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Short communication

The real-time determination of net water transport coefficient based on measurement of water content in the outlet gas in a polymer electrolyte fuel cell

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ABSTRACT

A numerical approach is developed to determine the real-time Net Water Transport Coefficient (NWTC) based on the experimental water vapor pressure for the cathode and anode outlet obtained by the optical humidity sensors with Tunable Diode Laser Absorption Spectroscopy (TDLAS). The results show that there are sharp vibrations for NWTC in the process of start-up and shut-down. And the time needed for the water transport balance increases with the increase in the current. The balanced NWTC ranges from −0.2 to 0.2, and it increases with the increase in the operation current in the present research. In the view of flooding prevention, it is reasonable to humidify the anode inlet gas with the lower temperature than that of cathode side by decreasing the osmotic-drag water from anode to cathode.

1. Introduction

Water management is very import for the operation of polymer electrolyte fuel cell (PEFC). On one hand, the insufficient water can cause the difficulty of proton conduction in the membrane. On the other hand, excessive water will hinder the mass transfer of the reactants and the product, which causes the degradation of the fuel cell performance [1,2]. Net Water Transport Coefficient (NWTC) is defined as the ratio between the net water flux through the membrane and the water produced in the cathode catalyst layer by the electrochemical reaction, which directly shows the water transport situation in a PEFC. Many excellent researches have been done to develop the methods for the determination of NWTC [3–13], which are based on the water conservation in a PEFC, and the water out of the cathode and anode are collected from the cathode outlet and anode outlet by some equipments for condensation, then the value of NWTC can be calculated according to the water mass of the collection. However, these researches are limited to the steady state application, and it is a challenge to obtain the real-time dynamic NWTC, which is very import to understand the water transport in the start-up and shut-down process and dynamic behavior during operation of a PEFC. Wang and co-workers [14,15] developed an instrumented cell with segmented flow plate, combining the functions of current collection and gas sampling with one pin (for gas chromatograph) for each segment, which is capable of measuring current and species distributions simultaneously from a single experiment. The two distribution data are subsequently combined in a material balance analysis to yield the net water transport coefficient distribution through the membrane. But this approach is limited by the response and analysis time the GC, so the dynamic behavior is not satisfied. It is good at the measurement of the NWTC distribution in a PEFC.

In this study, a numerical method combined with the experimental results obtained by Tunable Diode Laser Absorption Spectroscopy (TDLAS) humidity sensor for water pressure in cathode outlet and anode outlet was developed to obtain the real-time NWTC, which will be helpful for understanding the water transport in the operation of a PEFC including the start-up and shut-down process.

2. Experiments

In this study, two humidity sensors with TDLAS were used to measure the water content in cathode and anode outlet, which are made in Via Space Inc., and can work at the temperature as high as 110 °C. The response time of the sensors is about 1 s, that's enough to monitor the change of the water pressure changes in the cathode and anode outlet. In our experiments, the fuel cell works at the temperature of 80 °C, and the humidity sensors are kept at 100 °C, the pipes between the outlet and the sensors are kept at 90 °C, which permits the vaporization of the liquid water out of the fuel cell.

A JARI (Japan Automobile Research Institute) standard single PEFC was employed for the experiments. And the MEA (membrane electrode assembly) are composed of Nafion212 membrane

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Nomenclature

Parameters and variables

D	diffusion coefficient ($cm^2\ s^{-1}$)
F	Faraday's constant
i	current (A)
M	molar mass ($kg\ mol^{-1}$)
m	mass flow rate through the membrane
N	diffusion rate
P	pressure (Pa)
V	volume
v	velocity ($m\ s^{-1}$)
x	mass fraction

Greek letters

ρ	density ($kg\ m^{-3}$)

Subscripts

in	into the fuel cell
out	out of the fuel cell
across	through the membrane
reaction	by reaction
w	water
H_2	hydrogen
diffu	for diffusion
H_2O	water

$$\int_{t0}^{t1}(\rho v)_{\text{in}}\,dt=\frac{(\rho v)_{\text{in},t0}+(\rho v)_{\text{in},t1}}{2}(t1-t0)$$

$$\int_{t0}^{t1}(\rho v x_{\text{w}})_{\text{in}}\,dt=\frac{(\rho v x_{\text{w}})_{in,t0}+(\rho v x_{\text{w}})_{\text{in},t1}}{2}(t1-t0)$$

and TGP-H-060 carbon paper. The catalyst loading in the MEA is 0.5 mg cm^{-2} both for anode side and cathode side. The total active area of MEA is 5 cm × 5 cm. The serpentine flow field is used in this experiment. The experimental system is shown in Fig. 1.

