

Short communication

## Performance characterization of passive direct methanol fuel cells

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### Abstract

The performance of a fuel cell is usually characterized by a polarization curve (cell voltage versus current density) under stabilized operating conditions. However, for passive direct methanol fuel cells (DMFC) that have neither fuel pumps nor gas compressors, the voltage at a given current density varies with time because methanol concentration in the fuel reservoir keeps decreasing during the discharging process. The important question brought up by this transient discharging behavior is: under what conditions should the polarization data be collected such that the performance of the passive DMFC can be objectively characterized? In this work, we found that the performance of the passive DMFC became relatively stable as the cell operating temperature rose to a relatively stable value. This finding indicates that the performance of the passive DMFC can be characterized by collecting polarization data at the instance when the cell operating temperature under the open-circuit condition rises to a relatively stable value.

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**Keywords:** Passive DMFC; Open circuit voltage (OCV); Cell performance; Cell temperature; Waiting time

### 1. Introduction

Because its unique features, such as high energy density, compact system, and ease in handling liquid fuel, the direct methanol fuel cell (DMFC) has been recognized as a promising power source for mobile and portable applications. Over the past decade, extensive effort [1–8] has been made to the study of the active DMFC, in which the fuel is fed by liquid pumps and oxidant is supplied by gas compressors. However, these auxiliary devices not only make the fuel cell system complex but also decrease the achievable energy and power density due to the parasitic power losses. It may not be practical to operate the DMFC under such conditions for powering portable electronic devices. For this reason, passive DMFCs with neither pumps nor compressors have been proposed and studied [9–27]. This type of passive DMFC not only offers the advantage of simple and compact system but also makes it possible to eliminate parasitic power losses for powering ancillary devices required in the active DMFC. Because of these advantages, the passive DMFC has

received much more attention in the area of small fuel cells. Kim et al. [9] investigated the influences of various operating conditions on the performance of a passive, air-breathing, monopolar DMFC stack that consisted of six unit cells, such as temperature, methanol concentration and reactants feeding methods. Liu et al. [11] studied sintered stainless steel fiber felt as the gas diffusion layer in an air-breathing DMFC. The effect of methanol concentration was also studied in this work. Kim [12] developed a vapor-feed passive direct methanol fuel cell to achieve a high energy density by using pure methanol for mobile applications. Compared with a liquid-feed passive DMFC, the vapor-feed passive DMFC with humidified MEA maintained 20–25 mW cm<sup>-2</sup> power density for 360 h and performed with a 70% higher fuel efficiency and 1.5 times higher energy density. Abdelkareem and Nakagawa [13] investigated the effect of employing a porous carbon plate on the performance of a passive direct methanol fuel cell (DMFC) and found that the high methanol concentration could be used because of the increased mass-transfer resistance on the anode resulting from the porous carbon plate.

The performance of a fuel cell is usually characterized by a polarization curve (cell voltage versus current density). In an active DMFC, the polarization curve can be measured at any time

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when the cell operation reaches a stabilized condition since the concentration of reactants and the cell operating temperature can actively be controlled by methanol pumps and oxygen/air blowers. For the passive DMFC, however, the methanol concentration in the fuel reservoir decreases with time during the discharging process, leading to variation in the rate of methanol crossover, which, in turn, also cause the cell operating temperature to vary. As a result, the voltage at a given current density varies with time. This transient discharging behavior makes it difficult to objectively characterize the performance of the passive DMFC. A critical question is: under what conditions should the polarization data be collected such that the obtained polarization can truly reflect the performance of this type of passively operated fuel cell? Unfortunately, this point has never been addressed in the past. Most researchers reported their measured polarization curves but did not mention the conditions to collect experimental data. Our literature review turns out that different researchers started to measure the performance of their passive DMFCs at different instances after methanol was charged [13–15].

The objective of this work was to identify the operating condition under which the polarization data can be collected such that the performance of the passive DMFC can be objectively characterized. The experimental results indicated that for a given methanol concentration the measured voltages at different current densities kept increasing with the cell operating temperature, but became relatively stable when the temperature rose to a relatively stable value. Based on this finding, we suggest that the performance of the passive DMFC be characterized by collecting polarization data at the instance when the cell temperature becomes relatively stable.

