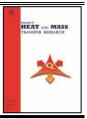


Journal of Heat and Mass Transfer Research

Journal homepage: http://jhmtr.journals.semnan.ac.ir



Investigation of purge time in cathodic dead-end mode PEMFC

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PAPER INFO

History:

Received 11 October 2013 Received in revised form 06 July 2014 Accepted 17 September 2014

Keywords:

Dead-End Mode PEMFC Thermodynamic Analysis Voltage Losses

Temperature

Purge Time

ABSTRACT

Recently, special type of fuel cells has been developed that operates in a Dead-End mode. Working in this condition, the Dead-End fuel cell is supplied with hydrogen almost at the same rate of consumption. It is noteworthy to mention that all of the water transport mechanisms have been considered in this simulation. Water accumulation that is directly proportional to the cell current is of a great importance and has a negative impact on the cell voltage and its performance. Hence, water and gas management in Dead-End mode should be handled properly. To do so, determining the suitable time of purge and its duration is valuable with a direct impact on cell performance. In this paper, the channel and gas diffusion layer have been considered as a single control volume and the blockage effect has been investigated by means of thermodynamic analysis. In order to obtain a reasonable assumption, we have studied three different scenarios: GDL flooding, channel flooding and GDL-channel flooding simultaneously. The influence of blockage effect rate of gas diffusion layer and channel on cell voltage drop, performance and purge time have been studied. Voltage drop curves in different operating conditions have been presented and the results show an acceptable agreement with experimental studies. These curves have been investigated for different current densities (0.5, 1 and 1.5 A/cm²), active areas (25, 50 and 100 cm²) and temperatures (60-80 °C). An Increase in temperature and in current density, reduces purge time interval, while increasing active area has an inverse impact. In high current densities, the effect of temperature variation can be neglected.

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1. Introduction

PEMFCs have received a considerable attention in comparison with other fuel cells because of their low operating temperature and less corrosion due to the implementation of a solid membrane [1, 2]. Having a low temperature operating condition make them suitable for automobiles, power generation devices and household usage. Also, the clean nature of PEM fuel cells favors the reduction of environmental problems [3]. The operating

condition of PEMFCs is classified as following: Open mode and Dead-end mode. The open mode operation needs higher rates of fuel and oxidant than that of complete reaction because of incomplete fuel utilization and the necessity of exhausting waterproduced. Also, to increase the fuel consumption rate, the residual fuel must be recirculated with external devices which in turn decrease the efficiency of the fuel cell. In order to overcome these drawbacks, dead-end operating condition has been proposed. Supplying the fuel at the rate of consumption is the main advantage of

the dead-end mode. Water managements and purge processes in these types of fuel cells arenecessary to avoid water accumulation in channels [3]. Indoor applications are also possible in this type of fuel cells due to negligible exhausted fuel.

Real et al. [4], obtained voltage loss versus time curves for a fuel cell stack with 46 cells. Asghari et al. [2] have studied on thermodynamic analysis of anodic dead-end fuel cell and have investigated voltage loss versus time and purge time frequency. Jong Won Choi et al. [3, 5] have done experimental studies on cathodic and anodic PEMFCs and have studied purge time at 10% of voltage losses in cathode and 5% voltage losses in anode for different current densities.

Mujumdar et al. [6] have investigated anodic dead-end PEMFC with commercial software FLUENT in which they have considered 0.4 voltage as a purge criterion. They have studied time variation of voltage dropfor different current densities and distribution of local current density as well as reactant gases and amount of saturation. They have also investigated the effect of anode inlet pressure increment on voltage drops, gases molar fraction and amount of saturation. Yongchan Kim et al. [7] have experimentally studied water transport in the membrane of anodic dead-end fuel cell. They have investigated the effect of relative humidity, air stoichiometry and different current densities on time variation voltage curves.

Chao-Yang Wang et al. [8, 9] have investigated two phase transport processes and have obtained saturation distribution in GDL. They have also considered capillary pressure and saturation distribution effect on polarization curve.

