

AN EXPERIMENTAL STUDIES ON IMPROVEMENT OF ANODIC DEAD-END MODE FUEL CELL USING PULSATION EFFECTS

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ABSTRACT

This paper describes experimental results performed on the basic purge characteristics of the anodic dead-end mode fuel cell, how to increase the purge period using the pulsation effect, and then how to operate anodic dead-end mode fuel cell without purge cycles.

In anodic dead end mode fuel cell, the purge is essential to avoid the flooding problems caused by the liquid water formed in the channel which can block the porosity of the GDL and reduce the active area. However, the un-reacted hydrogen can be discharged in purge process although it can be thought to be a little. Therefore, the purge frequency should be as short as possible for increasing the fuel efficiency. Experimental results show that it decreased when the current density decreases, the operation pressure increased. When the pulsation effect such as various frequencies or amplitudes in the outlet of anode channel was applied to fully humidified hydrogen, the number of purge was alleviated up to one third. In addition, when the dry hydrogen was supplied and oscillated in the channel, the pulsation effect can make the purge interval much longer, moreover, it can be an auxiliary humidifier using the back diffusive water vapor, which is a novel concept of the humidification. Finally, the purge cycle was eliminated by connecting the Nafion chamber to the outlet of anode, which can improve the fuel efficiency. The wall of the chamber is made of Nafion[®] 117 membrane that can transmit the water vapor selectively, which is also a novel concept of operating the dead-end mode fuel cell.

INTRODUCTION

There have been few researchers to study the dead-end mode fuel cell as mentioned in the section 1.1. Mocoteguy *et al.* [1] made experiments to identify the influence of the dead-end mode fuel cell's position in the stack on its performance. Difference between voltages of the first and the last cell of the stack was observed and this difference was explained by a water accumulation at the outlet and by higher partial pressure

NOMENCLATURE

A	[m ²]	Area
d	[m]	Diameter
D	[m ² s ⁻¹]	Diffusivity
f	[Hz]	Frequency
P	[bar]	Pressure
t	[s]	Time
T	[°C]	Temperature
V	[V]	Voltage
x	[-]	Mole fraction
Special characters		
λ	[-]	Stoichiometry factor
Subscripts		
ch		Channel
eff		Effective expression
fc		Fuel cell
l		Liquid
v		Vapour

of gases at the cell inlet. Tabe *et al.* [2] obtained the optimal performance at 60°C for the air-breathing anodic dead-end mode fuel cell. Himanen *et al.* [3] made an experiment about free-breathing PEM fuel cell on anodic dead-end mode in different hydrogen pressure, humidification levels and purge valve duty cycles. They found out that at higher hydrogen pressure, there was no clear drop in the cell voltage. Also, they demonstrated that water balance can be changed by increased hydraulic permeation and there were no significant differences in cell performance at different purge valve duty cycles. Dumercy *et al.* [4] reported some experimental results to have been performed on a three cell PEFC stack and in order to calculate the optimal flush frequency, a stack model was developed. As a result, the impact of the dead-end mode on the stack voltage depended strongly on the current density and the mean time between two flushes in the dead-end mode versus current was decreasing in higher current.

In the meantime, In the meantime, researches about pulsating flow have been done for a long time and the

researches were initially focused on transport of human blood. Experimental and theoretical studies on the oxygen diffusion in blood flow were done firstly by Patel *et al.* [5]. Edwards *et al.* [6] confirmed that Newtonian laminar flow with pulsation in a rigid circular tube promised a space and time averaged mass transfer rate. And then, effect of pulsation on oxygen transport to the human arterial wall was researched by Schneiderman [7]. He identified that the pulsating velocity fields were based on Womersley number and tidal volume by analytical works. Watson [8] reported a spreading coefficient of diffusing substance along a circular pipe could be enhanced by oscillatory flow. The increasing diffusivity was also taken numerically in some limiting cases.

Generally, the periodical purge process is needed for discharging the liquid water in the channel on dead-end operation since the liquid water can block the porosity of the GDL, thus make the fuel cell performance decayed according to time. However, un-reacted hydrogen in the channel can be discharged with the liquid water during the purge process, which can make the fuel efficiency lower. Therefore, the pulsation was introduced and applied to the dead-end mode fuel cell to increase the effective diffusivity of the water vapor, thus to increase time to be condensed, which makes the fuel efficiency of dead-end mode fuel cell higher.

