Transient Behavior of a Proton Exchange Membrane Fuel Cell under Dry Operation

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The transient behavior of a polymer exchange membrane fuel cell (PEMFC) with dry gases fed in is investigated in this paper. Periodical ramp sweeps were applied to the fuel cell. When dry gases are fed into the fuel cell, the drying out effect of the polymer electrolyte is measured during the sweep process. The polarization curve of the fuel cell and time-dependent membrane resistance is shown. A hysteresis effect of the fuel cell polarization curve is found. The “threshold”, defined as the match point of the forward and backward sweep current–voltage curve is introduced. In this paper, threshold indicates the status of the fuel cell membrane hydration. The transient behavior during load change is investigated when dry gases are fed into the fuel cell. The comparison between the ramp sweep and the step sweep experiments shows that the fuel cell could run stable at the threshold current density under a specific operating condition.

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During the past decade, proton exchange membrane fuel cells (PEMFCs) have been paid more and more attention in the research and development field. PEMFCs are on the way to the real market production. Although more and more research results on fuel cells have been published, most fuel cell investigations focus mainly on fuel cell steady-state behavior. In practical operation, the behavior of the PEMFC is not stationary but dynamic. When fuel cells experience a transient change, i.e., start-up, shut-down, load change, temperature change, and gas flow turbulence, etc., the performance of the fuel cells also changes. This transient operation may have some impact on fuel cell applications. Therefore, it is necessary to investigate the transient response in fuel cell applications. Recently, there has been growing interest in dynamic and transient behaviors of PEMFCs, and some researchers have published their investigative results in the dynamic behavior investigation of PEMFCs.1–5

Operating PEMFCs fed with dry gases will be an advantage in PEMFC applications. Proper hydration of the membrane electrode assembly is a critical factor in PEMFC operation. Stable operation with dry gases is one of the aims which fuel cells developers and researchers are pursuing now.6–11

For the PEMFC dynamic and transient behavior study, Hamelin and co-workers7 found the hysteresis phenomena in an MK5 fuel cell stack at 72°C when they measured the polarization curve with positive and negative load increments of 5 A every 0.15 s. In their experiments, the air and hydrogen are totally humidified inside the stack. They showed that the negative load increment is always higher than the positive load increment. They explained the phenomena related to the membrane conductivity via its water content, the water transmitted to the membrane from the humidified gases, which should be fairly constant for a given set of temperature and pressure.12 When the load increases, the water content of the membrane takes some time to reach equilibrium because the production rate is time-dependent. This results in a lower polarization curve. When the load decreases, the membrane contains the water required for efficient proton conductivity. Thus, they observed a higher polarization curve. They found that the hysteresis is reproducible during the load commutations.

Atkins et al.13 studied the PEMFC performance when dehydration of MEA occurs. They observed strong periodic fluctuations in current and cell resistance as the feed stream humidification level is diminished. They proposed that the fluctuation is due to the process involving cyclic hydration and dehydration of the anode. Kim and co-workers14 investigated reservoir and dilution effects on the dynamic behavior of a PEMFC. The fuel cell was fed in with humidified gases at fixed flow rates.

In a fuel cell, when operating conditions change, the interface of the electrochemical reaction shifts. To date, only the simulation result13 and ex situ measurement give the evidence of a three-phase interface shift.15 In HClO4 solution, Kamamura and co-workers16 conducted Fourier transform infrared (FTIR) measurements. They found that hydrophilic and hydrophobic domains at the interface between the Pt electrode and the Nafion membrane can be easily changed by a humidity change. During fuel cell operation the reaction interface could shift when the operation conditions change. The interface between the electrode and the membrane is not static but dynamic. Most of the research work on the dry operation is aimed at achieving stability of operation without external humidification of the fuel gases.

The transient behavior of a PEMFC fed with dry gases is studied in this paper. The aim is to understand the possibility of the stable operation with dry gases fed in.