Noteworthy, due to the importance of purge time in dead-end fuel cells, one has to refer to the time variation of voltage curvein order to obtain a suitable purge time at a specified voltage. Water accumulation in GDL is the main reason of voltage drop and consequently a fuel cell performance reduction. Considering the aforementioned works, this paperfocuses oninvestigating the effect of different current densities. Todo so, the time variation of voltage drophas been presented including thermodynamic analysis. In every water generation cycle, the active area is reducedby flooded region. Also, the effect of capillary pressure on water transport in GDL has been taken into the account.

2. Governing equations and Solution

All water transport mechanisms in fuel cells have been shown in figure1. The first mechanism, back-diffusion, occursdue to the concentration gradient between cathode and anode which leads water flow from cathode to the anode side. The second one is due to electro-osmotic drag in which every H^+ ion carries 1 to 5 water molecules from anode to the cathode side. The third and fourth ones are because of relative humidity of inlet gases. The last mechanism is the transportation of water vapor due to the re-circulation of air in the channel. This work is based on the assumption of volume fraction distribution of water.

Volume fraction distribution is the ratio of volume of water to the total volume of channel. According to this assumption, the produced water is redistributed between channel and GDL based on their volumeratio.GDL porosity and thickness have been considered to calculate the GDL effective volume.

Having considered all of the above mentioned mechanisms, net transport coefficient (α_d) is defined for a fuel cell.In this research, a constant value of 0.5 is assigned to the cathode [2, 12]. The

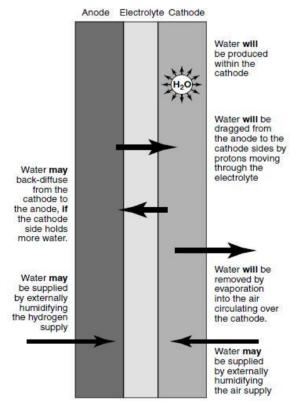


Fig. 1. Water transport mechanisms [11]

solution is based on control volume thermodynamic analysis. As expected, when a control volume is considered, the rate of inlet, outlet and generation in this control volume should be considered and calculated. The amount of generated water is calculated as follows:

$$\begin{split} \dot{n}_{H_2O,net,a-c} &= \dot{n}_{H_2o,drag} + \dot{n}_{H_2o,diff} + \dot{n}_{H_2o,perm,gas} \\ &+ \dot{n}_{H_2o,perm,cap} + \dot{n}_{H_2o,temp} \end{split} \tag{1}$$

$$\dot{n}_{H_2O,net,a-c} = \alpha_d \frac{iA}{F} \tag{2}$$

In the equation 1, the first term is a net value of water which moves through anode to cathode or contrariwise. The second term is the rate of water movement due to erector-osmotic drag. The third, fourth and fifth terms are the rate of water movement due to back-diffusion, gas permeability and capillary effects, respectively. The last term is the water iterance due to inlet humidification. These terms are shown in fig1. For prescribingthe control volume, one can write the continuity equation:

$$\frac{dn}{dt}\bigg|_{CV} = \dot{n}_{in,c} - \dot{n}_{out,c} + \dot{n}_{H_2O,gen} \tag{3}$$

Since the fuel cell is operating in dead-end mode, \dot{n}_{out} is equal to zero. By substituting equations 2, 4 and 5 in equation 3 and performing mathematical simplifications, equation 6 can be derived as:

$$\dot{n}_{H_2O,gen} = \frac{iA}{2F}$$

$$\dot{n}_{in,c} = \dot{n}_{H_2O,net,a-c}$$
(4)

$$\dot{n}_{in,c} = \dot{n}_{H_2O,net,a-c} \tag{5}$$

$$\frac{dn}{dt}\bigg|_{CV} = (\alpha_d + 0.5)\frac{iA}{F} \tag{6}$$

Channel and GDL Flooding is the main problem in dead-end fuel cells. The amount of accumulated water in the cathode side that has to be exhausted can be calculated by equation 6. GDL moisten occurs when the capillary forces distribute water and the active area is reduced accordingly. At the early stage, no liquid water is generated. Immediately after the channel saturation stage, liquid water will be generated. The maximum water vapor capacity in the channel is calculated as follows:

