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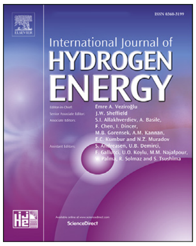

Effects of reformate on performance of PBI/H_3PO_4 proton exchange membrane fuel cell stack

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HIGHLIGHTS

- A five-cell high-temperature proton exchange membrane fuel cell is studied.
- The effect of different mixtures of hydrogen fuel is investigated.
- The influence of carbon monoxide on performance of PEMFC is examined.
- The effect of working temperature on the behavior of PEMFC is studied.
- The increase of temperature improves the carbon monoxide tolerate of PEMFC.

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ABSTRACT

The present study aims to examine the effect of nitrogen and carbon monoxide concentrations as well as the working temperature and the stoichiometry number on the performance of a self-made five-cell high-temperature Proton-exchange membrane fuel cell stack (PEMFC). The concentration of hydrogen in a reformed gas can be varied, and it may contain poisonous substances such as carbon monoxide. Hence, the composition of the fuel gas could affect the performance of the PEMFC. The polarization curve and the electrochemical impedance spectrogram are utilized to examine the behaviors of PEMFC. The cell temperature of 160 °C is found as an optimal working temperature in this study for high-temperature PEMFC. Measured results show that the stoichiometry of the anode gas has a minimal effect on the PEMFC performance. A high percentage of nitrogen makes hydrogen dilute and leads to poor cell performance. When carbon dioxide exceeds 3%, the pt-catalyst was covered with the CO and the cell performance significantly decreased. Finally, a raise of the PEMFC temperature boosted the catalyst energy and improved the detachment of the carbon monoxide and eventually enhanced carbon monoxide tolerance.

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Introduction

In recent years, due to the influence of extreme climate and greenhouse effects, green energy is a hot topic in many areas of recent researches. In this regard, fuel cells are a promising green technology, which among them, the proton exchange membrane fuel cells (PEMFCs) are capable of providing high efficiency, low noise and low pollution [1]. Besides, the fuel gas of a PEMFC is hydrogen, which can be obtained from natural gas. Apart from natural gas, hydrogen can also be achieved from renewable resources such as biogas, ethanol, and biomass [2]. Due to potential applications of PEMFCs in many portable and stationary applications, these fuel cells have been the subjects of various researches [2].

The development of PEMFCs was intensified when major companies started to use PEMFCs in their products. For instance, Toyota introduced a hydrogen fuel cell car the ‘Mirai’, while other major companies also introduced their products such as Hyundai (Tucson), Mercedes (B-Class), Honda (Clarity) [3]. Currently, PEMFCs, which are commonly used for system integration, are mostly low-temperature PEMFCs (LT-PEMFCs), which are mainly sensitive to the purity of hydrogen in fuel gas. The LT-PEMFCs primarily utilize perfluorosulfonic acid (Nafion) as the membrane. The structural integrity of this type of membrane is supported by a hydrophobic phase, functioning as the continuous phase, and a sulfonic acid group, which provides a hydrophilic phase for the water reservoir [4]. A charge carrier inside the Nafion membrane, water, is essential for the proton conductivity. Thus, keeping the membrane in a hydrated condition is necessary for the proper functioning of PEMFCs and the membrane inside them [5].

A crucial issue in PEMFCs is water management in the cathode [6]. The lack of an adequate amount of water leads to dehydration of the membrane and results in the reduction of the proton conductivity, which drastically elevates the cell resistance. In contrast, too much water floods the electro-catalyst cathode and limits the oxygen diffusion [7,8] and also reduce the output performance [9]. A typical working temperature of an LT-PEMFC is below 100 °C since the Nafion membrane requires an adequate level of moisture. However, a too low temperature of PEMFC reduces the kinetic reaction while a too high temperature reduces the moisture of the membrane and declines its charge transport capability. Hence, both water management and thermal management systems are inescapable parts of an LT-PEMFC. Very recently, Zhang and Jiao [10] addressed the issues of PEMFCs in a comprehensive review.

Another critical challenge of LT-PEMFC is the catalyst poisoning by carbon monoxide. The platinum, used as the catalyst to enhance the electrochemical reaction, is sensitive to carbon monoxide where a 10 ppm concentration of CO can notably reduce the performance of the catalysis by covering its surface [11,12]. Thus, a supply of hydrogen fuel with high purity (99.999%) is essential for LT- PEMFCs to avoid poisoning problems. However, the production of pure hydrogen is a costly process, which can also include the production of greenhouse gasses. Thus, many researchers tried to reduce the impact of CO on the reduction performance of LT-PEMFCs. Some of these efforts involve modifying the electro-catalyst, e.g., PtRu/C, using a catalyst with a high CO tolerant, and feeding of oxidants into the fuel. However, these approaches could not fundamentally overcome the problem, and they suffer from degrees of system complexity, system cost, a decrease in the durability and effectiveness of the reaction, and safety issues [3].

Research interest into the high-temperature PEMFCs (HT-PEMFCs) has raised in recent years to overcome the mentioned problems of LT-PEMFCs such as water management difficulties and carbon monoxide poisoning of the catalysis. HT-PEMFCs typically work at a temperature above 120 °C since a temperature lower than 120 °C can result in the formation of liquid water. In an HT-PEMFC, the increase of temperature alters the operating conditions of the fuel cell such as the changing of the charge transfer resistance and protons as well as the kinetic reaction. At higher operating temperatures, the high-temperature energy can force most of the poison away from the catalyst, so an HT-PEMFC has a better tolerance to poisonous gases than LT-PEMFCs. Hence, the increase of temperature improves the tolerance of the catalysis to carbon monoxide impurities as much as 3% or more [13]. This amount of allowable impurity is promising for developing simple hydrogen reformer techniques such as methanol, partial oxidation of hydrocarbons, gasification of coal, natural gas steam reformer [3].

A proton exchange membrane, commonly used in HT-PEMFCs, is made of Phenylbenzimidazole (PBI). Unlike the Nafion membrane, commonly used in LT-PEMFCs, a PBI membrane has a relatively high glass transition temperature 420–426 C and also has good mechanical and chemical properties in high-temperature environments. In addition to PBI, there is also ABPBI material, which is a high-temperature film similar to PBI. Although ABPBI has better mechanical strength, simpler structure, and a lower price compared to PBI [14], the PBI has better durability than ABPBI [15]. A proper amount of water can increase transport efficiency, but too much water will carry away the phosphoric acid and reduce transfer efficiency. Besides, if the gas is not humidified, the phosphoric acid is easily dehydrated to pyrophosphoric acid when the cell-temperature raises to about 140 C [16]. If the temperature is too high, the phosphoric acid dehydration will be accelerated [17], increasing impedance and reducing the fuel cell performance.

