Operation of a PEM Stack with High Impurity Anode Feeds in a Recycle Mode

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Abstract A Ballard PEM stack (Nexa^{TM} power module) was utilized in this work, providing 1200 watts of unregulated DC power at a nominal output voltage of 26 VDC. In deference to normal operational procedures, high levels of inert gases were deliberately added to the anode feed. Fuel exhaust management in the Nexa^{TM} system was carried out by adding a manual exhaust line into the exterior fuel exhaust purge line. This exhaust management system provided the opportunity to optimize the exhaust flow rate and increase system efficiency in a recycle mode. This type of operation provides a dual use of membranes in the MEAs as both gas purifier and as solid electrolytes. The PEM stack was successfully operated with up to 7.5% nitrogen in the absence of a palladium-based hydrogen separator. In further experiments, a hydrocarbon reformate containing high levels of CO_2 and H_2O was also used in the Nexa^{TM} stack after troublesome CO and H_2S poisons were removed. Both fuels successfully ran the Nexa^{TM} stack. Recycle operation may be used to reduce the size and complexity of the fuel processing system at a specified power level.
Keywords: Fuel cell operation; exhaust gas management; PEMFC.

A PEM fuel cell stack has many operational methods to obtain high fuel-gas efficiency (Boehm *et al*., 2001 and Preidel *et al.,* 2003). This means that a fuel cell stack including its control system needs various optimal methods to convert chemical energy to electricity as efficiently as possible. Fuel gas, air oxidant (or pure oxygen), water vapor and liquid, heat generation, gas exhaust treatment, power production and energy efficiency are the main issues of PEM fuel cell management. Parameters from these operation have close relationship. It is summarized that the PEM system has four main areas of operation including gas management, water management, thermal management, and power (energy) management. The operation diagram is shown in Figure 1. Power management reduces the energy self-consumption and increases power output for electric work. It involves the optimization of power consumption related to the electrode structure, air compressor, system controller, and air(water)-cooling fans/motors. Water and thermal management exhibit a close relationship widely investigated in order to develop MEAs and operate the FC system safely (Marshall *et al*., 1994 and Ahmed *et al*., 2002). Gas management is the primary design issue of the fuel cell system for MEA membrane and system safety concerns. This is essential for the system to maintain operation after start-up and to prolong its operational life time. The gas pressure in anode and cathode channels directly influences the system's energy efficiency. Higher pressure causes gas compressor to use more energy. Here, the anode side fuel gas and its exhaust management are discussed in detail for higher fuel efficiency.

The fuel gas and exhaust stream at the anode side undergoes an electrochemical oxidation of hydrogen by reacting with water to lose some electrons. The product of hydrated protons moves forward to the membrane with high protonic conductivity. Most protons pass through the hydrated membrane by diffusion. The other protons with water are moved through the ionomeric membrane from the anode to the cathode by electroosmotic drag. The chemical reaction occurs at the cathode side, producing water and heat. Some water is necessary to have mass transport by back-

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diffusion to the anode side for further hydrogen electro-oxidation. Because heat is maily generated at the cathode side, the effect of water vapour in the gas stream at the anode side is neglected when the fuel cell system is operated at *ca.* 200 W stack power and no more than 30°C stack temperature. The PEM system including a stack was bought from Ballard Power Systems for the experiment. The Ballard Nexa^{TM} power module was fed with hydrogen and high levels of inert gases. The PEM system is a fully automated fuel cell system using a hydrogen fuel supply. The design requires no more than 0.01% of total inert gases. A manual purge line was added into the Nexa^{TM} exhaust line in order to use the system for the fuel exhaust test. Making use of the auto purge line, the FC system was able to be started normally and shut-down safely by the system controller.

$$H_2\,(g) + 2H_2O\,(aq) \rightarrow 2H_3O^+\,(aq) + 2e^- \qquad (1)$$

$$H_3O^+\,(aq) \rightarrow H_2O(aq) + H^+ \qquad (2)$$

The flow rate of the manual purge stream was adjusted by using a back pressure valve in the exhaust line. The accurate flow rate was measured by a gas bubble meter. The flow rate was accurately measured for feeds of either pure hydrogen or high levels of inert gases. After the fuel cell system was started-up at a 200 W stack load and run for approximately 20 minutes to reach a steady state, the hydrogen fuel with inert gases was fed into the FC system replacing the pure hydrogen fuel. The purge cell voltage was recorded by the NexaMon software from Ballard. The Agilent 6890 gas chromatography system with enhanced integrator was employed to measure the compositions of the fresh and exhaust gas streams.