$$m_{\nu,\text{max}} = \frac{P_{sat} v_{ch}}{RT} \tag{7}$$

$$R = \frac{R_g}{M} \tag{8}$$

When water vapor reachesthe maximum water vapor capacity in the channel, liquid water will be generated. Accordingly, water accumulation reduces the active area of each cell as it is shown in figure 2.a. Consequently, this reduction increases the consumption of current density which results in a cell voltage drop according to the following equation:

$$V = V_{oc} - \eta - Ir \tag{9}$$

Although, equation 9 is not a time-dependent equation, but cell potential will be reducedby current density increment at each time due to reduction of the active area. Consequently, time variation of cell potential curve can be obtained. Figure 2.a shows geometry of the model. Schematic of water transport and distribution in GDL is presented in Figure 2.b.

Equations 10 and 11 state the capillary correlations and have been considered in this research.

$$Q_{H_2O,Pore} = \frac{\pi r_{pore}^4 \Delta P}{8\mu_{water} L_{pore}}$$
 (10)

$$\Delta P = \frac{2\gamma_{water}\cos\theta}{r_{pore}} \tag{11}$$

Table 1 shows geometrical parameters.

Table 1. Specifications and Geometrical parameters

	Parameter	Value
1	Cell temperature (°C)	70
2	Fuel cell active area (cm ²)	25
3	GDL thickness (μm)	300
4	GDL volume (m ³)	0.0000007 5
5	Channel volume (m ³)	0.000003

3. Results

To obtain the time variation of the voltage drop, a few operating parameters have to be set. The fuel cell is operating at $70^{\circ}C$ and 10% of reduction in maximum voltage is chosen to trigger the purge process.Furthermore, values of 25cm2and 1A/cm2 are assigned to cell active area and current density, respectively. Flooding and reducing of active area increase the current density in each step and subsequently reducethe cell voltage. In this manner, one can determine the net voltage drop.Initial current density can be obtained by knowing the operating voltage usingthe polarization curve. Figure 3 represents the time variation of cell voltage. There is an acceptable agreement between the experimental data and the present study.

The deviation of the present study (8-9%) from experimental data can be explained by assuming the single phase fluid and neglectingthe pressure drop along the channel. In the experimental work, a serpentine channel for cathodic dead-ended fuel

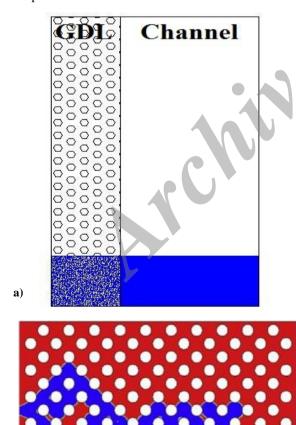


Fig. 2. a) Geometry of the model, b) Water distribution in GDL [10]

cell has been considered and the value of purge time has been set to 90% of the maximum voltage. Table 2 shows the experimental operating

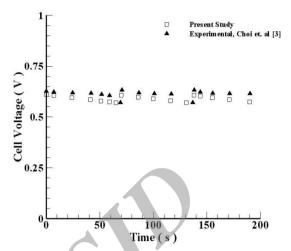


Fig. 3. Time variation of cell voltage

Table 2. Experimental operating conditions

	Parameter	Value
1	Cell temperature (°C)	70
2	Fuel cell active area (cm ²)	25
3	Relative Humidity	100%
4	Stoichiometry factor	1.0
5	Reference voltage to start the purge	90% maximum voltage

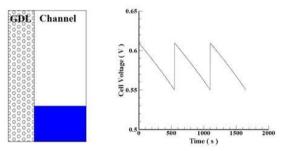


Fig. 4. Voltage drop curve with channel flooding assumption

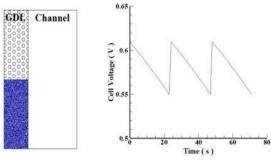


Fig. 5. Voltage drop curve with GDL flooding assumption

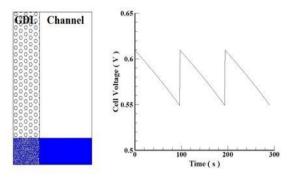


Fig. 6. Voltage drop curve with GDL-channel flooding assumption

conditions which are needed for validation and numerical procedure[3]. Although the simulation has been done using a single phase model, but the effect of liquid phase on the cell active area has alsobeenconsidered. In each step, the area that has been blocked by the accumulated liquid water is being reduced inthe active area. Thermodynamic analysis assumptions are shown in figures 4, 5 and 6. In this case, different conditions have been considered to obtain a logical result. Having considered the channel filled with water and no liquid water in GDL, Figure 4 has been obtained which obviously shows an incorrect prediction of the purge process. Now as a second step, it is