Very recently, Nalbant et al. [18] investigated the energy and exergy performance benefit of an HT-PEMFC for an integrated cogeneration system. The operation temperature was which operates between 160 °C and 200 °C. The outcomes revealed that the anode stoichiometric ratio was the most influential parameter, affecting the performance of the integrated system. The operating temperature of 160 °C was found the best operating temperature for the maximum performance. Zhu et al. [19] employed a data-driven model to study the performance of HT-PEMFCs. The results of this theoretical study show that the increase in the operating temperature enhances performance. Chen and Su [20] successfully developed a new HT-PEMFC using stamped 304 stainless steel bipolar plates. Nalbant et al. [21] proposed a 1-D semi-empirical model for an HT-PEMFC operating between 160 °C and 200 °C. The feeding gas mixture could be hydrogen and carbon monoxide.

Considering HT-PEMFCs, most of the literature studies are mainly focused on single-cell PEMFCs, and there are only a few studies regarding multi-cell (stack) PEMFCs. The literature review shows that increasing the temperature of an HT-PEMFC helps to improve performance and reduce the internal impedance of the cell. A decline in the supplied hydrogen concentration reduces the hydrogen diffusion and consequently deteriorates the fuel cell performance. The presence of carbon monoxide gas poisons the PEMFC catalyst and reduces the performance of the fuel cell. The higher the concentration of carbon monoxide, the worse the fuel cell performance. Fixing the concentration of carbon monoxide and increasing the temperature of the fuel cell help to increase the resistance of the fuel cell to poisonous substances. Considering the gas mixture for fuel cells, Pinar et al. [22] performed experiments to investigate the effect of the stoichiometry of anode (hydrogen) and cathode (oxygen) gases on a fuel cell performance. They performed tests for the various stoichiometry of the cathode as 1.0, 1.5, 2.0, 3.0, 4.0. It was found that the increase of the stoichiometry notably improves the performance, but the increased performance is not apparent for a stoichiometry of 2.0. Indeed, raising the stoichiometry up to 2.0 saturates the cathode. At the anode side, the increase of the stoichiometry to 1.2, 1.5, 2.0, and 2.2, shows a trend of behavior similar to the cathode, and a rise in the stoichiometry enhances the cell performance. However, the stoichiometric number 2.2 is worse than that of 2.0. This is since excessive hydrogen dehydrates the proton exchange inside the fuel cell, which results in a drier membrane and increasing the internal impedance of the fuel cell. Hence, excessive hydrogen leads to a decrease in performance.

Jalani et al. [23] changed the stoichiometric number of cathode gas (air) to 1.4, 2.0, 2.5, 6.0 for a fixed cell temperature of 160 C. They studied the polarization curve and found that the higher the stoichiometry number, the better the fuel cell performance. Since only about one-fifth of the air is oxygen, if the air is replaced with oxygen, better fuel cell performance could be obtained. Liu et al. [24] further studied the changes in the internal catalyst of the fuel cell. The literature review shows that the rate of adsorption and detachment of air is slower than that of hydrogen, and hence, the reaction of the cathode portion is more pronounced on the fuel cell performance than that of the anode portion. After the operation, the catalyst in the cathode portion will be more concentrated than the anode portion. Hence, the contact area of the catalyst dramatically reduces at the cathode side, which makes the interaction of the oxygen with the catalyst difficult. Various aspects performance improvements for PEMFCs such as amino acid clusters [25], using a dot matrix and sloping baffle cathode for fuel cells flow field [26], Low-Pt membrane electrode assemblies [27], subzero startup assistance [28], improving the oxygen reduction reaction by templated growth of non-precious metal catalyst on porous carbon [29], and reduction of mass transport loss by freeze-drying of cathode catalyst layers [30] are explored by recent researchers. Moreover, anion-exchange membrane fuel-cells also have been subject to various recent studies [31,32].

Considering the poisoning effect, most of the literature-works were mainly studied the LT-PEMFCs and HT-PEM single fule cells. The experiments on HT-PEMFC stacks are scarce, but all had reported common phenomenon: carbon monoxide poisoned the fuel cells, and fuel gas also affected the performance of the fuel cells. Bhatia and Wang [33] explored the effects of hydrogen concentration on a single-cell performance and its toxic resistance. It was found from the experiment that the fuel cell performance under the hydrogen concentration of 40% is only slightly worse than that of a pure hydrogen state. However, further reducing the hydrogen concentration lead to fuel cell starvation at the catalyst. Moreover, the carbon monoxide can be easily combined with the catalyst surface, which reduces the interaction of hydrogen. As a result, diluting hydrogen supply increases the cell impedance and degrades the fuel cell performance. Qi et al. [34] addressed the effect of using single, binary and ternary contaminant mixtures, containing bromomethane, acetonitrile, and propene, on the performance of PEMFCs. It was found that the hydrolysis of acetonitrile led to the ammonium-ions formation and enhanced the membrane resistance by an improvement of ions exchange with membrane protons. The accumulation of bromide on the surface of the catalyst reduced the surface area of the catalyst.

Yan et al. [35] reported not only carbon monoxide but also carbon dioxide affects the fuel cell performance. A fuel cell can be poisoned by carbon monoxide, produced by reverse water gas shift reaction (RWGS) [36]. The influence of operating conditions on a degradation mechanism PBI membranes was investigated in Ref. [37] at high-temperatures. Meyer et al. [38] addressed the carbon degradations in PEMFCs by using electrochemical impedance spectroscopy of the catalyst. Moreover, the degradation behaviour of anion-exchange membrane fuel-cells is also investigated by Maurya et al. [39]. In addition to carbon monoxide, which poisons the fuel cell, the sulfurized material [40,41] and iron ions [42] are also harmful to the fuel cell. In recent years, there have been quite a lot of studies on the number of PBI and Poly (2,5-benzimidazole) (ABPBI), and the influence of catalyst components on fuel cell performance [43,44]. The purpose was to improve fuel cell performance and increase poisoning resistance. Among them, Hu et al. [45] employed Pt–Mo as a catalyst instead of a conventional Pt–Ru catalyst. The results show that the fuel cell performance of the Pt–Ru catalyst is better than that of the Pt–Mo catalyst in the case of pure hydrogen. However, after introducing 25–1000 ppm of carbon monoxide, it was found that the Pt–Mo catalyst is significantly more resistant to poisoning than the Pt–Ru catalyst. Sung et al. [31] performed experiments on the performance recovery of low-temperature PEM single cell poisoned by carbon monoxide. During the experiment, 53 ppm of carbon monoxide was introduced into the anode gas while the voltage of the fuel cell was fixed at 0.6 V. Then, the air was introduced to the cell, and the current were measure. It was found that the airflow increased the cell current. The higher the stoichiometry of the air, the higher the current was. However, the current recovery from 5% to 20% of the excess air was not much different.