3. Numerical method

In the anode side of a PEFC, the total mass conservation can be considered as follows without liquid water:

$$\int_{t0}^{t1}(\rho v)_{\text{in}}\,dt-\int_{t0}^{t1}(m_{\text{w}})_{\text{across}}\,dt-\int_{t0}^{t1}(m_{\text{H}_2})_{\text{reaction}}\,dt=\int_{t0}^{t1}(\rho v)_{\text{out}}\,dt+\oint_{v}\frac{d\rho}{dt}\Delta t\,dV \quad (1)$$

The above equation means the total mass flowing in is equal to that of flowing out plus consumption by the reaction, water through the membrane and the change of the total mass in the anode side due to the density. The value of t1–t0 is the time interval between each neighboring experimental data.

As for the water mass conservation in the anode side, it can be calculated as:

$$\int_{t0}^{t1}(\rho v x_{\text{w}})_{\text{in}}\,dt+\int_{t0}^{t1}(m_{\text{w}})_{\text{across}}\,dt=\int_{t0}^{t1}(\rho v x_{\text{w}})_{\text{out}}\,dt+\int_{t0}^{t1}N_{\text{w,diffu}}\,dt+\oint_{v}\frac{d\rho x_{\text{w}}}{dt}\Delta t\,dV \quad (2)$$

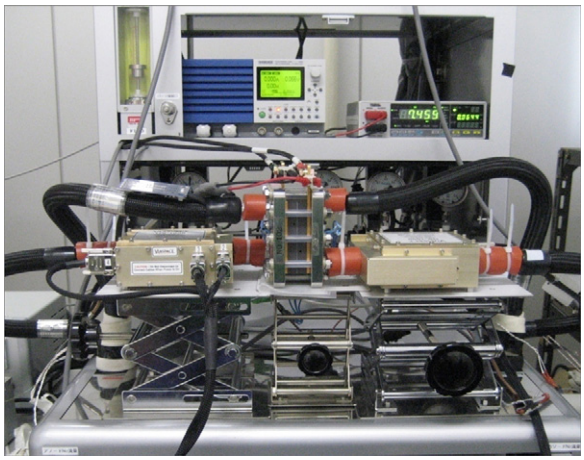

Fig. 1. Experimental system for the measurement of water in the outlet gas of a PEFC.

The above equation means the total water mass flowing in is equal to that of flowing out plus water through the membrane, diffusion, and the change of the water mass in the anode side due to the concentration.

The value of flowing in and flowing out for total mass and water can be estimated as follows:

$$\int_{t0}^{t1}(\rho v)_{\text{out}}\,dt=\frac{(\rho v)_{\text{out},t0}+(\rho v)_{\text{out},t1}}{2}(t1-t0)$$

$$\int_{t0}^{t1}(\rho v x_{\text{w}})_{\text{out}}\,dt=\frac{(\rho v x_{\text{w}})_{\text{out},t0}+(\rho v x_{\text{w}})_{\text{out},t1}}{2}(t1-t0) \quad (3)$$

And the consumed hydrogen, the net water flux through the membrane can be calculated as:

$$\int_{t0}^{t1}(m_{\text{H}_2})_{\text{reaction}}\,dt=\frac{i}{2F}M_{\text{H}_2}(t1-t0)$$

$$\int_{t0}^{t1}(m_{\text{w}})_{\text{across}}\,dt=\alpha\frac{i}{2F}M_{\text{H}_2\text{O}}(t1-t0) \quad (4)$$

where α is the NWTC.