VOLTAGE AND PURGE CHARACTERISTICS ON ANODIC DEAD-END OPERATION

Before showing the experimental result, it is needed to explain some definitions in this study. Fig. 1 shows the voltage variation and purge characteristics on anodic dead-end operation. As shown in Fig. 1, the pressure except the purge process was representative of the operating pressure on dead-end operation. Time period between two purges was defined as purge interval. And then, the criteria to open the purge valve

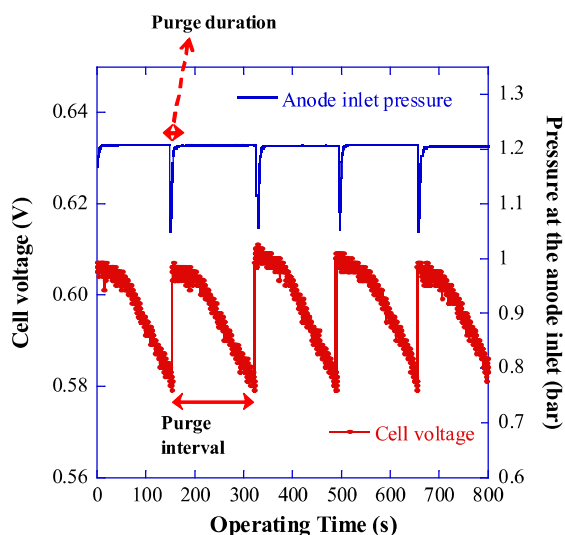


Figure 1 The voltage and pressure variation on anodic dead-end mode fuel cell

was set as 5% off value of the maximum voltage for avoiding the degradation of MEA due to the excessive liquid water. Finally, three terms such as FAFH (fully humidified air and hydrogen), FADH (fully humidified air and dry hydrogen), and DADH (dry air and hydrogen) were used for explaining the humidification conditions.

There are only three species in the anode channel: The nitrogen, the water vapour, and the hydrogen. Thus, it is essential to investigate preliminarily what can influence on the voltage drop on dead-end operation. Fig. 2 shows the experimental result of the voltage variation and mean purge interval for different combinations of the nitrogen concentration in the anode flow on anodic dead-end operation. From the results, it could be known that not the nitrogen but the liquid water is more influential factor on the cell performance and purge interval. Fig. 3 also show the voltage variation and mean purge interval for different operating pressure in the anode inlet. From these results, mean purge interval is shorter up to 46% when the operating pressure is increased from 1.1 bar to 1.3 bar while the maximum voltage performance is 3.1% higher. This is because the partial pressure of the water vapour is increased when the operating pressure is higher, that is, the water vapour can be condensed more quickly. Therefore, it is better to choose lower operating pressure as possible for obtaining longer purge interval, which can make the fuel efficiency higher.

IMPROVEMENT OF PURGE CHARACTERISTICS WITH PULSATION EFFECTS

Although mean purge interval can be longer when the operating condition is changed, the hydrogen should still be discharged during the purge process. In this chapter, therefore, flow pulsation is adopted to enhance the uniformity of the water vapour in the anode channel. It has been well reported,

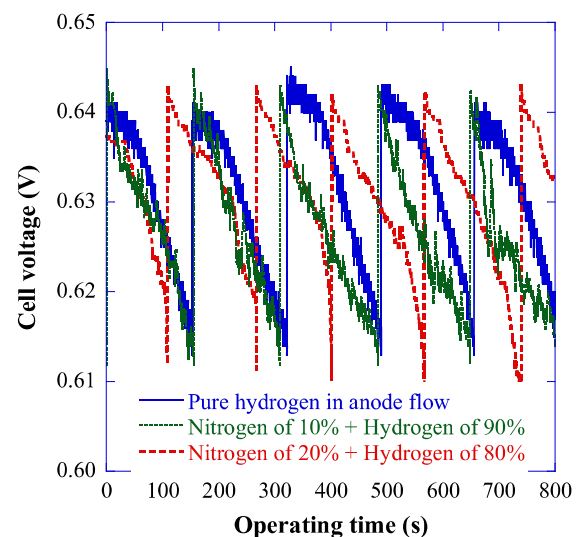


Figure 2 The voltage variation for various combinations of hydrogen and nitrogen concentration feeding conditions