Experimental

Test fuel cell.—The test fuel cell is a single cell which is composed of meander-shaped flow fields machined in graphite plates both on the cathode and anode side. The PRIMEA 5510 with 25-μm membrane thickness by Gore and TGP-H-060 by Toray (0.20 mm in thickness, no poly(tetrafluoroethylene) are used as the membrane electrode assembly (MEA) and the gas diffusion layer (GDL), respectively, unless otherwise noted. The active area of the MEA is only 1 cm2. The gas in the flow field is then assumed to be distributed evenly.

Test stand.—The Solartron 1286 electrochemical interface and 1255 HF frequency response analyzer are connected to the test fuel cell. The load of the test fuel cell is controlled by Solartron. The fluxes of the reactants (hydrogen and air) flows are controlled by digital mass flow controllers (series EL-Flow from Bronkhorst High-Tech. B.V. Netherlands). When the fuel cell operates in wet mode, before the gases are fed into the test fuel cell, they pass through the stainless steel humidifiers in which the water temperature could be controlled by the test software. The humidity sensors are Rotronic Hygrometer 1-155°C, by Rotronic Messgeraete GmbH. The pipes from the humidifiers to the test fuel cell are heated by heating wires. When the humidified gases are fed in, the temperature of the gas lines controlled by the test software is always 2°C higher than the temperature of the test fuel cell to prevent condensation of water from the reactant streams in the gas pipes.
The Fisherbrand FBC 720 is connected to the cooling channel of the test fuel cell at the cathode side, and the test fuel cell could be kept isothermal during the measurement. The fuel cell test software is programmed based on LabView 7.0, from National Instruments. All the experimental parameters, i.e., cell voltage, current density, gas flow rate, and test cell temperature, are controlled by the software.

The fuel cell test is performed in potentiostatic or galvanostatic mode. Typically, a voltage is imposed on the cell and the load is varied to maintain it. The LabView based data acquisition system can be used to automatically generate fuel cell polarization curves. The resistance of the MEA is measured at 10 kHz during fuel cell operation.

Contact angle measurements.—To get the liquid water transport properties of the gas diffusion media, contact angle measurements are performed for different gas diffusion media samples. The samples are at least 3 × 3 cm to avoid significant changes of the sample surface. The contact angle is measured by the optical contact angle measurement system OCA 20, from DataPhysics Instruments GmbH. For each measurement, a 15-μL deion water droplet is dropped by placing the tip of the syringe close to the sample surface. The contact through angles of GDLs are obtained the software of the contact angle measurement system.

Results and Discussion

Ramp sweep measurement.—Before the dry hydrogen and air are fed in, the test fuel cell is conditioned with humidified hydrogen and air. Then, the gas is switched to dry gases for the designed ramp sweep measurement. During the ramp sweep measurements, the cell voltage or current is varied periodically between the upper and lower limit with fixed gas flow rates on the anode side and the cathode side. The transient behavior of the fuel cell is studied by means of dynamic sweeps. The illustrations of the “forward” and “backward” sweep are given in Fig. 1, in which “forward” means from high cell voltage to low cell voltage or from low current density to high current density. “Backward” means from low cell voltage to high cell voltage or from high current density to low current density, respectively.

In Fig. 1, the forward sweep is indicated by dark squares and the backward sweep is indicated by blank circles. During the forward sweep the amount of water that is removed by the gases reduces the self-humidification of the membrane. The proton conductivity of the membrane is not as high as for a fully hydrated membrane. During the backward sweep, with more humidity inside the MEA, the proton conductivity of the membrane is higher than during the forward sweep in the same cell-voltage region. In Fig. 1, it can be seen that there is a point marked with a star designating the intersection of Forward and backward sweep, when the fuel cell operates under dry gases. This point is called the threshold. During the forward sweep, the drying out effect of the MEA is the dominant factor before the threshold current density. After the threshold the water generated makes the MEA fully humidified and even flooding occurs. During the backward sweep, when the current remains higher than the threshold and excess liquid water has accumulated inside the MEA, the fuel cell still has mass-transport limitation. When the sweep passes through the threshold toward the low-current-density region, the water production rate reduces and the flooding effect disappears, but the membrane maintains a higher hydration status than during the forward sweep. This results in a higher fuel cell performance as compared to the forward sweep process.

