a balance between the average oxygen mole fraction and the cell relative humidity, flooding is not significant so the in-house GDL outperforms the E-TEK GDL at all temperatures under dry operation.

Fig. 8a and b show membrane ionic resistance of the in-house GDL MEA and the E-TEK GDL MEA, respectively, as a function of current density at different temperatures between 60 and 80 °C, all at an anode stoichiometry of 1.3 and a cathode stoichiometry of 1.5. A horizontal line of 0.10 Ω cm<sup>2</sup> in each figure is a reference line added for easier comparison of resistance values between the two plots. It is clear that the E-TEK GDL MEA has higher membrane resistance than the in-house GDL MEA at all conditions. Resistance values of the E-TEK GDL MEA also increase more significantly with current density than those of the in-house GDL MEA, which remain relatively constant with current density except at the 75 and 80 °C conditions.

When constant stoichiometry is used (as in the case of this study) higher current densities mean higher inlet gas flow rates that can cause more cell “dry-out”. At the cell inlet area, there is the highest amount of dry inlet flow and the least amount of accumulated water produced. Thus, cell “dry-out” is likely to happen at the inlet more than any other areas of the cell causing non-uniform membrane resistance throughout the cell active area. The in-house GDL MEA is

more suitable for dry operation than the E-TEK GDL MEA with less membrane resistive loss and less inlet “dry-out”.

### 3.5. System analysis for the dry operation

Mallant [17] presented an analysis of fuel cell system complexity by considering water and heat management issues in running a fuel cell system at different operating conditions. The system included a fuel cell stack, inlet gas compressors, inlet gas humidifiers, exit gas condensers, and heat exchangers. The analysis was based on real elemental cell performance (operating on pure hydrogen and air) which was scaled up to a stack size for the calculation. Net power output, stack heat production, duty condenser, net cooling duties, and relative pressure drop factor were presented. These parameters provide practical fuel cell operating conditions.

Mallant’s algorithm was applied to the results obtained in this work so to compare practical fuel cell operation at saturated conditions with dry conditions. The elemental cell performance at saturated conditions used in the analysis was from the published “state-of-the-art” commercial MEA performance of various companies [18–20]: DuPont Fuel Cells, (Wilmington, DE), 3M (St. Paul, MN), and Gore Fuel Cell (Elkton, MD). The elemental cell performance at dry operations used in the analysis was from the performance at the optimized conditions presented in this work (Table 3). The calculation steps were taken from Mallant [17] where elemental cell performance from 5 to 7 cm<sup>2</sup> MEA active

Table 4

Summary of system evaluation calculation results comparing operation at saturated conditions and operation at dry conditions.

	Units	UConn <sup>a</sup>	UConn <sup>a</sup>	UConn <sup>a</sup>	DuPont MEA <sup>b</sup>	3M MEA <sup>c</sup>	Gore 56 MEA <sup>d</sup>
Operating conditions							
Cell temperature	°C	60	70	80	65	70	70
Cell pressure	atm	1	1	1	1	1	1
Inlet cathode RH	%	0	0	0	100	100	100
Air stoichiometry	–	3	2	1.5	1.7	2.5	2
Hydrogen stoichiometry	–	1.3	1.3	1.3	1.25	1.5	1.2
Operating current density	A/cm <sup>2</sup>	0.4	0.4	0.4	0.4	0.4	0.4
Operating voltage	V	0.658	0.645	0.605	0.75	0.78	0.73
Calculation results							
Stack power obtained	kW	32	31	29	36	37	35
Air compressor power losses	kW	0.6	0.4	0.3	0.4	0.5	0.4
Humidifier work required	kW	NR <sup>e</sup>	NR <sup>e</sup>	NR <sup>e</sup>	–14	–28	–22
Total stack heat production	kW	28	28	30	33	32	34
Condenser heat production	kW	NR	NR	NR	5	19	14
Summary							
Net power (normalized <sup>f</sup> )	kW	29	28	27	34	30	35
Net cooling duty required	kW	28	28	30	24	23	24
Net non-stack duty required	kW	28	28	30	52	79	68
Cell efficiency <sup>g</sup>	%	53	52	49	60	63	59

<sup>a</sup> From the elemental cell performance reported in Table 3.

<sup>b</sup> From [18].

<sup>c</sup> From [19].

<sup>d</sup> From [20].

<sup>e</sup> NR stands for “not required”.

<sup>f</sup> Normalized to a hydrogen stoichiometry of 1.2.

<sup>g</sup> Cell efficiency calculated based on the lower heat value of hydrogen (240 kJ/mol).

area cells was used for stack calculations of 12 m<sup>2</sup> in total active area.