Thomassen et al. [46] investigated the effects of gas mixture on the stack performance of HT-PEMFC, including adjusting the hydrogen concentration, which are 100%, 80%, 60%, and 40%, while the equilibrium gas was nitrogen. As a result, it was found that diluting hydrogen by using nitrogen reduced the available amount of hydrogen for reaction in the fuel cell. Therefore, the performance of the low hydrogen concentration at a high load was significantly lower than that of a high hydrogen concentration. Zuliani et al. [47] conducted a study on HT-PEMFC systems. The fuel gas was a hydrogen-rich gas, which was produced from natural gas. The analysis of the power consumption of each part showed that the most energy-consuming part of the system was in auxiliary equipment of the system such as water pump, air compressor, and cooling system. It is important to note that HT-PEMFCs are more natural to heat recovery due to higher operating temperatures. Authayanun et al. [2,48] studied the use of glycerol and methane to reform hydrogen to supply HT-PEMFCs. It was found that glycerol produces hydrogen more efficiently than methane, and produces less CO, but more CO_2. Increasing the operating temperature of the reformer can also increase the amount of hydrogen production while also reduces CO emissions. Shabani et al. [49] performed an excellent review on the poisoning of PEMFCs.

Lüke et al. [50] designed a five-cell liquid-cooled HT-PEMFC stack and introduced a mixture of 42% hydrogen, 1% carbon monoxide, and 57% nitrogen as a fuel stream. The heat dissipation part only allowed the cooling liquid to flow through the gas. The cold aisle drained excess heat, and there was no additional water cooling channel. Based on the outcomes, it was concluded that reducing the hydrogen concentration and adding carbon monoxide would also cause the performance of the stack to decrease, but the toxic resistance was higher than that of a single cell. Moreover, the influence of the hydrogen concentration was also lower than that of a single cell. The liquid-cooled type controlled the cell temperature better than the air-cooled type; so that the internal temperature and the current density of each cell were relatively average. Supra et al. [51] inherited the design of Lüke et al. [50] to explore the internal changes in the stack. The effect of the mesh flow field on characteristics of PEMFCs was also addressed by Bao et al. [52].

The literature review shows that various aspects of HT-PEM with single cells have been investigated; however, there are few studies on the overall performance of a stack of fuel cells. Therefore, the present work aims to examine the effect of the stack temperature, the nitrogen concentration, and carbon monoxide concentration on the performance and behaviour of an HT-PEMFC stack.

Experimental setup and research method

Experimental setup

The equipment structure of this work is shown in Fig. 1. To test various concentrations of nitrogen, hydrogen, and carbon monoxide in the reformed gas, a gas mixture module and gas analysis module are utilized. The gas mixer adjusts the portion of each gas and sends it to the gas analyzer. The gas analyzer determines the proportion of the composition of the recombination gas to ensure the correct composition of the gas mixture before it enters the PEMFC test section. Then, the voltage, current, and power of the PEMFC are measured through a fuel cell test system.

The PEMFC test module of this study consists of a stack of five single cells, and the reaction area of a single cell is 24 cm^2. A bipolar plate is designed with five serpentine flow channels to serve as a flow field, with a width, depth, and a pitch of 0.8 mm. The literature review [48,53] shows that a serpentine flow channel results in better performance; so that the inner flow channel of the existing stack is mainly a snake-shaped flow-channel. An actual photo of the PEMFC test module (stack) is depicted at the bottom of the schematic figure (Fig. 1). The membrane electrode assembly of this work is a Celtec®-P 1000 [54] series produced by BASF Fuel Cell GmbH, a thickness of 863 μm, and an anode partial platinum content of 0.45 mg cm^{-2}. The cathode portion has a platinum content of 1 mg cm^{-2}. The hermetic gasket, used in the stack, is a self-made oil seal gasket made of Viton® with a hardness of 60°. The three different sizes are 44 mm × 24 mm, 31 mm × 28 mm and 65 mm × 65 mm, and the thickness is 1 mm. Viton® materials are resistant to high temperatures, deformation, and elasticity, making them ideal for making airtight coils for HT-PEMFC stack.

To adjust the operating temperature of the PEMFC stack, four heating rods are utilized to uniformly heat the PEMFC test module and maintain the adjusted operating temperature. The input voltage of each of the heating rods is 110 V with a maximum output power of 200 W. So that the operating temperature can be quickly increased in a short time to reach the temperature required for the experiment. The outside of the PEMFC stack is covered with a heat-insulating cover made of silicone material to keep the operating temperature fixed. The gas mixer consists of four electronic flow controllers to control the hydrogen, nitrogen, carbon dioxide, and carbon monoxide. For experimental purposes, two flow controllers are used to control the high and low flow of carbon monoxide. Software, provided by Tokyo Instruments, controls the flow