During the ramp sweep process, the resistance of the membrane is measured at 10 kHz. The time-dependent cell voltage, current, and membrane resistance are shown in Fig. 2. In Fig. 2, the fuel cell runs at 40°C, ambient pressure, with a gas flow of 25 and 50 mL/min on the anode and cathode side, respectively. The MEA resistance is the upper triangle. At the beginning when the measurement starts, the membrane resistance shows a very high peak because it is switched from humidified to dry gases. As the sweep proceeds, water generated as the product of the electrochemical reaction makes the membrane hydrated. The membrane resistance reduces to between 0.05 and 0.07 Ω cm². From the second sweep cycle onward, the membrane resistance shows periodic behavior in the range between 0.05 and 0.07 Ω cm². This corresponds to the periodic voltage and current sweep. In the high-current-density region, compared with the threshold, flooding occurs. Furthermore, because more liquid water accumulates, the reactant gases have a high mass-transport resistance. This effect leads to mass-transport limitation, as can be seen in the current–voltage (I–V) curve.

It can be seen that the change of the cell resistance shows a strong hysteresis effect. In the backward ramp sweep, the water production rate decreases but the water accumulated inside the MEA affects on the membrane conductivity. Therefore, during the backward-ramp sweep, the hysteresis effect is observed.

At the beginning of the experiment, a strong increase of the cell resistance is observed, which is caused by the preconditioning of the fuel cell. Before the test cell operates under dry gases, fully humidified gases are fed in for the test cell preconditioning. Then, the dry gases are fed in. When operating close to the open-circuit voltage, the fuel cell can hardly maintain a steady-state operation under dry gases. At the beginning while the dry gases are fed in, the membrane...
has a drying out effect which is reflected in the high cell resistance of the first sweep cycle. Although there is a strong increase in the cell resistance at the beginning of the experiment, a decrease in cell resistance is achieved during the course of the experiment. During the backward sweep, the cell resistance remains at a low level. In the following second sweep cycle, the cell resistance begins to show a slight change. The subsequent cycles are identical to the second one. Then, the fuel cell shows a dynamic equilibrium operation.

The influence of the liquid water accumulation on the electrochemical reactions can be seen from the simulation results. According to the simulation result, in the membrane the fraction of expanded channels is negligible at the beginning of the first cycle. The liquid water saturation is still low at the highest current density when the forward sweep is performed. The accumulation of liquid water increases during the backward sweep, and the cell resistance increase indicates the membrane is hydrated. This leads to the observed hysteresis behavior. Compared with the lower current density region (less membrane hydration) and higher current density region (flooding possibility), threshold is a good point to operate the fuel cell under dry gases, it is able to get a hydrated membrane and without flooding.

**Analysis of the threshold for Gore 5510 (25 μm) and Toray paper.**—As the threshold is related to the fuel cell operating conditions, there are some factors which could take effect on the location of the threshold. In this section, different sweep rates (sweep durations), different temperatures, and different gas flow rates are applied to analyze their effect on the threshold and hysteresis. Unless it is specified in the paper, the measurements use Gore Primea 5510 as MEA and Toray paper as GDL in the test cell.

**Sweep rate.**—In Fig. 3, the test cell runs at 50°C, and gas flow rates on the cathode side (air) and the anode side (hydrogen) are 40 and 20 mL/min, respectively. The differences are the ramp sweep rate, 5, 10, and 20 mV/s, respectively. The test cell runs under potentiostatic ramp mode, and the sweep range is 0.05–0.85 V. In Fig. 3, the thresholds for 20, 10, and 5 mV/s are marked Threshold_{20} (846 mA/cm², 0.492 V), Threshold_{10} (743 mA/cm², 0.537 V), and Threshold_{5} (716 mA/cm², 0.564 V), respectively.