The mass change in the time interval from $t0$ moment to $t1$ moment can be estimated as:

$$\oint_{V}\frac{d\rho}{dt}\Delta t\,dV=V\left[\left(\frac{\rho_{\text{in},t1}+\rho_{\text{out},t1}}{2}\right)-\left(\frac{\rho_{\text{in},t0}+\rho_{\text{out},t0}}{2}\right)\right] \quad (5)$$

$$\oint_{V}\frac{d\rho x_{\text{w}}}{dt}\Delta t\,dV=V\left[\left(\frac{\rho_{\text{in},t1}x_{\text{w,in},t1}+\rho_{\text{out},t1}x_{\text{w,out},t1}}{2}\right)-\left(\frac{\rho_{\text{in},t0}x_{\text{w,in},t0}+\rho_{\text{out},t0}x_{\text{w,out},t0}}{2}\right)\right] \quad (6)$$

While the water diffusion from inlet to outlet can be estimated by:

$$\int_{t0}^{t1}N_{\text{w,diffu}}\,dt=\frac{1}{L}\frac{D_{\text{w}}}{RT}\left(\frac{p_{\text{w,out},t0}+p_{\text{w,out},t1}}{2}-\frac{p_{\text{w,in},t0}+p_{\text{w,in},t1}}{2}\right)\Delta t M_{\text{H}_2\text{O}} \quad (7)$$

In the above equations, the inlet water pressure can be obtained according to the inlet humidified temperature, and the outlet water pressure can be obtained by the experimental data. As for the outlet

total pressure, it is equal to the atmosphere pressure in the experiment, and inlet total pressure is adjusted to assure that NWTC is equal to about zero when there is no current. By this way, the above equations are solved to obtain the NWTC and outlet velocity. And the positive value of NWTC means water moves out of the anode side, the negative value means water moves in the anode side as well. The numerical work was accomplished in Matlab software.

4. Results and discussions

Figs. 2–4 show the water pressure in the cathode and anode outlet under the constant current of 5, 8 and 10 A. The humidified temperature for cathode and anode inlet gas are 75 °C respectively, the inlet flow rate for anode is 200 ml min^{-1} which is same as that of cathode. According to the results in Figs. 2–4, it can be seen that there is no liquid water accumulated in the cathode side for the case 5 A, and there is slight flooding in cathode for the case of 8 A, while the serious flooding occurred for the case of 10 A for the measured voltage is quickly decreased. So Figs. 2–4 represent the three general states in the operation of a PEFC respectively.

Figs. 5–7 show the real-time MWTC obtained by the method in the present research. The values of NWTC without current are near to zero, which demonstrates the correctness of the choice of the inlet pressure. Actually, the inlet pressure is very close to the outlet pressure in the present research, which is also proved by the other research that the pressure loss in anode side is very small [16].

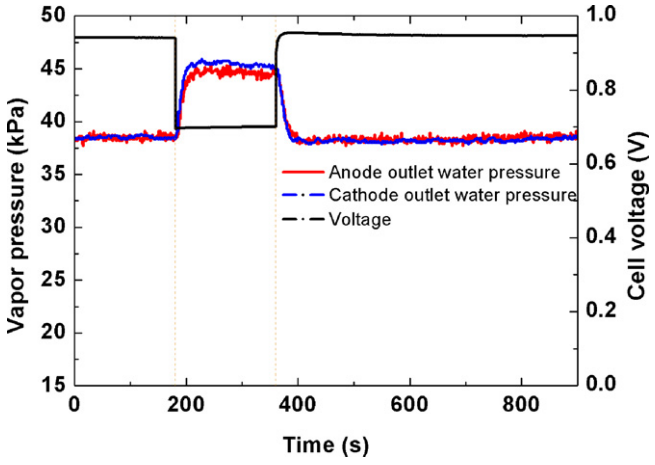

Fig. 2. Outlet water pressure for anode and cathode, and voltage, for the current of 5 A for base case.

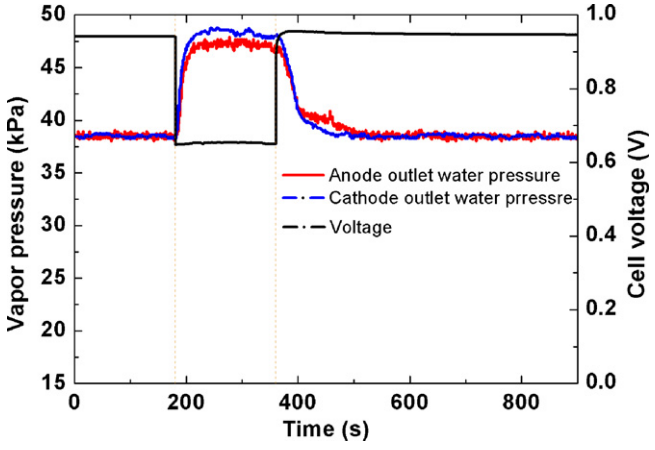

Fig. 3. Outlet water pressure for anode and cathode, and voltage, for the current of 8 A for base case.