assumed that the GDL is filled with water and the channel is dry. This procedure also yields the wrong prediction of purge process. At the final step, the previous assumptions are corrected and a new approach is presented. This method is based on the linear distribution of water in the channel and GDL, according to the volume fraction of each part, and does include the capillary effect. Figure 6 represents the results obtained by the latter approach.

Implementing the simulation in the three above mentioned methods, yields the values of 19, 378 and 66 seconds for the purge time, respectivly. All of the simulation are conducted at the current density of 1A/cm². As it is indicated in Figure 6, 66 seconds is the reasonable time of purge for a typical Dead-End fuel cell. Figures 7.a, 7.b and 7.c show the effect of current density on the voltage drop curves. It is confirmed that increasing the current density reduces the purge interval.

Due to an increase in the temperature, a reduction in the purge time has been shown in Figure 8. The increment in temperature reduces the maximum water vapor capacity according to equation 7 which accelerates the water generation in the channel. Consequently, the blockage will

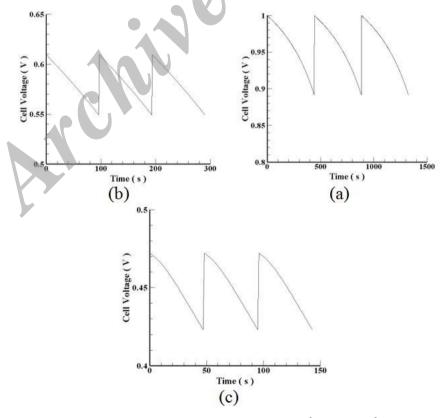


Fig. 7. Voltage drop in different current densities a) 0.5 A/cm², b) 1 A/cm² and c) 1.5 A/cm²

occurfaster and the purge time will reduce. Figure 9 represents the influence of active area on the purge time interval. When the surface area increases, the effective volume increases as well. Accordingly, the maximum water vapor capacity in the channel will increase which will delay the condensation process and liquid water generation. Consequently, the cell voltage drops slower.

Figure 10 shows the effect of active area on purge time at different temperatures. Purge time reduces due to the temperature increment. The influence of temperature on purge time for different current densities has been presented in figure 11.

The effect of temperature on purge time in low current densities is more important in comparison with higher current densities.

Figure 11 represents the temperature effect on purge time for different current densities. It has

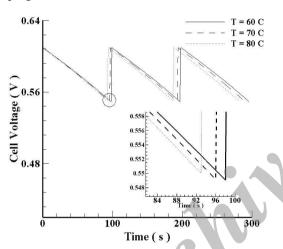


Fig. 8. Effect of temperature on voltage drop curves

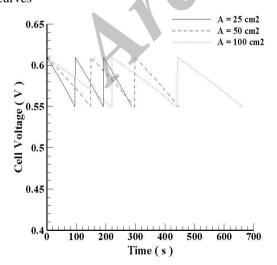


Fig. 9. Effect of active area on voltage drop curves

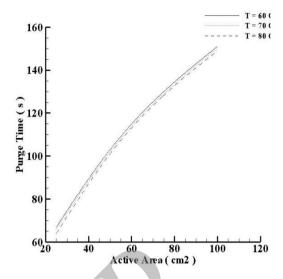


Fig. 10. Effect of active area on purge time at different temperatures

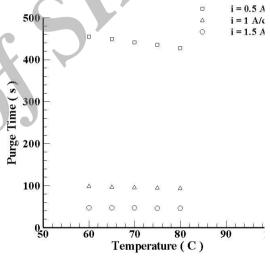


Fig. 11. Effect of temperature on purge time for different current densities

been shown that at high current densities, the effect of temperature variation can be neglected.