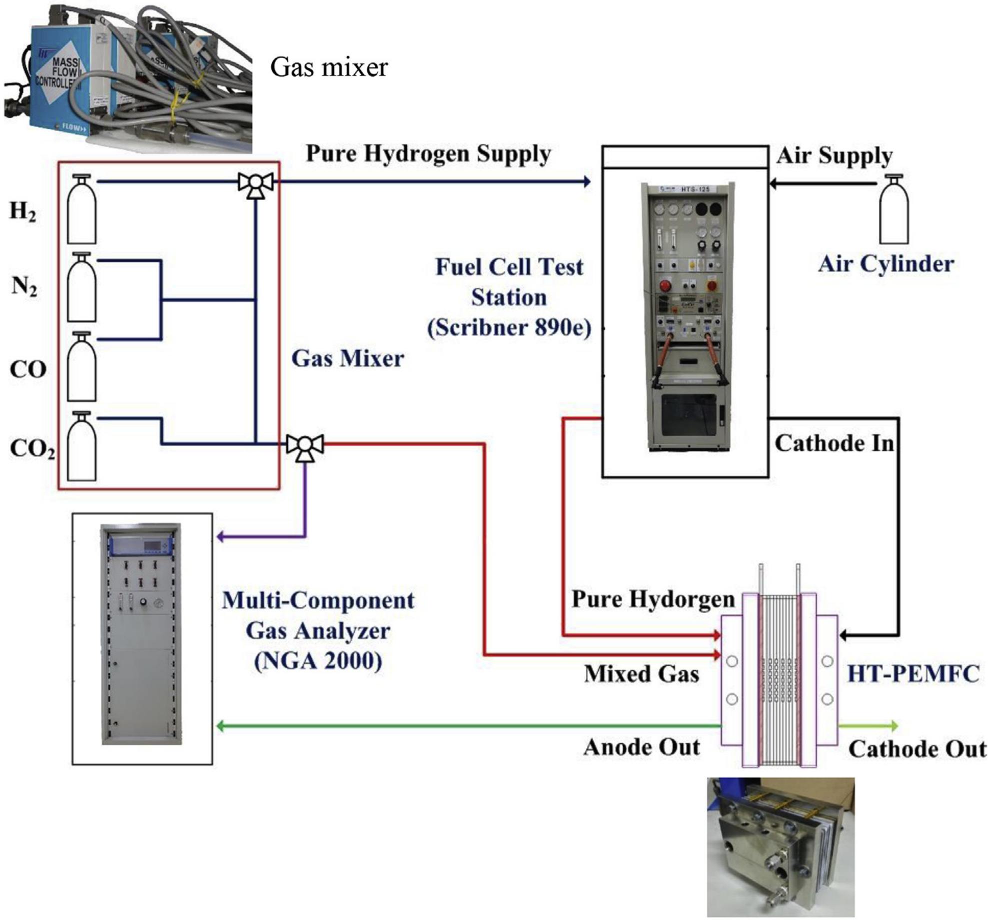

Fig. 1 – Schematic view of the experimental setup.

control, and the error values of the four flow controllers are all within ±2% F.S.

A fuel cell test system (Scribner 890e) is adopted to test and control the PEMFC stack. The test device is capable of not only controlling and recording the current but also recording the voltage and the power, which are essential for performance analysis. In this work, before experimental testing, the fuel cell test system is calibrated with accuracy within 1%. Therefore, the uncertainty of the results is within 1% of the measured data. The temperature control and functions such as electrochemical impedance spectroscopy (EIS) are also available as functions of the test device. Both the anode and cathode gas input sections have a flow meter and a bubble humidifier, which can control the temperature and humidity of the gas entering the fuel cell, and also, they can adjust the stoichiometry of the intake fuel. So, most aspects of the fuel cell can be tested and analyzed in the present experiment. The gas analysis module, utilized in the current experiment, is NGA2000 produced by EMERSON. It is mainly used to analyze the proportion of various gases in the mixed gas in real-time, and also it can analyze the composition of the gas, discharged from the fuel cell, and record the data.

Research method

In the present study, the polarization curves and ESI measurements were utilized. A polarization curve demonstrates the overall performance of a fuel cell; however, it is not adequate for analysis of the individual losses inside the fuel cell. EIS is a common method capable of measuring the electrochemical impedance of the fuel cell parts individually. The basic principle of the ESI is to obtain a voltage response by applying a small sine-wave current-disturbance to the fuel cell under fixed operating conditions. The input sine waves current ($I(t)$) and the response voltage ($V(t)$) are in the following forms:

$$I(t) = I_m \sin(\omega t) \tag{1}$$

$$V(t) = V_o \sin(\omega t + \theta) \tag{2}$$

where I_m is the scan current, V_o is the response voltage, ω is the frequency, and θ is the phase angle. Resistance is the ability to block current flow. In addition to the concept of resistance, impedance also includes time and frequency. Therefore, it is known by Ohm's law as $R = V/I$. Impedance adds the concept of time as $Z = V(t)/I(t)$. Therefore, the substitution of Eqs. (1) and (2) can be obtained as:

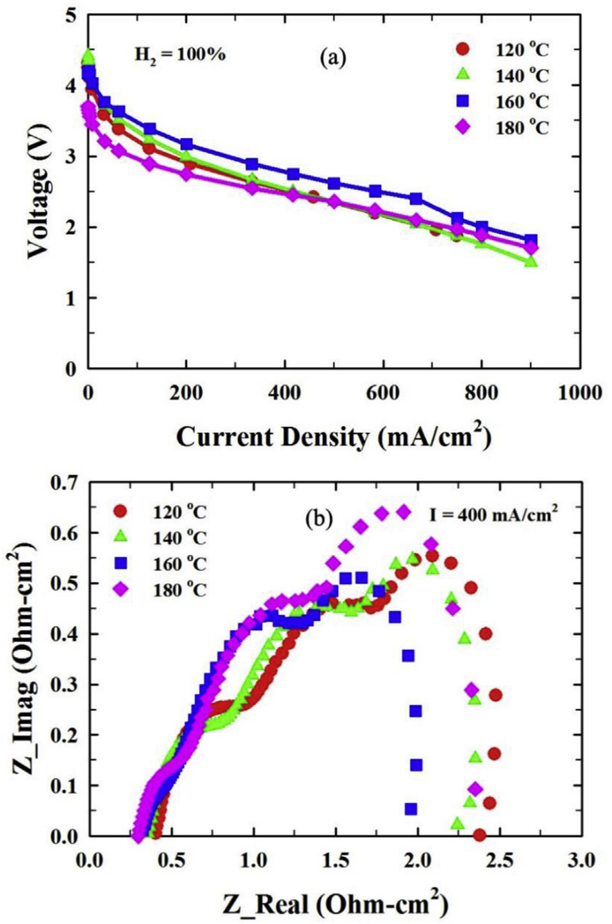

Fig. 2 – Effect of stack temperature on the performance. (a) I–V curves, (b) electrochemical impedance spectrogram.

$$Z(\omega) = \frac{V(t)}{I(t)} = Z_{Real}(\omega) + Z_{Imag}(\omega) \quad (3)$$

where Z_{Real} is the real impedance, and Z_{Imag} is the imaginary impedance.