**Thresholds are 40 and 20 mA/s, respectively.** For a galvanostatic sweep, a similar trend is shown in Fig. 4 where the sweep range is 0–1400 mA/cm². In Fig. 4 there are three different sweep rates—10, 20, and 40 mA/s—the corresponding thresholds are Threshold_{10} (915 mA/cm², 0.518 V), Threshold_{20} (930 mA/cm², 0.507 V), and Threshold_{40} (1025 mA/cm², 0.443 V). The sweep durations of each cycle are 280, 140, and 70 s for the three different sweep rates, 10, 20, and 40 mA/s, respectively.

Because the test cell runs with dry gases, the highest cell resistance should appear at the highest cell voltage (lowest current density). The time-dependent resistance curve, however, shows the hysteresis effect. This is due to the water transport delay in the cell (see Table I). In Table I, it is shown that the time delay expressed as $\Delta T(I_{\text{max}}-R_{\text{max}})$ and $\Delta T(I_{\text{max}}-R_{\text{min}})$ reduces with increased sweep rate. The hysteresis effect becomes weak. Because these four measurements are only different from each other on the sweep rate, the difference is caused only by the difference in drying out time. The maximum cell resistance is inversely proportional to the sweep rate. The minimum cell resistances are almost close to the fully humidified membrane resistance, because the cell resistance does not reduce further.

From the I-V curve, the threshold current density is getting higher when the sweep rates become faster. When the wet gases are fed in, no such hysteresis I-V curve is observed. The phenomenon can be explained as the membrane drying out effect becomes weak when the duration of the cell exposed to the dry gases becomes shorter. In Fig. 5a-c which corresponds to the measurement of Fig. 3, the time-dependent cell resistance and current trends are shown separately.

**Gas flow effect.**—Figure 6 shows the effect of different gas flow rates on the threshold changes. The operating conditions are 30°C, sweep rate 5 mA/s. Different gas flow rates are applied on the cathode side and the anode side, respectively. From Fig. 6a, it can be seen that with the increase of the gas flow rate, the threshold current density moves to a higher value. In Fig. 6b the cell resistance shows the reason. With the highest gas flow rate case 1 shows the highest cell resistance 0.15 Ω, resulting in the corresponding threshold in Fig. 6a showing a high value of 920 mA/cm². This concludes that

**Table I. Hysteresis of the cell resistance.**

<table>
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<tr>
<th>Sweep rate (mV/s)</th>
<th>20</th>
<th>10</th>
<th>5</th>
</tr>
</thead>
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<tr>
<td>$R_{\text{max}}$(Ω)</td>
<td>0.0552</td>
<td>0.0556</td>
<td>0.0625</td>
</tr>
<tr>
<td>$R_{\text{min}}$(Ω)</td>
<td>0.0460</td>
<td>0.0470</td>
<td>0.0460</td>
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<tr>
<td>$\Delta T(I_{\text{max}}-R_{\text{max}})$</td>
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<td>17</td>
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<tr>
<td>$\Delta T(I_{\text{max}}-R_{\text{min}})$</td>
<td>18</td>
<td>51</td>
<td>102</td>
</tr>
</tbody>
</table>
case 1 easily has the membrane drying out effect. Another possible reason is that the liquid water can be removed from the MEA and the GDL. Then the water-transport-driven pressure becomes less. Therefore, the fully hydrated region of the membrane decreases under the dry gases.