## 2. Experimental

### 2.1. Membrane electrode assembly (MEA)

A pretreated Nafion 115 membrane with a thickness of 125  $\mu\text{m}$  was employed in this work. The pretreatment procedures included boiling the membrane in 5 vol%  $\text{H}_2\text{O}_2$ , washing in DI water, boiling in 0.5 M  $\text{H}_2\text{SO}_4$  and washing in DI water for 1 h in turn. The pretreated membranes were kept in the DI water prior to the fabrication of MEAs. Single-side ELAT electrodes from ETEK were used in both anode and cathode, where carbon cloth (E-TEK, Type A) were used as the backing support layer with 30 wt% PTFE wet-proofing treatment. The catalyst loading on the anode side was  $4.0 \text{ mg cm}^{-2}$  with PtRu black (1:1 a/o), while the catalyst loading on the cathode side was  $2.0 \text{ mg cm}^{-2}$  using 40 wt% Pt on Vulcan XC-72. Furthermore,  $0.8 \text{ mg cm}^{-2}$  Nafion<sup>®</sup> ionomer was coated onto the surface of each electrode. Finally, MEA with an active area of  $4.0 \text{ cm}^2$  were fabricated by hot pressing at  $135^\circ\text{C}$  and 4 MPa for 3.0 min. More detailed information about the MEA fabrication can be found elsewhere [28].

### 2.2. Single cell fixture

As shown in Fig. 1, the MEA mentioned above was sandwiched between an anode and a cathode current collector. The

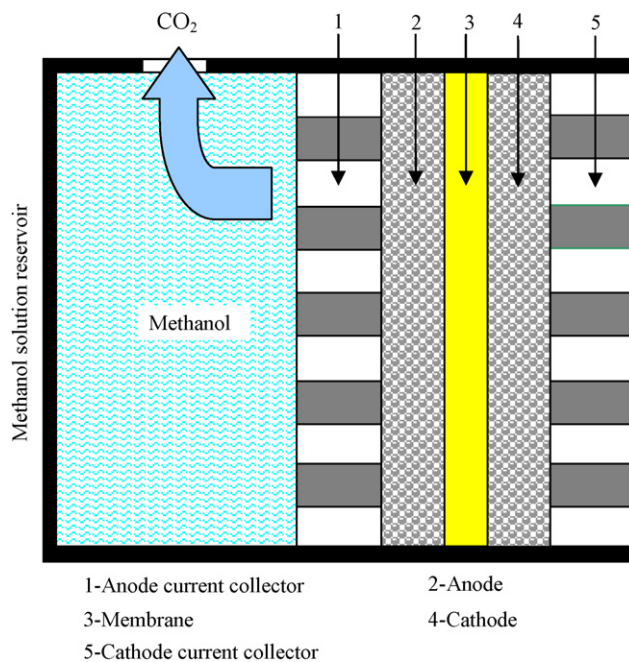


Fig. 1. Schematic of the passive DMFC.

entire cell setup was then held together between an anode and a cathode fixture, both of which were made of transparent organic glass. A 5.0 mL methanol solution reservoir was built in the anode fixture. Methanol was transferred into the catalyst layer from the built-in reservoir, while oxygen, from the surrounding air, was transferred into the cathode catalyst layer through the opening of the cathode fixture. The cell temperature was measured by a thermocouple (Type T), which was installed on the outer surface of the anode gas diffusion layer. The electrical current collectors were made of 316L stainless steel plates of 1.5 mm on the anode and 1.0 mm on the cathode in thickness. A plurality of 2.6 mm-circular holes was drilled in the both current collectors, serving as the passages of fuel and oxidant, which resulted in an open ratio of 47.8%. A 200-nm platinum layer was sputtered onto the surface of the perforated-plate current collectors to reduce the contact resistance with the electrodes.

### 2.3. Electrochemical instrumentation and test conditions

An Arbin BT2000 electrical load interfaced to a computer was employed to control the condition of discharging and record the voltage–current curves. The voltage–current curves were collected by consecutive current steps from the zero current (OCV) to high current. For each discharging current point along the  $I$ – $V$  curve, a 60-s waiting time was needed to obtain the stable voltage at the last second. The cell operating temperature was measured by the Arbin BT2000 built-in function.