Experimental procedure

In the present study, the experiments were performed with pure hydrogen with no poisoning carbon monoxide. The temperature of the stack was fixed at the control temperature of the experiment, and when the stack reached a stable temperature the polarization curve was measured and recorded. The stoichiometry of the gas was controlled by the gas mixer and monitored by the gas analysis module.

The stack was tested for various current densities of 200 mA, 400 mA, and 600 mA and various mixture combinations, and then, the ESI curves were measured and plotted. After then, the experiments were repeated for a new working temperature of the stack. The effect of different nitrogen concentrations or gas mixture also performed in the same way by introducing the gas mixtures to the stack.

To investigate the effect of carbon monoxide as the poisoning agent, CO was introduced to the stack as a portion of the mixture gas. The poisonous mixture gas was introduced to the stack for 30 min until the PEMFC, and its voltage reaches an equilibrium status, and then the polarization curves were measured and plotted.

Results and discussion

This study mainly explores three variables that affect the stack: the temperature, the concentration of fuel gas, and the concentration of poison gas. Polarization curves and the ESI are measured for each experiment.

The effect of temperature on the performance of the PEMFC stack

The literature review shows that PEMFC provides better performance at a high temperature. This part of experiment tends to study the effect of stack temperature on the stack performance at various temperatures of 120 C, 140 C, 160 C, and 180 C while the anode gas is pure hydrogen and the

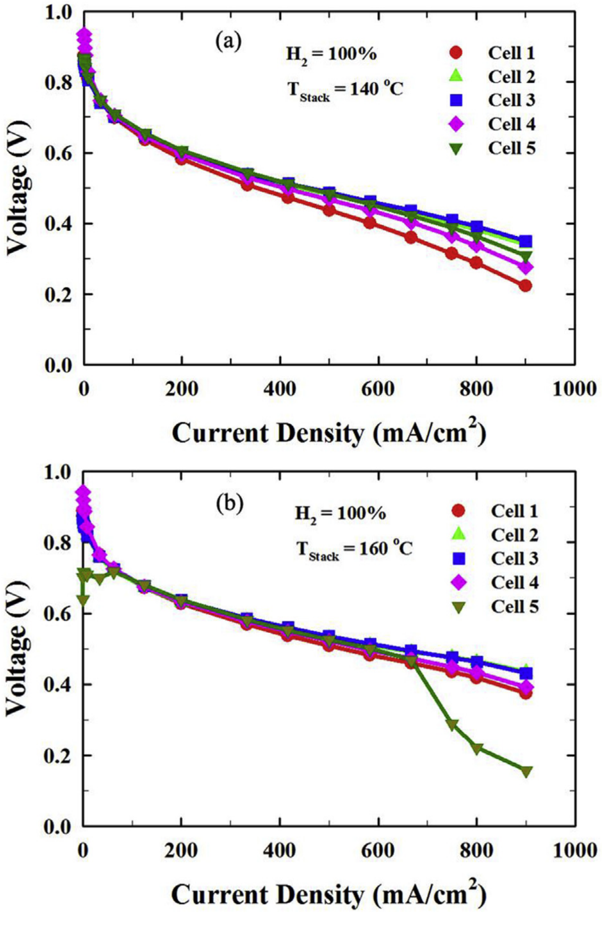

Fig. 3 – The performance of each cell on HT-PEMFC stack. (a) $T_{Stack} = 140$ °C, (b) $T_{Stack} = 160$ °C.

cathode gas is air. The stoichiometric ratio of the anode to cathode is 1.2/2.0.

Fig. 2 depicts the I–V curves and ESI plots of the PCMFC stack for various working temperatures. The outcomes of Fig. 2 (a), in agreement with the literature results, show that the performance of PEMFC gradually improves by increasing the PEMFC temperature from 120 C to 160 C. However, the performance is attenuated when the working temperature rises to 180 C. The open-circuit voltage (OCV) at 180 C is also slightly lower than other temperatures.

Increasing the temperature of the PEMFC enhances the performance, but at 180 C, the performance is drastically reduced by the drop of the PEMFC voltage for a fixed current. It is clear that the optimal operating temperature of the PEMFC is about 160 C. From Fig. 2 (b), it can be observed that the impedance semicircle has a third-circle at high load, and it is inferred that a slight concentration polarization occurs at high load. Between 120 C and 160 C, increasing the temperature reduces the PEMFC impedance, which improves the PEMFC's performance, but at 180 C, the impedance increases significantly, which degrading the PEMFC's performance.

Fig. 3 illustrates the I–V curves for each cell performance for two working temperatures of $T_{Stack} = 140$ C and $T_{Stack} = 160$ C. At low current densities, the stack is working naturally, and the heating conditions, gas distribution and reactions are uniform in most cells. When the working temperature is $T_{Stack} = 140$ C, the voltage trends for all cells are stable, and the performance of Cell 3 and Cell 2 is better than other cells. The performance of Cell 1 (close to the anode gas inlet side) is poor. When the PEMFC temperature elevates to 160 C, the performance of all cells is quite close, except for Cell 5, which shows a significant performance drop at high current densities. This performance drop presumably is because of the higher temperature inside the PEMFC, which causes a rapid decline in performance. Indeed, in the case of $T_{Stack} = 160$ C, the performance of Cell 3 is relatively good, and the performance of Cell 5 is relatively unstable.

Influence of stoichiometry values on PEMFC performance

A stoichiometry of 1.2 for anode side shows that the provided amount of hydrogen to the reaction is 20% more than that of the required amount of hydrogen for the reaction. Similarly, a stoichiometric amount of 2 for air indicates that the amount of the air passes through the PEMFC stack is twice the required air for the reaction. In this part of the experiment, the effect of changing the stoichiometries of the hydrogen and air on the performance and impedance of the PEMFC is studied. To aim this purpose, the impact of the anode gas (hydrogen) and