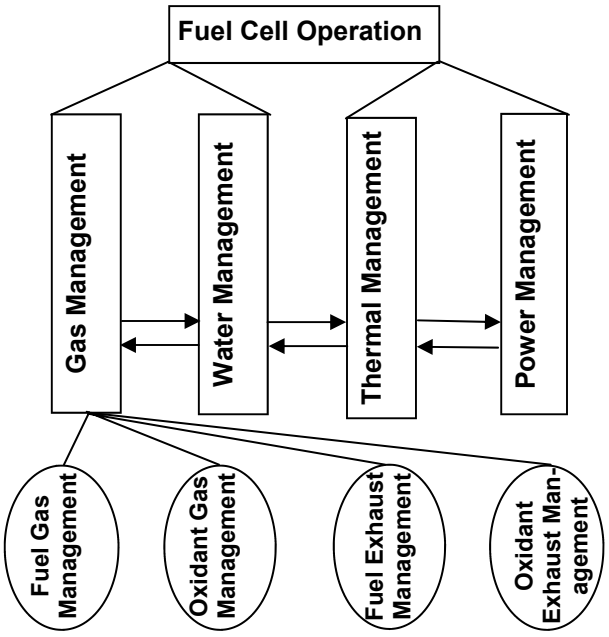

Figure 1. Schematic operation diagram of the PEM fuel cell system.

The flow rate of fuel gas in fuel cells can be determined by measuring the exhaust flow and the change in gas composition. After the gas stream flows into the common fuel cell inlet, it is assumed that the gas stream is uniformly distributed to every MEA unit. At a steady state after the fuel gas has arrived in each cell, hydrogen fuel is consumed at an approximately equal rate in each cell. At each cell outlet, the gas composition is viewed as the same, but the flow rate increases with the cell numbers. It is also supposed that the gas composition is the same at the auto purge exhaust and the manual purge outlets. From a mass balance and the above mentioned assumptions, the inlet/outlet flow rates and the average flow rate of auto purge are then obtained

$$u_0 = \frac{y_{e2} \cdot mI}{(x_{01} - y_{e1}) \cdot 2F} \qquad (3)$$

$$v_0 = \frac{1 - x_{01}}{x_{01} - y_{e1}} \cdot \frac{mI}{2F} \qquad (4)$$

$$v_c = \frac{1 - x_{01}}{x_{01} - y_{e1}} \cdot \frac{mI}{2F} - v_e \qquad (5)$$

Flow rates shown in the above equations are in mol/sec but are also converted to ml/sec by using the ideal gas assumption at 1 atm and 20°C for convenient description. The equation (5) shows that the flow rate of auto purge exhaust is a function of the inlet/outlet gas compositions, number of fuel cells, stack current, and the manual purge flow rate.