All the experiments of the passive DMFCs were performed at room temperatures of  $20.9$ – $21.6^\circ\text{C}$  and the relative humidity of 66–72%. Prior to the performance test, the MEA was installed in an active cell fixture and activated at  $70^\circ\text{C}$  about 24 h. During the activation period, 1.0 M methanol was fed at  $1.0 \text{ mL min}^{-1}$ ,

while oxygen was supplied under atmospheric pressure at a flow rate of  $50 \text{ mL min}^{-1}$ .

### 3. Results and discussion

#### 3.1. Transient discharging behavior

Fig. 2 shows the measured polarization curves of the passive DMFC filled with 3.0-M methanol solution at different waiting times (see the legends). Here, the waiting time is defined as the length of time that passes from the instance when methanol is filled into the fuel reservoir to that when a polarization curve measurement is started. It can be seen from Fig. 2 that at rather low current densities ( $<3 \text{ mA cm}^{-2}$ ) including the open-circuit condition, the measured voltages increased as the waiting time was changed from 1 min to 10 min and then decreased to a stable value for other longer waiting times. At middle and high current densities, however, the measured voltages kept increasing with increasing the waiting time, but became stable for the waiting time longer than 40 min.

To explain the possible mechanism leading to the transient discharging behavior of the passive DMFC, the variation in the open-circuit voltage (OCV) of the passive DMFC with time was measured for a period of 2.0 h after charging 3.0 M methanol into the 5.0-mL reservoir. The transient OCV, along with the measured transient cell temperature, is presented in Fig. 3. It is seen from Fig. 3 that the OCV remained to be near zero before charging the fuel, while the cell temperature stayed at room temperature. After the fuel was filled, over the entire period the OCV exhibited two peaks with the representations of Peak I and II in Fig. 3, finally decreased to a stable value of 0.545 V. At the beginning, once the fuel was filled, the OCV increased rapidly (about 15 s) to Peak I with a voltage of 0.9 V, and then declined quickly (about 18 s) to a value of 0.69 V. The formation of Peak I of the OCV can be attributed to two main reasons: hydrogen evolution on the anode and the low mixed overpotential on the cathode. First, when the methanol is filled into the fuel reservoir at the anode, it immediately permeates to the

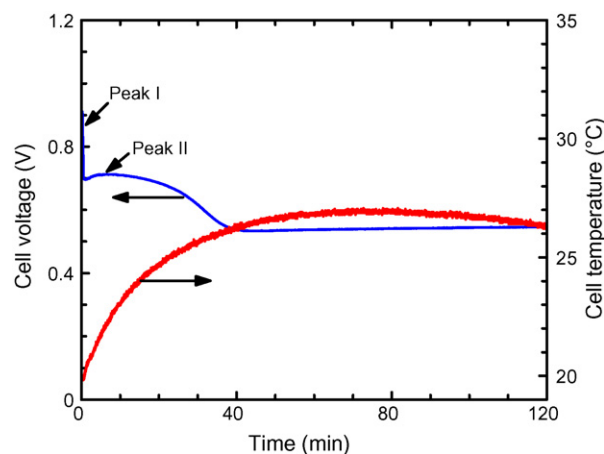


Fig. 3. Transient behaviors of the OCV and cell temperature. Anode: 3.0 M methanol; cathode: room temperature:  $21.2^\circ\text{C}$ , relative humidity: 68%.