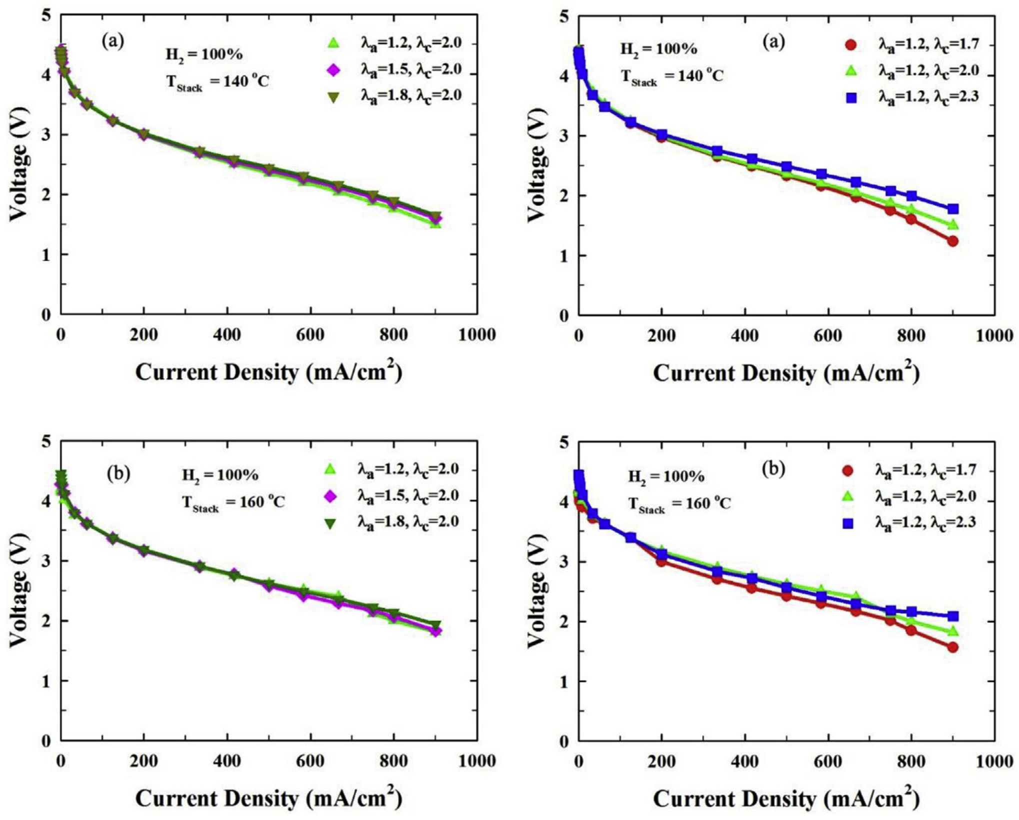

Fig. 4 – Effect of anode/cathode stoichiometries on stack performance. (a) $T_{Stack} = 140$ °C, (b) $T_{Stack} = 160$ °C.

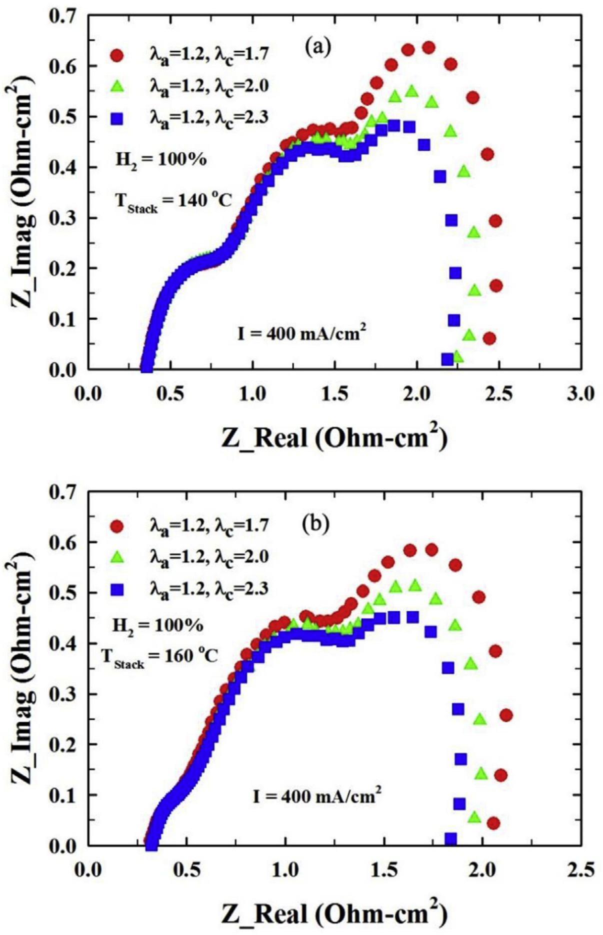

Fig. 5 – Effect of cathode stoichiometry on the stack impedance. (a) T_{Stack} = 140 C, (b) T_{Stack} = 160 C.

cathode gas (air) on the performance of the PEMFC stack are explored when the current density is fixed at 400 mA cm^{-2}.

The effect of anode stoichiometry and cathode stoichiometry on the stack performance are presented in Fig. 4. The results are reported for two stack temperatures of (a) T_{Stack} = 140 C, (b) T_{Stack} = 160 C. As seen, the gradual growth of the stoichiometric number of hydrogen raises the performance slightly when T_{stack} = 140 C. The same trend of the results can be observed for the temperature of T_{stack} = 160 C. Moreover, increasing the stack temperature slightly improved performance, but the increase was not significant. Fig. 4 also demonstrates that the higher the air stoichiometry, the better the performance when the amount of hydrogen is fixed. The performance improvement is notable in Fig. 4 for cathode regardless of the stack temperature.

Fig. 5 illustrates the effect of cathode stoichiometry on stack impedance for two stack temperatures of (a) T_{Stack} = 140 C, (b) T_{Stack} = 160 C. As seen, the increase of the air stoichiometry steadily shrinks the impedance semicircle. In terms of Ohmic impedance change, the change of the metering number to the Ohmic impedance is not apparent; only the rise of the stack temperature can significantly reduce the Ohmic impedance. The highest stoichiometry has the lowest impedance and remains the same at different temperatures. The trend is that the maximum drop is 12.1% at 140 C and 12.2% at 160 C. Therefore, it can be concluded that increasing the stoichiometry of air can effectively reduce the charge transfer impedance and mass transfer impedance. By arranging the above research results, the effect of changing the stoichiometry of the cathode on the performance and impedance of the stack is more evident than changing the stoichiometry of the anode, because the oxygen reduction reaction (ORR) of the cathode is slow than the hydrogen oxidation reaction (HOR) of the anode. When the stack is under lower loading (lower current density), the ORR reaction is much more apparent than the HOR reaction, so the HOR reaction is mostly negligible; but at higher current density, the HOR reaction becomes visible, so the ORR reaction and the HOR reaction must be considered simultaneously [55].