This work mainly discusses management of the anode fuel gas and its exhaust stream. For the Nexa^{TM} system, the fuel and exhaust gas management on the anode side is conducted by auto purge exhaust if the fuel cells are operated at an unacceptably low cell voltage. The well-developed commercial product has the advantages of requiring low maintenance, being fully automated, portable, and highly integrated. The disadvantage of the Nexa^{TM} system is that it is not convenient to utilize hydrogen feeds with high levels of inert gases or reformate gases, because frequent purging and system restoration wastes fuel energy and results in efficiency loss, and may also cause system failure with highly frequent exhaust release. The Nexa^{TM} system at a 200 W stack power level fed by pure hydrogen, was tested for membrane dry-out resulting in no voltage diminution during a testing period of 48 minutes at an exhaust flow rate of 5 ml/sec. The FC system (Nexa^{TM} #527) was tested at 7.5% nitrogen content, balanced with pure hydrogen. The stack and control system were successfully operated for start-up and the duration of inert gas intake. The single fuel cell (*i.e.,* MEA voltage (No.13, 33 and 47 from the anode to the cathode side) was measured at a level of 0.70 V at 200 W stack power, but the dynamic voltage signals were difficult to collect simultaneously for single separated fuel cells. The system from National Instruments was set up in order to obtain enough dynamic information for fuel cell diagnosis. The purge cell voltage reduced gradually and the system purged for voltage restoration and performance recovery. After an auto purge in the fuel exhaust line, the purge cell voltage increased to the highest level and then dropped slightly. At this moment, the manual purge valve was opened by a small amount and the purge cell voltage gradually increased as shown in Figure 2. The flow rate was able to be kept at a minimum level and the purge cell voltage was also maintained as a constant. If a voltage drop or rise occurred, a small adjustment was necessary to keep this parameter constant. This minimum flow rate is called a critical flow rate, a useful parameter deciding the auto purge frequency.

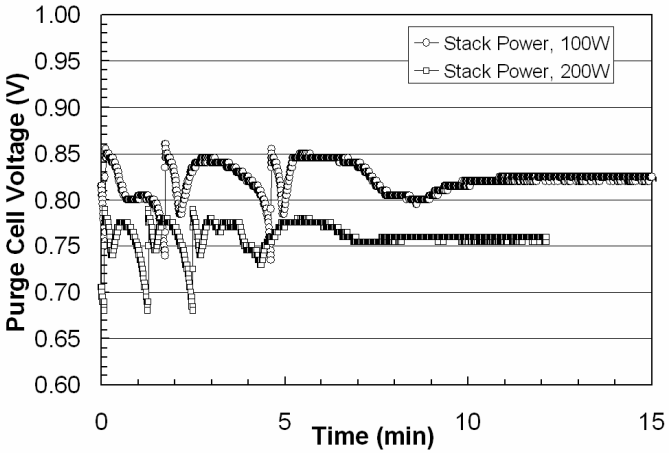

Figure 2. Purge cell voltage as a function of operation time.

Carbon dioxide is more difficult than nitrogen to obtain a good gas mixture in the lab because carbon dioxide (1.964 mg/ml) is 22 times heavier than hydrogen (0.0893 mg/ml) at 1 atm and 0°C (STP). The FC system was successfully operated with a *ca. 7.*5% carbon dioxide* feed for 50 minutes possibly even longer if the system had an exhaust flow rate of more than 1.70 ml/sec. From the work in the lab test, nitrogen demonstrated a good capability for mixing with hydrogen at 800 psig pressure.

As mentioned for the Nexa^{TM} system operation, it is not difficult to notice that there exists a critical flow rate between the auto purge and manual purge route. If the manual exhaust flow rate is lower than the critical value, it will start the auto purge operation. If higher than the critical value, there is no need for auto purge. This is potentially beneficial for fuel recycle mode design and increasing the fuel efficiency. The critical value can be approximately measured by manually adjusting the back pressure valve. The auto purge subsystem stops when the manual purge flow rate reaches a certain limit. At that point, the purge voltage increases very slowly or maintains a maximum purge cell voltage but may not start

*Pressure has some difference between high and low pressure chambers. The pressure drop ratio over the pressure relieve valve is estimated as 0.67. The initial data without this consideration was obtained as a composition of *ca.* 5%.

any more auto purges.