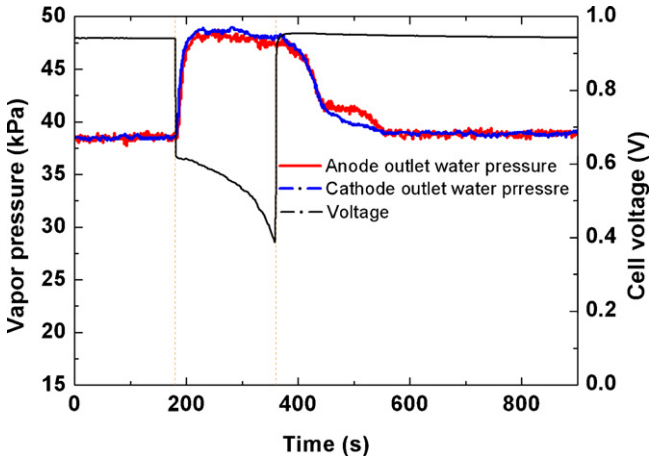

Fig. 4. Outlet water pressure for anode and cathode, and voltage, for the current of 10 A for base case.

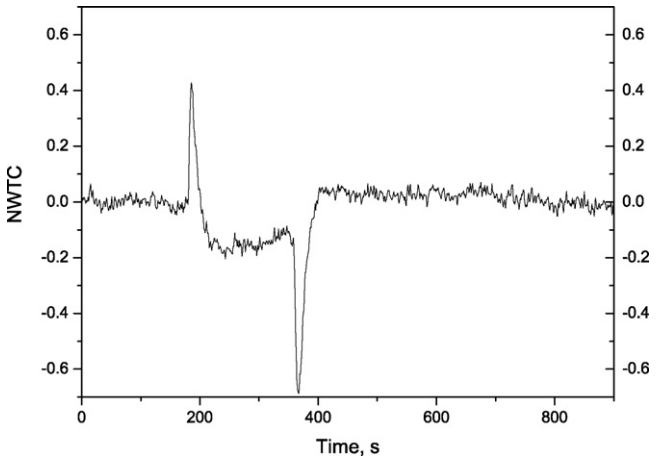

Fig. 5. Real-time NWTC for 5 A for base case.

It can be seen that the NWTC increases quickly after the current is on with the positive value, which means that the water moves out of the anode side quickly. And then, after about a few seconds, the NWTC decreases quickly until it reached the nearly steady value, which means the flowing out rate of the water from anode side decreases quickly until the approximate balance for water transport is built. The time interval between the current-on

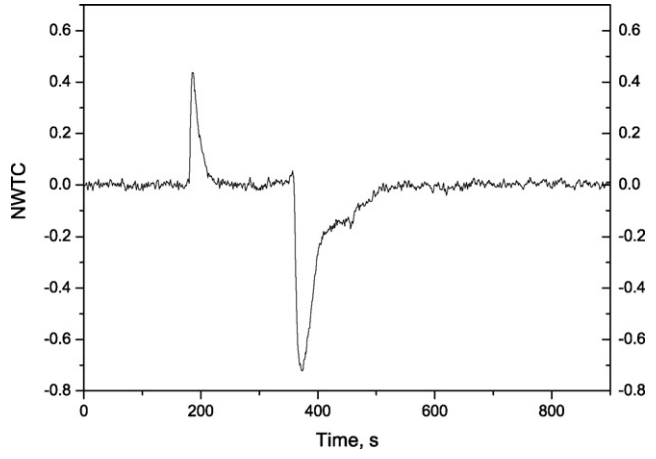

Fig. 6. Real-time NWTC for 8 A for base case.