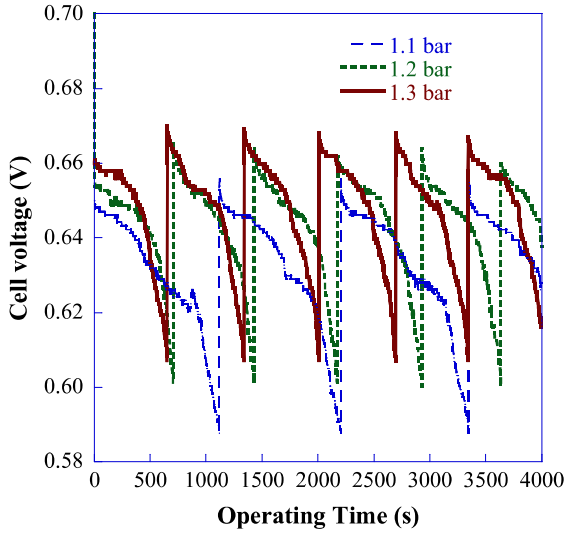


Figure 3 The voltage variation for different operating pressures at the anode inlet

both experimentally and numerically, that flow pulsation can increase the diffusion between two species that have a concentration gradient due to enhanced dispersion. In fact, the diffusion is increased by up to three to four orders of magnitude above the molecular diffusion coefficient. By changing the frequency and the amplitude of the pulsation, the purge performance of the dead-end mode fuel cell is compared with that in the absence of flow pulsation. Alejandro *et al.* [11] presented the time variation of liquid water in the GDL as shown in Eq. (1).

$$\frac{ds}{dt} = \left(\frac{1}{\rho_l \varepsilon A_{fc}} \right) \frac{\partial W_l}{\partial y} - \frac{R_{evap} M_v}{\rho_l} \quad (1)$$

where s , ρ_l , ε , A_{fc} , W_l , y , M_v , and R_{evap} represent fraction of liquid volume to the pore volume in the GDL, liquid water density, porosity of the GDL, active area of the fuel cell, liquid water mass flow rate, thickness' direction of the GDL, water vapour molecular weight, and molar evaporation rate, respectively. From the equation, the small variation of the fraction, s , according to time can make the active area blocked slowly. Furthermore, all components are decided according to the operation conditions such as the humidity, current density, operating temperature, and pressure except the molar evaporation rate. The molar evaporation rate can be expressed in Eq. (2).

$$R_{evap} = \gamma \frac{P_{sat} - P_v}{RT} \quad (2)$$

where γ , P_{sat} , and P_v mean the volumetric condensation coefficient, saturation pressure, and the partial vapour pressure, respectively. As shown in Fig. 4, the larger molar evaporation rate is expected to make the water vapour condensed very slowly if the water vapour concentration, p_v is lower by pulsation.

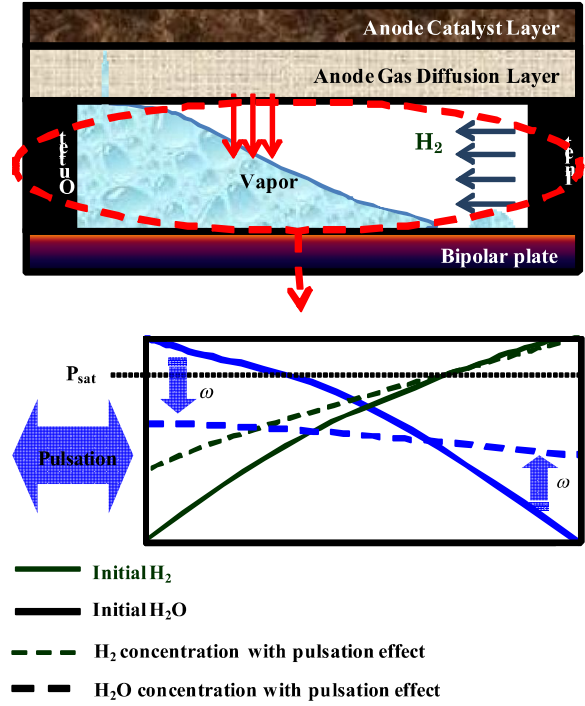


Figure 4 Schematic of the anode channel on dead-end operation

FAFH condition with pulsation effects

Fig. 5 shows the variation of mean purge interval when the various pulsation frequencies are applied to the outlet of the anode channel in FAFH condition. From the result, mean purge interval is increased almost linearly with the root frequency, which is well matched with the analytical results of many previous works that the effective diffusivity of the water vapour is increased with the root frequency.