Effect of nitrogen and carbon monoxide concentrations on stack performance

The introduction of nitrogen into the anode side causes dilution of the hydrogen, which reduces the hydrogen concentration and affects the performance of the stack. Hence, the behaviour of PCMFC for dilute values of hydrogen is studied by using various amounts of nitrogen. The nitrogen with various amounts of 25%, 50% or 75% is utilized while the working temperature of the PCMFC stack is fixed at 140 C. Fig. 6 displays the effect of variation of the concentration of nitrogen and carbon monoxide on the PCMFC behaviour. The labels of (a) and (b) denote the I–V curves and EIS plots, respectively. It can be seen that increasing the concentration of nitrogen makes the dilution of hydrogen more significant, and the performance of the stack gradually declines at the polarization curvet. When the nitrogen concentration is 25%, the performance of the fuel cell is decreased slightly. However, if the nitrogen concentration increases to 50%, the performance decline is noticeable, and after the nitrogen concentration raises to 75%, the performance degradation is more remarkable.

The effect of nitrogen concentration on the stack impedance is also investigated in Fig. 6. The impedance semicircle starts to show an expanding-outward trend by the gradual increase of nitrogen concentration. The outward expansion is quite significant in the case of the nitrogen concentration is 75%. It is apparent that the hydrogen at this time cannot be adequately supplied to the stack for the reaction. In the study, the anode was introduced into different concentrations of carbon monoxide, which were 1%, 3%, and 5%, respectively, and the hydrogen is utilized as the equilibrium gas. When carbon monoxide is introduced into the stack, it reacts with the platinum on the catalyst layer, so that the hydrogen cannot react smoothly with the catalyst after exposing to

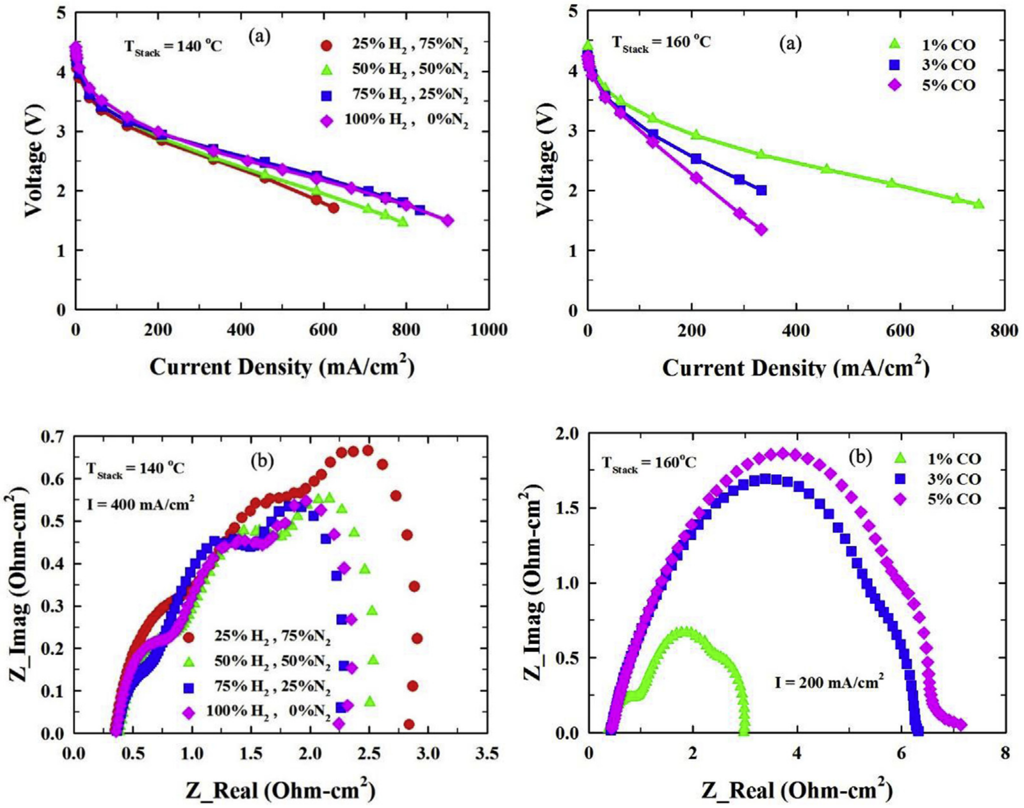

Fig. 6 – Effect of nitrogen/carbon monoxide concentrations on stack performance. (a) I–V curves, (b) electrochemical impedance spectrogram.

carbon monoxide, which results in a decline in the performance of the stack. It can be seen from Fig. 6 that the higher the concentration of carbon monoxide, the more severe the performance declines. The performance of the stack exposed to 5% of carbon monoxide roughly is like half of its performance when it is exposed to only 1% of carbon monoxide. Due to the poor performance of the stack, the EIS experiment was performed with only a fixed operating current of 200 mA. It can be observed that when the concentration of carbon monoxide is increased from 1% to 3%, the impedance increase is quite significant. When the carbon monoxide concentration further elevates to 5%, its effect on the impedance curve diminishes, and the impedance semicircle is slightly expanded outward. It is speculated that when the concentration of carbon monoxide is 1%, only a portion of the platinum catalysts is covered by the carbon monoxide, which partially affects the performance of the stack. The increase of the concentration from 1% to 3% covers most of the platinum on the catalyst. So the impedance is significantly increased, and also the performance of the stack is reduced. After the carbon monoxide concentration raised to 5%, the increase in impedance limited. The limited increase of the impedance is since most of the platinum on the catalyst is already covered by carbon monoxide, and only very few portions of catalysts are remained uncovered and can be exposed to a further increase of the carbon monoxide.

Effect of stack temperature on carbon monoxide tolerance

An experiment was conducted by introducing 1% carbon monoxide into the anode gas and using hydrogen as the equilibrium gas. Fig. 7 indicates that the performance is the worst when the stack temperature is 120 C. The gradual growth of the stack-temperature improves the stack's performance. Here, the EIS diagram is obtained for a fixed current of 200 mA due to the poor performance of the stack. Moreover, since the EIS of the stack could not be fixed for the current of 200 mA at $T_{stack} = 120$ C, it could not be compared in Fig. 7 (b). It can be clearly observed in Fig. 7 (b) that increasing the temperature of the stack can significantly reduce the impedance and the impedance semicircle.