4. Conclusion and discussion

Determining the suitable purge time is the key to avoid the performance reduction in a Dead-End fuel cell. In this study, thermodynamic based analysis including

capillary effect has been conducted. Different operating conditions have been studied, including temperature and active area effects. An increase in temperature reduces purge time interval, while increasing active area has an inverse impact. Results indicate that purge time decreases according to current density increment.

Nomenclature

- A Area (m^2)
- *i* Current Density (A/cm²)
- F Faraday Constant (C/mol), 96485
- n Mole of Water (mol)
- r Pore radius (m)
- ΔP Capillary pressure difference (N/m²)
- L Pore length (m)
- P Pressure (N/m^2)
- V Volume (m³)
- m Vapor mass(Kg)
- R Gas Constant (J/(Kg.K)), 8.314
- M Molecular weight(Kg/mol)
- t Time(s)

Greek symbols

- α Water transfer Coefficient
- μ Viscosity((N.s)/m²)
- θ Contact angel(deg)
- γ Surface tension(N/m)

Subscript

- Vapor
- max Maximum
- gen Generation
- H_2O Water
- diff Diffusion
- temp Temperature
- perm Permeability
- a Anode
- cap Capillary
- g Gas
- CV Control Volume
- oc Open circuit

Superscript

Rate (1/s)

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بررسی زمانبندی تخلیه در پیل سوختی پلیمری انتها بستهی کاتدی

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اطلاعات مقاله

دریافت مقاله: ۱۹ مهر ۱۳۹۲ پــذیرش مقالــه: ۲۶ شــهریور ۱۳۹۳

واژگان کلیدی:

پیل سوختی پلیمری، انتهابسته، بررسی ترمودینامیکی، افت ولتاژ، زمانبندی تخلیه، دما.

چکیده

در سالهای اخیر نوع خاصی از پیلهای سوختی، تحت عنوان انتهابسته، توسعه ایافتهاند. در این شرایط عملکردی به طور معمول تغذیه هیدروژن معادل میزان مصرف خواهد بود. آب انباشته شده که ارتباط مستقیم با جریان الکتریکی سل دارد، حایز اهمیت بوده، تأثیر منفی بر ولتاژ و عملکرد سل خواهد داشت. لذا مدیریت آب و گازهای عبوری در شرایط انتهابسته باید به درستی صورت پذیرد. در ایس راستا تعیین زمان بندی مناسب برای تخلیه و نیز مدتزمان بازبودن شیر خروجی جهت تخلیه، تأثیر مستقیمی بر روی عملکرد سل خواهد داشت. در این مقاله کانال و لایهی نفوذ گازی به عنوان یک حجم کنترل واحد در نظر گرفته شده است و اثرات انسداد مسیر با روش ترمودینامیکی مورد بررسی قرار گرفته است. شایان ذکر است که در این شبیهسازی کلیهی مکانیزمهای انتقال آب در نظر گرفته می شود. برای رسیدن به فرضی منطقی، سه سناریوی مختلف مورد مطالعه قرار گرفته است: غرقاب شدن GDL، غرقاب شدن کانال و غرقاب شدن همزمان GDL و کانال. بر این اساس، تأثیر میزان انسداد لایه نفوذ گازی و کانال بر روی افت ولتاژ، عملکرد و زمان بندی تخلیه بررسی شده است. منحنی های افت ولتاژ در شرایط عملکردی متفاوت ارائه شده است و نتایج هم خوانی مناسبی را با نتایج آزمایشگاهی نشان میدهند. این منحنیها برای چگالیهای گوناگون جریان (۰/۵، ۱ و ۱/۵ آمپـر بـر سـانتيمتر مربـع) و نيــز سـطوح فعـال (۲۵، ۵۰ و ۱۰۰ سـانتيمتر مربع) و دماهای (۶۰ الی ۸۰ درجه سلسیوس) مختلف مورد بررسی قرار گرفتند. افزایش دما و چگالی جریان باعث کوتاهتر شدن فاصلهی بین تخلیههای مختلف شده است؛ درحالی که افزایش سطح فعال تأثیری معکوس داشته است. در چگالیهای جریان بالا، اثر تغییرات دما می تواند چشم پوشی شود.