At the manual exhaust outlet, the GC gas samples for N_2 composition were taken after recording data at different exhaust flow rates. Exhaust flow rates, gas compositions, and fuel consumption rates in all the stack channels were measured or calculated. The auto purge flow rate is a dynamic value; thus, an average flow rate was approximated and substituted into this data. The measured N_2 exhaust concentration decreased with increasing the manual exhaust flow rate. The manual flow rates are dynamically measured as the critical flow rate. From the calculations, the auto purge rates were close to zero, and in actuality, no auto purge was observed during the test process. This type of operation provides a dual use of membranes in the MEAs as both gas purifier and as solid electrolytes. Optimization of the fuel and exhaust gas management would potentially increase fuel efficiency. In the recycle mode, single cell voltage response, gas concentration profiles and pressure gradients are the most important parameters for safe fuel cell operation. Recycle operation may be used to reduce the size and complexity of the fuel processing system at a specified power level.

In further experiments, a hydrocarbon reformate containing high levels of CO_2 and H_2O was also used in the Nexa^{TM} stack after troublesome CO and H_2S poisons were removed. Because small amount of poisonous carbon monoxide comes into the fuel cell system, the overall stack voltage drops gradually. The voltage of the purge cell at the end of the stack was measured slightly higher voltage than the average cell voltage as shown in Figure 3. This means that a concentration gradient of carbon monoxide exists inside the fuel gas distribution channel. The front fuel cells in the stack are more likely to receive the poisons causing temporary catalyst deactivation. This phenomenon will be further examined in the diagnostic analysis of the fuel cell system.

The addition of the manual purge line to the exhaust system makes advantageous use

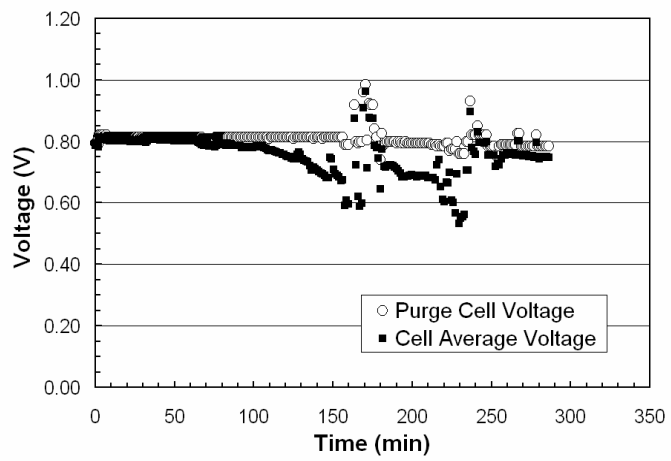

Figure 3. Nexa^{TM} fuel cell system operation using a hydrocarbon reformate containing CO_2 and H_2O after CO and H_2S poisons removal.

of the commercial product's low maintenance, full automation, mobility, and high integration. This provided a dual use of membranes in the MEAs as both gas purifier and as solid electrolytes. The Nexa^{TM} PEM fuel cell system successfully utilized hydrogen feeds with *ca.* 7.5% inert gases. This operational method eliminated the need for a high temperature palladium separator and/or gas purifier. It also reduced the auto purge frequency required for stack performance recovery. The critical flow rate for the gas exhaust stream at a specified power level was obtained by manual adjusting of the manual purge valve. Further work on the dual exhaust management in a recycle mode operation could potentially save fuel usage and improve its system efficiency.

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List of Symbols

F Faraday constant, 96487 A s mol^{-1}

I current through fuel cell stack, A

u gas flow rate at inlet side, mol/sec in equations (*2.404X10^4 ml/sec at 20°C, 1 atm)

v gas flow rate at the outlet side, mol/sec in equations (*2.404X10^4 ml/sec at 20°C, 1 atm)

x_{i1} fuel inlet volume fraction (hydrogen) for the cell i

x_{i2} fuel inlet volume fraction (inert gas) for the cell i

y_{i1} outlet hydrogen volume fraction for the cell i

y_{i2} inert gas volume fraction at the outlet for the cell i

Subscripts

0 fuel gas inlet/exhaust outlet at 1 atm and 20°C

1 hydrogen

2 inert gas

c auto purge outlet

e manual exhaust outlet