The performance after poisoning is much worse than that of an intact stack. Hence, the poisoning effect is quite remarkable. The impedance of the poisoned stack increased by 3.91 and 1.29 times when the stack temperature 140 C and 160 C, respectively. In the case of $T_{stack} = 140$ C, the increase of impedance is quite large, which led to a drastic reduction of the stack performance. As the temperature rises from 120 C to

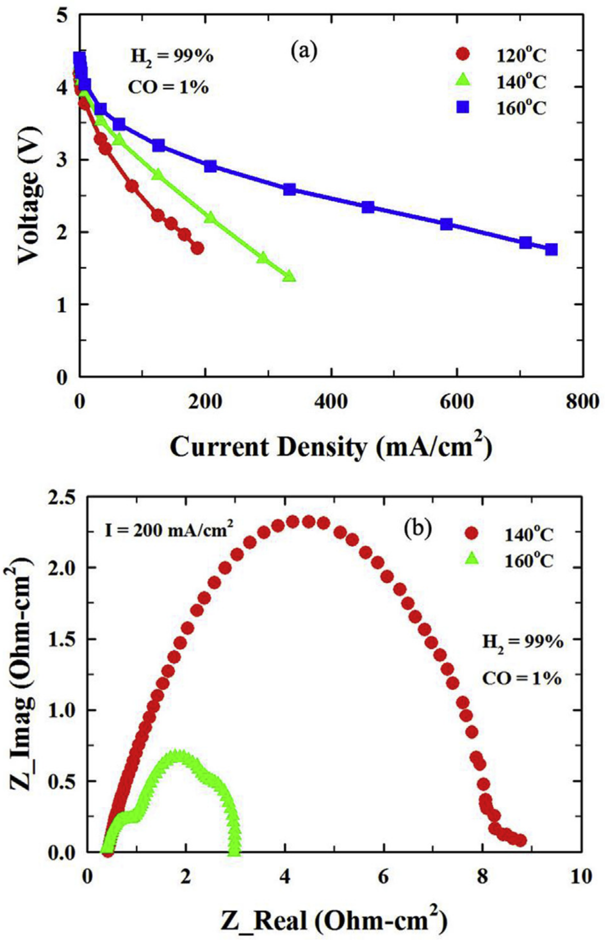

Fig. 7 – Effect of 1% CO poisoning on the stack performance. (a) I–V curves, (b) electrochemical impedance spectrogram.

160 C, the performance of the poisoned stack enhances. Hence, this finding is in agreement with the literature review, in which increasing the fuel cell temperature helps to increase the tolerance to carbon monoxide.

Effect of hydrogen concentration on stack performance under poisoning conditions

The temperature of the fixed stack is kept fixed at $T_{stack} = 160$ C, while the anode gas flows with a constant concentration of 1% carbon monoxide, and the hydrogen is diluted with 24% nitrogen to produce a hydrogen flow with a total concentration of 75%. When the hydrogen is diluted by nitrogen, changing the partial pressure of hydrogen makes the reaction of hydrogen and catalyst more difficult. In this case, the stack polarization plot and ESI plot are depicted in Fig. 8. As can be seen in Fig. 8, the performance after dilution has a significant decline, and the impedance semicircle also has a significant outward expansion, which increases the impedance notably. Using the diluted hydrogen considerably increased the impedance by 1.3 times.

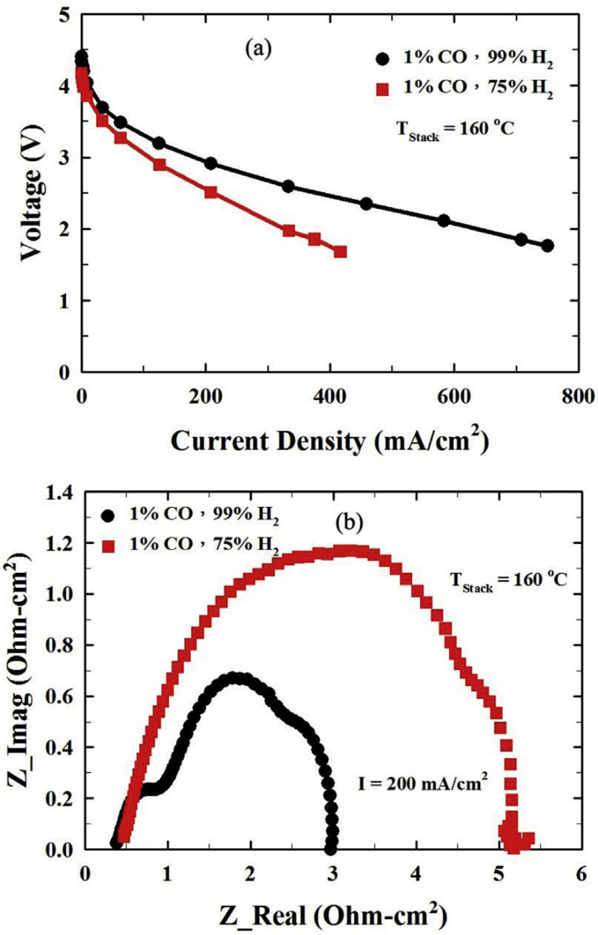

Fig. 8 – Effect of hydrogen concentration on the performance under poisoning conditions. (a) I–V curves, (b) electrochemical impedance spectrogram.

Conclusions

In this work, an experimental setup for analysis of a PBI/H_3PO_4 PEMFC was built. Then, the effect of working temperature, the concentration of fuel, air, carbon monoxide on the performance and impedance of the fuel cell were addressed. The main outcomes of the study can be summarized as follows:

1. Increasing the temperature of the stack reduces the ohmic impedance and thereby improves the performance of the stack. The optimal operating temperature of the stack is about 160 C.
2. Changing the stoichiometry of the anode side has no significant effect on improving fuel cell performance and reducing impedance. Conversely, increasing the stoichiometry of the cathode side contributes to increased stack performance and reduce internal impedance.
3. When the nitrogen concentration is higher, the hydrogen concentration becomes lower, which causes the sum of the mass transfer impedance and the charge transfer impedance inside the fuel cell to increase, which affects the performance of the stack. Increasing the load and reducing

the amount of the supplied hydrogen led to the phenomenon of the concentration polarization.

4. Increasing the concentration of carbon monoxide declines the performance of the stack. At a fixed carbon monoxide concentration, the higher the temperature of the PEMFC stack, the better the poisoning resistance and the better the performance of the stack.

In the present study, only the effect steady-state poisoning was investigated on the stack performance. However, the transient behaviour of poisoning gas could be of interest. Hence, the study of transient poisoning behaviour of the stack could be subject to future studies.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2020.03.219.

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