DADH condition with pulsation effects

Eckl *et al.* [9] presented that the operation with dry gases is possible if the amount of product water is sufficient to saturate the outlet gases, respectively if the following criterion is satisfied

$$1 \geq \left(\lambda_{H_2} - 1 + \frac{\lambda_{air}}{2x_{O_2}} - \frac{1}{2} \right) \times \frac{P_{sat} T_{fuelcell}}{P - P_{sat} T_{fuelcell}} \quad (3)$$

where λ_{H_2} represents the hydrogen stoichiometry, x_{O_2} is the fraction of oxygen in the airflow (usually 0.21), P is the inlet pressure of the air in bar and P_{sat} is the saturation pressure of water vapour, depending on air temperature. For anodic dead-end mode operation ($\lambda_{H_2}=1$), a critical air stoichiometry for internal humidification can be derived from Eq. (4).

$$\lambda_{air,critical} = 0.21 \left(\frac{2P}{P_{sat} T_{fuelcell}} - 1 \right) \quad (4)$$

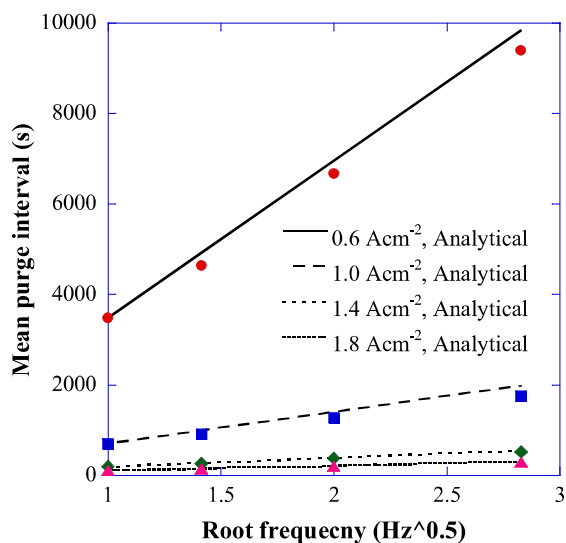


Figure 5 The variation of mean purge interval for various pulsation frequencies

As pressure varies with airflow for various current densities, $\lambda_{air,critical}$ is a function of saturation pressure, operating temperature, and also current density. In this study, critical stoichiometry ratio of the air was calculated as about 3.3 for self-humidifying condition. Fig. 6 shows the time history of the cell voltage in these conditions. The maximum voltage was 0.595 V which was about 16% lower compared with the result in conditions of dry hydrogen and 60% humidified air, while mean purge interval was about 4720 s, which is 1.65 times longer. At a glance, this operation condition is not desirable and reliable since the ohmic loss of the fuel cell caused by low ion

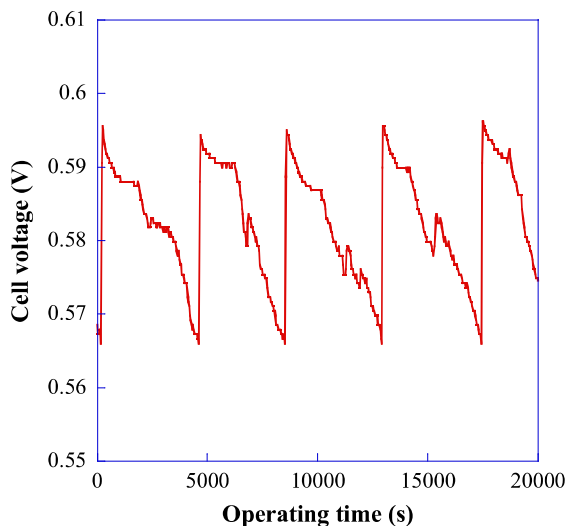


Figure 6 Time history of the cell voltage in DADH condition

conductivity of the membrane is very large. However, the pulsation can help the membrane humidified by dispersing the water vapor near the outlet of the channel. The experiment has been done for investigating the cell potential variation according to the frequency in the conditions of the current density of 1.4 Acm⁻², the dry air stoichiometry ratio of 4.0, the operating temperature of 65°C, and the hydrogen pressure of 1.1 bar. When the frequency increases, the voltage decay rate were about 8.2 μ V/min, 5.7 μ V/min, 4.2 μ V/min, and 3.1 μ V/min, respectively, which were very smaller than that without the pulsation. Furthermore, there has never been any purge process for 7 hours in any frequency from 1 Hz to 8Hz. From the results, mean purge interval can be predicted as 61.9 hrs, 89.2 hrs, 121.1 hrs, and 173.4 hrs, which were about from 47.6 times to 133.4 times longer period without the pulsation effects. Accordingly, it is concluded that the pulsation effect on the dead-end mode fuel cell is more helpful as the fuel cell is operated in DADH condition.