cathode through the Nafion<sup>®</sup> membrane due to the concentration difference. The permeated methanol will react directly with oxygen in the cathode catalyst layer, reducing the local oxygen concentration. Because part of the gas diffusion layer is exposed to the sounding air via the openings and the remaining part is covered by the ribs, the opening region exhibited a much lower mass-transfer resistance than did the rib region. As a result, the above reaction will quickly reduce the oxygen concentration under the ribs, whereas the oxygen in the openings remains relatively rich. This non-uniform distribution of oxygen on the cathode can lead to hydrogen evolution on the anode [8]. Subsequently, the hydrogen generated in the gas evolution period will be oxidized electrochemically in the anode catalyst layer, resulting in a lower overpotential on the anode. Secondly, since the methanol concentration on the cathode at the beginning is rather low, the mixed overpotential is very small. As such, these two effects contributed to a higher OCV of Peak I shown in Fig. 3. The following rapid decline in the OCV after Peak I was because the hydrogen generated in the gas evolution period was completely oxidized and the rate of methanol crossover increased. After about 10 min, the second OCV peak (Peak II) then appeared, followed by a gradual decrease to a relatively stable value of 0.545 V in 40 min. This is because the increased temperature as a result of the exothermic reaction between the permeated methanol and oxygen on the cathode enhanced the electrochemical kinetics at the both the anode and cathode. On the other hand, the higher temperature resulted in a higher rate of methanol crossover and thus an increase in the mixed overpotential. The combined effect of the increased cell temperature and mixed overpotential led to the Peak II. Apparently, this behavior resulted in a lower OCV at 1-min than that at 10-min after the cell was charged. As a result, the cell performance measured at the 1-min waiting time was lower than that measured at the 10-min waiting time at the rather low current densities including the OCV. In addition, since the cell voltage decreased with the time after 10 min, the measured performances with the waiting time from 10 min to 40 min gradually decreased at low current densities, as shown in Fig. 2. However, this is not the case at middle and high current densities. The cell voltages at middle

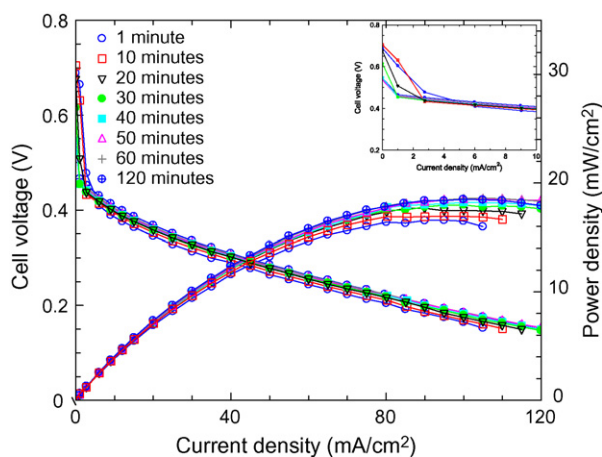


Fig. 2. Comparison in the cell performance measured at different waiting times. Anode: 3.0 M methanol; cathode: room temperature:  $21.6^\circ\text{C}$ , relative humidity: 72%.

and high current densities increased with the waiting time. This is because the cell temperature continuously increased in 40 min after the fuel injection shown in Fig. 3. The increased cell temperature led to the faster electrochemical kinetics on both the anode and cathode and thereby the increased cell performance. As a result, the measured performance of the passive DMFC increased with the waiting time at middle and high current densities. After about 40 min, the cell temperature almost remained at 26.8 °C with a slight increase followed by a slight decrease, while the OCV remained at a relatively stable value of 0.545 V. The increase in the cell temperature is because of the exothermic reaction between the permeated methanol and oxygen on the cathode. The cell temperature decreases during this period can be attributed to two aspects: first, the heat loss from the cell to the ambient may be enhanced because of the evaporation of the accumulated water; secondly, the methanol concentration in the fuel reservoir decreased with the time, causing a decrease in the rate of methanol crossover and hence the lowered heat generation rate and cell temperature. However, since the variation of the cell temperature was small, the cell temperature remained relatively stable, resulting in a relatively stable OCV of 0.545 V. The relatively stable cell temperature and OCV led to the almost same performance of the passive DMFC measured at the waiting time longer than 40 min. To further illustrate the transient discharging behavior of the passive DMFC, the cell voltage corresponding to the current density of 80 mA cm<sup>-2</sup> measured at different waiting times are shown in Fig. 4. It is seen that the cell voltage kept increasing with the waiting time but became relatively stable when the waiting time was longer than 40 min. It is interesting to notice that the variation trend in the cell voltage with the waiting time shown in Fig. 4 is similar to the cell operating temperature shown in Fig. 3. This fact reveals that the transient discharging behavior of the passive DMFC depends mainly on the cell operating temperature. In summary, the measured polarization curves kept varying with the waiting time as a result of the increased cell temperature, but the voltages became relatively stable when the cell temperature rose to a rel-

atively stable value. The experimental results indicated that the performance of the passive DMFC can be more objectively characterized by collecting polarization data at the instance when the cell temperature rises to a relatively stable value.