**Temperature effect.**— In Fig. 7a and b, the fuel cell operating conditions are gas flow rate 50 mL/min for air on the cathode side and 25 mL/min hydrogen on the anode side. The sweep rate is 10 mV/s. For the clarity of the figure, only the identical curves after the 2nd cycle of each measurement are plotted. The comparison between 30, 40, and 50°C fuel cell temperature is shown. In Fig. 7a, the 30°C I-V curve approaches its Threshold at 537 mA/cm², 0.605 V, the 40°C I-V curve approaches its Threshold at (778 mA/cm², 0.453 V), and the 50°C I-V curve approaches its Threshold at (1072 mA/cm², 0.409 V).

The lower current density of Threshold is due to the low electrochemical reaction rate, less drying out effect, and earlier flooding region of the sweep. The width of the 50°C curve shows a stronger drying out effect before its threshold. From Fig. 7b, it can be seen that the 50°C measurement shows the highest cell resistance, because the drying out effect becomes stronger at higher temperature. Therefore, the 50°C forward sweep shows the lowest fuel cell performance before 600 mA/cm², although the high temperature benefits the electrochemical reaction.

**Different GDLs.**— From the above experiments, the threshold shows the hydration status of the MEA. The hysteresis in the current density is caused by an increase in the mass-transport limitation on the cathode side. The reason is the accumulation of water on the cathode side. For different GDLs, the threshold could be used to compare the water management characteristic during fuel cell dry operation.

In Fig. 8, there are three different GDLs used to understand the threshold location and gas transport properties in the test fuel cell. The three GDLs are Toray carbon paper, Toray carbon paper + a microporous layer, and SGL 20 BC + a microporous layer. Contact angle measurements are implemented to understand the hydro-
Phobicity of the GDLs. The measured contact angles for the Toray paper, microporous layer, and SGL 20 BC are 131.9, 138.7, and 145.6°C, respectively. From the contact angle values, it can be concluded that the SGL 20BC is the most hydrophobic GDL, while the Toray paper has the minimum hydrophobicity. From the open-circuit voltage, it can be seen that the SGL 20 BC with an additional microporous layer shows the highest open circuit voltage, the Toray paper with an additional microporous layer shows the second-best open-circuit voltage, and with only Toray paper the open-circuit voltage is the lowest one.

From Fig. 8, a trend is shown that the low contact angle leads to a low threshold current density, i.e., Toray. For the high hydrophobicity SGL 20 BC + microporous layer, there is no threshold even when the test cell runs at 1200 mA/cm². The high hydrophobicity results in good gas transport passages which can keep the GDL from liquid water flooding. Therefore, the liquid water concentration is lower at the three-phase interface inside the MEA. When the test cell runs under dry gases, if there is insufficient liquid water or water vapor, the membrane can easily dry out; therefore, no threshold could be observed. The higher the contact angle, the more hydrophobic is the medium. Hydrophobicity is a property that leads to a strong driving force pushing liquid water out of the GDL. As a consequence, the flooding effect is reduced. The SGL 20BC does not show any flooding. The lower part of the “8” is missing. Therefore, if a less hydrophobic GDL is used for dry gas operation, it will benefit the membrane with respect to the drying out effect under a certain operating condition. Then, it is possible for the fuel cell to maintain a stable performance under the dry gases.

Different membrane thicknesses.— The water content in the polymer membrane also has impact on the threshold location. In Fig. 9, two catalyst-coated membranes with different thicknesses exhibit a difference of the threshold location. The 25-µm-thick membrane with low water content shows a lower Threshold₂₅ current density (920.7 mA/cm², 0.1099 V), while the 35-µm-thick membrane with higher water content has a higher threshold current density (1013 mA/cm², 0.2058 V).

Step sweep under dry gases.— Besides the ramp sweep tests of the test cell, Fig. 10a, a step sweep is also implemented in the test cell, Fig. 10b. Both Fig. 10a and b are measured at 50°C, with dry air 50 mL/min on the cathode side and dry 25 mL/min hydrogen on the anode side. Sweep rate 10 mV/s.