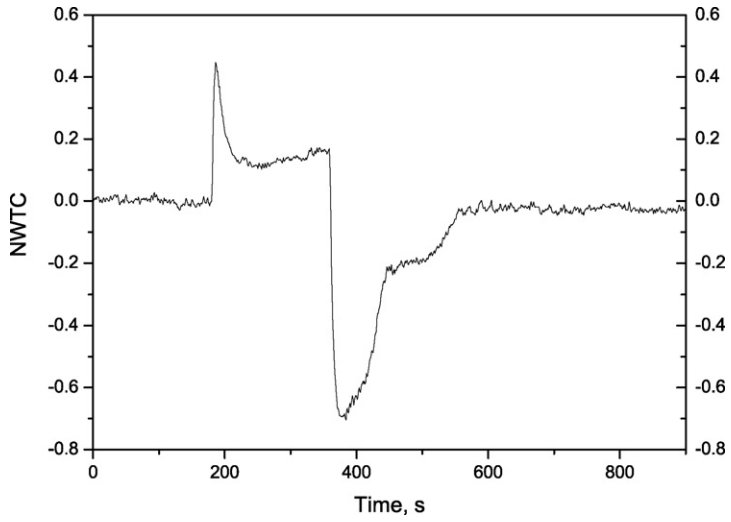

Fig. 7. Real-time NWTC for 10 A for base case.

moment to the approximate balance moment is the time needed for the balance of water transport in a PEFC for start-up. According to the comparison of the above time interval among Figs. 5–7, it can be seen that the time needed for the balance of water transport increases with the increase in the operation current.

The quick increase and decrease in the start-up maybe caused by the transport difference between the osmotic-drag and the back-diffusion. When there is current, the water is produced in the cathode catalyst layer, so the water will diffuse from cathode side to anode side through the membrane, and at the same time, the conduction of proton causes the osmotic-drag of the water out of the anode side. But for the anode side, the pathway for the water out of anode by osmotic-drag and water in anode side by back-diffusion are different, it is obvious that water in anode side by back-diffusion needs to move through the membrane, and when the water moves out of the anode side by the osmotic-drag at the beginning moment, the water of back-diffusion has not reached anode side yet, which cause the quick increase in the NWTC, and with time going on, the water of back-diffusion reached the anode side, so the net water transport from anode to cathode decreases. The speed of decrease is obviously lower than that of increase.

It can be seen that the NWTC quickly decreased after the current is off, which is caused by the fact that the water continuously diffused from cathode to anode, but the osmotic-drag is stopped due to the shut-down of the current. If there is no liquid water in the cathode side, the NWTC will increases quickly to zero due to the removal of the high humidity gas in the cathode side as shown in Fig. 5, but if there is liquid water in the cathode side, the NWTC will increases slowly due to the water back-diffusion from cathode side to anode side until the liquid water is fully removed which takes long time for the serious flooding case shown in Fig. 7.

The obtained values of NWTC in the present research range from −0.2 to 0.2 except for the start-up and shut-down process. The NWTC increases with the increase in the current, and when the current is larger than 8 A, the NWTC is larger than zero, which means net water transports from anode to cathode, but according to the water pressure in Figs. 3–4, it can seen that there is already flooding in the cathode side. And the net water transport from anode to cathode will deteriorate the flooding. So in the view of flooding prevention, the osmotic-drag should be deduced, and it is reasonable to humidify the anode inlet gas with the lower temperature than that of cathode side. So, the osmotic-drag from anode to cathode may decrease and is less than the back-diffusion from cathode to anode, and part of excessive water in cathode can be removed.

5. Conclusions

A numerical approach is developed to determine the real-time NWTC based on the experimental water vapor pressure for the cathode and anode outlet obtained by the optical humidity sensors with Tunable Diode Laser Absorption Spectroscopy (TDLAS). This approach is based on the fact that there is no liquid water in the anode side, and the real-time results can be obtained due to the real-time measurement of outlet water pressure, which is achieved by the TDLAS humidity sensor with the quick response and high accuracy. The results show that NWTC increases and decreases in the process of start-up and shut-down. And the time needed for the water transport balance increases with the increase in the current. The NWTC ranges from −0.2 to 0.2 in the present research for the nearly steady state. Also, the NWTC increases with the increase in the operation current for the nearly steady state. In the view of flooding prevention, it is reasonable to humidify the anode inlet gas with the lower temperature than that of cathode side by decreasing the osmotic-drag water from anode to cathode.

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