### 3.2. Effect of methanol concentration

Fig. 5 compares the polarization curve measured at the waiting time of 1 min and that measured at the stable cell temperature with 2.0 M and 4.0 M methanol operations. It is seen that for the 2.0 M and 4.0 M methanol operations the performance measured at the stable cell temperature was higher than that measured at the 1-min waiting time. This is simply because the cell temperature at the steady state was higher than that at the beginning. The increased cell temperature speeded up both the methanol oxidation and oxygen reduction reactions, thereby leading to the improved cell performance measured at the stable cell temperature. It is also interesting to notice that the performance difference between the stable cell temperature and the 1-min waiting time with the 4.0 M methanol operation was much higher than that with the 2.0 M methanol operation. This is because the rate of methanol crossover at 2.0 M methanol is lower than that at 4.0 M, causing a lower steady-state temperature, as evidenced from the measured temperature shown in Fig. 6. Therefore, the improvement of the cell performance at 2.0 M methanol was lower than that at 4.0 M methanol at their stable temperatures. In addition, it is seen from Fig. 5 that the performance measured at the 1-min waiting time between 2.0 M and 4.0 M did not show significant difference, except 2.0 M methanol yielded higher voltages than did 4.0 M methanol at low current densities as a result of the lower rate of methanol crossover. However, the performance measured at the stable cell temperature with the 4.0 M methanol operation was much higher than that with the 2.0 M methanol operation. This phenomenon is caused by the increased cell temperature resulting from the methanol crossover. When the cell performance was measured at the 1-min waiting time, the heat generated by the exothermic reaction between the per-

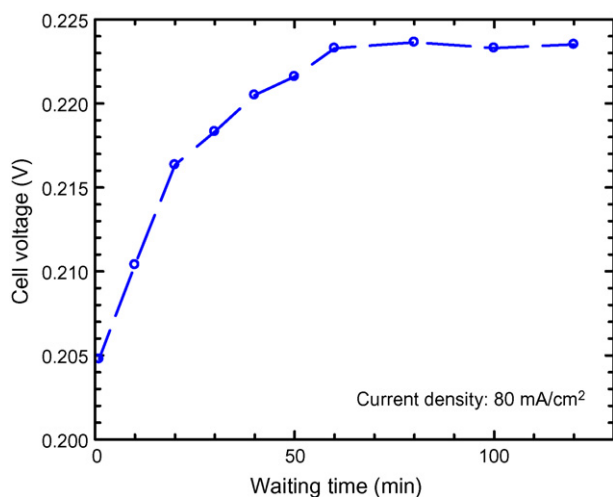


Fig. 4. Variation in the cell voltage corresponding to the current density of 80 mA cm<sup>-2</sup> measured at different waiting times. Anode: 3.0 M methanol; cathode: room temperature: 21.2 °C, relative humidity: 68%.

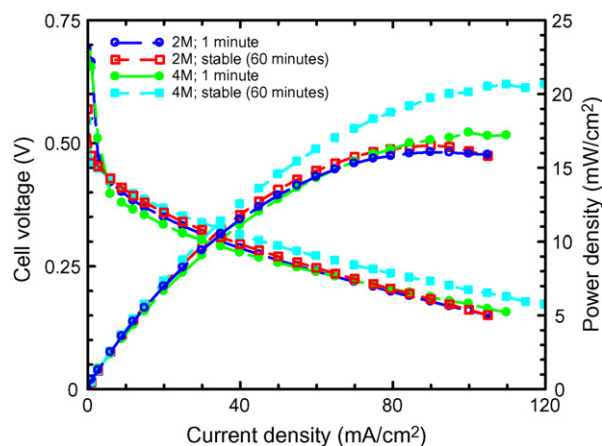


Fig. 5. Comparison in cell performance measured at the 1-min waiting time and the stable condition for the 2.0 M and 4.0 M methanol operations. Anode: 2.0 M and 4.0 M methanol; cathode: room temperature: 20.9 °C, relative humidity: 66%.