Figure 7. (a) Influence of temperature on the threshold: Threshold₃₀ (537 mA/cm², 0.605 V), Threshold₄₀ (778 mA/cm², 0.453 V), and Threshold₅₀ (1072 mA/cm², 0.409 V). (b) Cell resistance during the sweep process at different temperatures. Gas flow 50 mL/min dry air on the cathode side, and 25 mL/min dry hydrogen on the anode side. Sweep rate 10 mV/s.

Figure 8. Thresholds of different GDLs. Test cell temperature 30°C, sweep rate 20 mA/s. Gas flow rates 200 mL/min air on the cathode side, 100 mL/min hydrogen on the anode side, respectively. Threshold₃ₐ (738 mA/cm², 0.574 V), Threshold₃ₐ+₅ (1037 mA/cm², 0.366 V), and Threshold₃ₐ+₅ > 1200 mA/cm².

Figure 9. Thresholds of different membrane thicknesses. Cell temperature 30°C, dry gas. Sweep rate 5 mA/s. Gas flow rates are 400 mL/min on the cathode side, 200 mL/min on the anode side, respectively. Membrane thicknesses are 25 and 35 µm, respectively. Threshold₃ₐ (920.7 mA/cm², 0.1099 V), and Threshold₃ₐ > 1013 mA/cm², 0.2058 V.)
gen on the anode side. In Fig. 10a, the threshold is shown as (712 mA/cm², 0.55 V), while in Fig. 10b the step sweep is performed. It starts from low cell voltage and runs at a potentiostatic mode. The voltage step is 100 mV and keeps a certain cell potential for 120 s. The current and cell resistance are recorded during the process. From Fig. 10b, high cell resistance can be seen when the sweep begins, step 1 as marked in the figure, due to the dry gases fed in. About 60 s later, the cell resistance drops to around 0.05 Ω cm² while the current keeps falling; This can be explained in that as the membrane is fully humidified, liquid water can hardly be removed with the same gas flow. This corresponds to backward 2 of higher current density than the threshold current density in Fig. 10a. For the following steps 2, 3, and 4, the current density keeps reducing when the cell runs at each potentiostatic mode, and during this period the cell resistance does not change. In step 5 when current density is close to the threshold in Fig. 10a, the test cell shows a current density increase at the end of step 5. Meanwhile, the cell resistance also shows a slight increase. After step 6, the cell resistance increases suddenly. This is due to the low water production rate and results in the drying out of the membrane. In this way it can be validated that when the test cell runs around the threshold current density in dry gases, a relative stable fuel cell operation is possible. A test was made to run the fuel cell with dry gases fed in, and a relative stable current output was obtained at the threshold without significant resistance change (Fig. 11).

Figure 10. (a) Ramp sweep at 50°C, in dry gas; sweep rate 5 mV/s. (b) Step sweep at 50°C, in dry gas; step interval 100 mV/step. Gas flow rates are 50 mL/min dry air on the anode side, and 25 mL/min dry hydrogen on the cathode side.

Figure 11. Stable operation at the threshold. Gas flow rates are 50 mL/min dry air on the cathode side, and 25 mL/min dry hydrogen on the anode side. Cell temperature 50°C, in potentiostatic mode, 500 mV.

Conclusions

In this paper, ramp sweeps were implemented to the small test fuel cell under dry gas operation. Under dry gas operation the I-V curve shows a shape that resembles an “8”. One can roughly divide the curve into an upper region where drying-out effect can be seen and a lower region that is dominated by the flooding of the GDL. The regimes are divided by the intersection of the forward curve and the backward sweep curve. We call this point the threshold. The threshold shows the dynamic equilibrium status of the MEA under dry gas operation. The impact of the operating conditions on the threshold has been discussed. Compared with ramp sweep, step sweep is also performed on the test fuel cell. The results show that when using dry gases under certain operating conditions (GDL, gas flow rate, temperature, etc.), stable operation is obtained at around the threshold current density. When the threshold is determined, a good point of operation to start the fuel cell is obtained.

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