Table 4 shows all input parameters, calculation results, and important parameters in summary. “Operating conditions” include air stoichiometry, hydrogen stoichiometry, operating current density, and operating cell voltage obtained from experimental polarization curves [18–20] at 400 mA/cm<sup>2</sup>. “Calculation results” include stack power, air compressor power losses, humidifier work required, total stack heat production, and condenser heat production. All results except stack power are heat and energy requirements that need to be managed for the cell to maintain a certain operating condition. The required humidifier work is negative because heat consumption is needed to maintain the humidifiers at a certain temperature (not heat production by the system that needs to be removed). Net power normalized to hydrogen stoichiometry is calculated from the cell performance (voltage, current density, and total cell area) and is normalized to the same hydrogen stoichiometry to have the same cost.

All commercial MEAs operated at saturated conditions show 10–17% higher net power output (30–35 kW) when compared to that obtained from dry operation (27–29 kW). Net cooling duty required by the dry operation (28–30 kW) is 22–25% higher than that of the commercial MEAs operated at saturated conditions (23–24 kW). Some of the heat produced from the stack is used to heat up the humidifiers resulting in lower net cooling duties. While humidifiers can be managed to consume the waste heat produced from the stack and the condensers, they are not always desirable due to the added complications and more stringent controls of heat flow in the overall system. The net non-stack duty required (second to last row of Table 4) shows the total non-stack duty which is the sum of all duties which do not add to the system net power output, but are required to be managed to maintain each operating condition: air compressor power, humidifier work required (absolute value), stack heat release, and condenser heat production. If the net non-stack duty has a lower value the system is less sophisticated. Dry operation has 46–62% less total non-stack duty when compared to commercial operation at near-saturated conditions (28–30 kW compared to 52–79 kW).

Furthermore, less equipment is required for dry operation since no humidifiers and condensers are needed.

#### 4. Conclusion

Two cells with a similar in-house composite membrane, but with different cathode GDLs have been used to evaluate feasibility of fuel cell operation with no external humidification. The in-house GDL is better at preventing cell “dry-out” while the E-TEK\_V.2.11 carbon cloth GDL is more hydrophobic.

The influence of inlet humidification levels on fuel cell performance was evaluated. Removing the cathode humidification from both cells while maintaining the inlet an-

ode saturated causes little cell performance loss (5–6% at 400 mA/cm<sup>2</sup>). As the inlet humidification is removed from both the anode and the cathode, the cell temperature and the inlet gas stoichiometry have significant influence on the cell performance. Too high of a cell temperature causes too low of an exit cathode relative humidity in the cell, but too low of a temperature may lead to “flooding”. Since the saturated vapor pressure of water exponentially increases with cell temperature, there is an optimum temperature window for maximum performance. Too high of a flow stoichiometry causes cell “dry-out” while too low of a flow stoichiometry results in an oxygen partial pressure that is too low causing mass transport losses.

Conditions, in terms of cell temperature and cathode stoichiometry, for maximum cell performance for dry operation have been found. At constant stoichiometry, at a cell temperature of 75 °C the saturated vapor pressure is high enough to avoid flooding while the cell relative humidity is still high enough to have high proton conductivity. Different cathode stoichiometry optima for maximum cell performance have been found for different operating temperatures while the anode stoichiometry was maintained constant at a practical value of 1.3. The cathode stoichiometry optima are 3, 2.5, 2, 1.5, and 1.5 for the cell temperature of 60, 65, 70, 75, and 80 °C, respectively. The cell relative humidity at these optimum conditions at different temperatures was found to be about 60%. The Nafion<sup>®</sup>-based MEA (with Nafion<sup>®</sup>-based composite membrane and Nafion<sup>®</sup> in the electrode layers as the proton conductor) can be used with no significant resistive loss when the cathode exit relative humidity is higher than 60%.

The in-house GDL shows superior performance at low relative humidity conditions, while the higher hydrophobicity of the E-TEK GDL shows superior performance at saturated inlet conditions. Using the in-house GDL enables dry operation with a small power output loss compared with saturated conditions.

An overall system analysis was conducted to compare fuel cell operation at selected saturated conditions with that at dry conditions using the experimental performance obtained in this work. When the operating temperature, the cathode stoichiometry, and the MEA are optimized, dry operation can be effective. The net power output is reduced by at most 17% while the total non-stack duty is cut by over 46% and the humidifiers and condensers are eliminated making the system a lot simpler and more efficient. To increase the efficiency of a fuel cell operated in a dry condition, the cell can be run at a lower current density, but with a cost increase due to a bigger stack that is needed for the same total power.

While this work shows positive polarization curve results under dry operation for 5 cm<sup>2</sup> elemental cells, scale-up of a membrane electrode assembly for dry operation is expected to raise more serious difficulties than the scale-up of an MEA for near-saturated conditions. Difficulties may also include flow field design [6] (to avoid local “dry-out” in the cell, especially at the inlet), startup and shutdown procedures,

cell endurance, and a lack of thorough research data. Nevertheless, this work shows that it is possible to run a fuel cell with no external humidification with little loss compared to saturated operation as long as critical parameters are optimized.

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