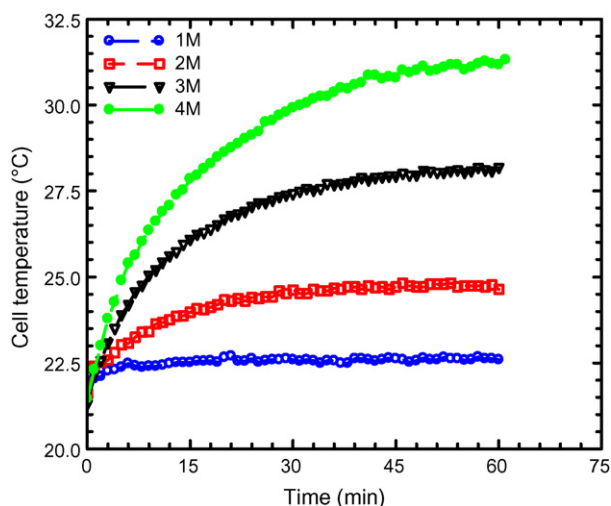


Fig. 6. Variation in cell operating temperature. Anode: 1.0–4.0 M methanol; cathode: room temperature: 20.9 °C, relative humidity: 66%.

meated methanol and oxygen was smaller because of the lower rate of methanol crossover. Hence, the cell temperatures for the both 2.0 M and 4.0 M methanol operations were the almost same, leading to the almost same cell performance. However, when the performance of the passive DMFC was measured at the stable cell temperature, the 4.0 M methanol operation showed a higher cell temperature because of the higher heat generation rate on the cathode resulting from the higher rate of methanol crossover. The increased cell temperature led to the faster electrochemical kinetics on both the methanol oxidation on the anode and oxygen reduction on the cathode and thereby the significantly increased cell performance. These results are in good agreement with those reported elsewhere [21]. As a consequence, these experimental results further confirm that the higher methanol concentration yields a higher performance as a result of the increased cell temperature caused by the increased methanol crossover, indicating that the temperature effect on the passive DMFC is a key factor for improving the cell performance. More importantly, these experimental results indicated that in order to truly characterize this type of fuel cell, the polarization data of the passive DMFC can be collected at the instance when the cell temperature under the open-circuit condition becomes relatively stable.

### 3.3. The condition to measure polarization curves

The experimental results discussed above indicate that the timing to start collecting polarization data is critical to truly reflect the performance of the passive DMFC. In this work, we suggest that a polarization curve be measured at the instance when the cell temperature under the open-circuit condition rises to a relatively stable value. If more than one polarization curves are needed, the measurement of each following-up curve has to be started up by cooling down the cell to a temperature lower than the stabilized value during the previous polarization curve measurement. Otherwise, the measurement will be made under a condition which deviates from the defined condition. To further elaborate this, we show two polarization curves for the 3.0 M

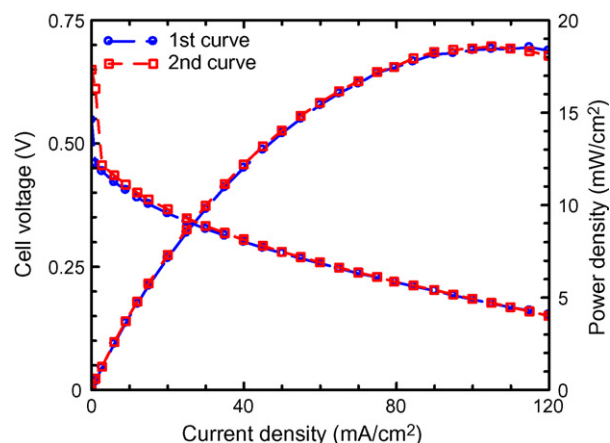


Fig. 7. Comparison of two polarization curves measured without interruption. Anode: 3.0 M methanol; cathode: room temperature: 20.9 °C, relative humidity: 68%.