PERFORMANCE IMPROVEMENT WITH NAFION[®] CHAMBER

From the previous studies, water permeation from liquid water increases with the temperature and the water activity difference across the Nafion[®] membrane. In addition, water permeation from humidified gas into the dry air goes through a maximum with the water activity difference across the membrane. Permeation is dependent on membrane thickness. With this self-diffusion, the auxiliary chamber was made and connected to the outlet of the anode for discharging the water vapor as shown in Fig. 7. Fig. 8 shows that the voltage variation of the single cell for 5 days is very stable like that on open mode operation in FADH condition for three current densities of 1.0 1.4, and 1.8 Acm⁻². The voltage was not decayed for 5 days for all current densities although the pulsation was not applied. Therefore, the purge process was not also needed due

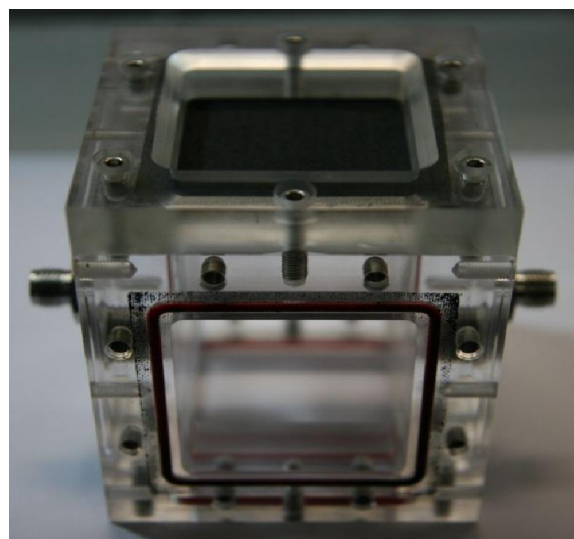


Figure 7 The picture of the Nafion[®] chamber

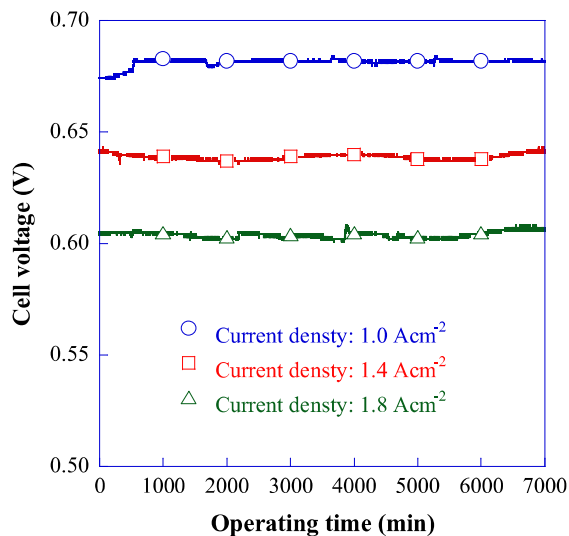


Figure 8 The voltage variation of the single cell connected with Nafion® chamber for 5 days in FADH condition

to the selective water vapor transmission characteristics of Nafion® 117 membrane, which could make the fuel efficiency the highest since the hydrogen has been never discharged during the purge process.

CONCLUSION

In this study, experimental studies were conducted to understand the basic characteristics of the purge cycles, to increase purge interval, and to increase the fuel efficiency in anodic dead-end mode fuel cell. Two novel operating methods were proposed for increasing the fuel efficiency of the dead-end mode fuel cell system.

First, the pulsation effects were applied to the outlet of the anode channel in FAFH condition. Mean purge interval increased according as the root frequency increased. The longest mean purge interval was measured as 546 s with the pulsation frequency of 8 Hz and the amplitude of 20 mm, which was 3.4 times longer than that without the pulsation. The pulsation effects were also applied to the outlet of the anode in DADH condition. The pulsation frequency of 8 Hz in DADH condition could make mean purge interval up to about one hundred times longer as well as the hydrogen hydrated as an auxiliary humidifier using back diffusive water vapor.

Second, the dead-end mode fuel cell was operated with the selective water separator. The purge process in the single cell could be completely eliminated by connecting the Nafion® chamber to the anode in FADH condition.

If the size of Nafion® chamber and the pulsation generator could be optimized and compacted, furthermore, two methods suggested in above chapters could be verified in the fuel cell stack as well as the single cell, these dead-end operation methods can be the most attractive ways to have the maximum fuel efficiency due to eliminating the purge process.

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