methanol operation in Fig. 7, where the first polarization curve was measured at the instance when the cell temperature under the open-circuit condition rose to a stable value, whereas the second polarization curve was measured immediately after the first one was completed. From this figure, it is seen that the second curve shows slightly higher voltages at low current densities, including the OCV, than does the first one, although at middle and high current densities there is almost no difference between the two curves. To explain why the second curve gives higher performance, we now look at Fig. 8, where the cell operating temperature history during the course of the two consecutive polarization curve measurements. Clearly, the second polarization curve was measured at an elevated temperature compared to that for the first one. This explains why the second curve gives higher voltages, particularly at low current densities. Hence, the measurement of each following-up polarization curve has to be started up by cooling down the cell to a temperature lower than the stabilized value during the previous polarization curve measurement. This can be further evidenced by the two polariza-

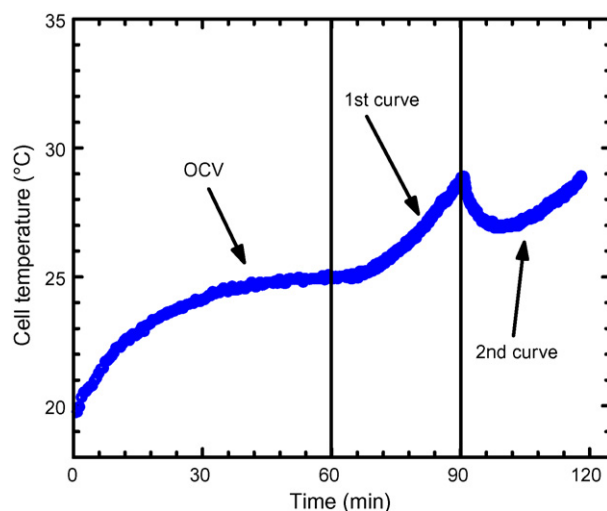


Fig. 8. Comparison in cell operating temperatures. Anode: 3.0 M methanol; cathode: room temperature: 20.9 °C, relative humidity: 68%.

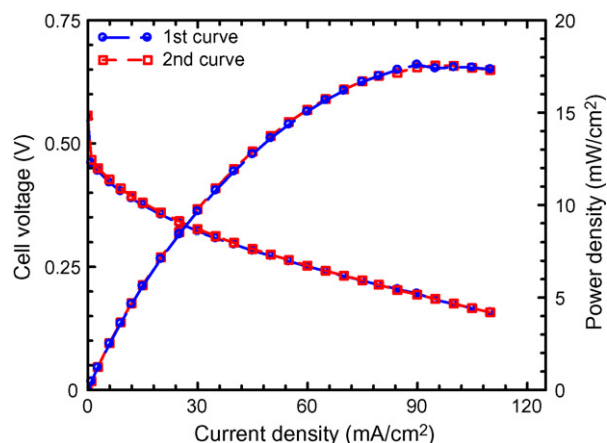


Fig. 9. Comparison of two polarization curves measured with interruption. Anode: 3.0 M methanol; cathode: room temperature: 21.4 °C, relative humidity: 68%.

tion curves shown in Fig. 9, where the two polarization curves became almost identical. This time the second curve was measured not immediately after the first curve. Instead, after the first polarization curve was completed, methanol was removed from the cell; the second curve was measured under the condition by refilling methanol into the fuel reservoir and until the cell temperature rose again to the stable value. Hence, these experimental results further indicated that the performance of the passive DMFC can be more objectively characterized by collecting polarization data at the instance when the cell temperature rises to a relatively stable value under the open-circuit condition, particularly in case more than one polarization curves are needed.

### 3.4. Concluding remarks

The experimental results presented in this paper have shown that the polarization curve of a passive DMFC kept varying with the waiting time, which is defined as the length of time that passes from the instance when methanol is filled into the fuel reservoir to timing to start measuring a polarization curve. However, the voltages at different current densities for a given methanol concentration became relatively stable when the cell temperature under the open-circuit condition rose to a stable value. The experimental results also indicated that the variation in the performance of the passive DMFC was closely related to the change in the cell temperature, which depends primarily on methanol concentration in the fuel reservoir under a given ambient condition. The results obtained in this work suggest that the performance of the passive DMFC be objectively characterized by collecting polarization data at the instance when

the cell temperature under the open-circuit condition rises to a relatively stable value.

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