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Determination of the optimal operating temperature range for high temperature PEM fuel cell considering its performance, CO tolerance and degradation

Caizhi Zhang [a,b,*], Weijiang Zhou [b], Mohsen Mousavi Ehteshami [b], Youyi Wang [c], Siew Hwa Chan [a,b,*]

[a] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] Energy Research Institute @ Nanyang Technological University, 50 Nanyang Avenue, Singapore 637553, Singapore
[c] School of Electrical & Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

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ABSTRACT

The objective of this study is to propose guidelines for the operating temperature range of High-Temperature Proton Exchange Membrane Fuel Cell (HT-PEMFC) considering the overall performance, CO tolerance and durability. To study the effect of temperature on HT-PEMFC performance, polarization curves of the cell operating on respective hydrogen and hydrogen/CO mixture were measured at 5 different temperatures. The electrochemical impedance spectroscopy (EIS) was used to characterize the internal resistances and the results provided the electrochemical analyses and explanations of the temperature effect on the HT-PEMFC. In addition, the stability tests (100 h) were also conducted, which were useful for trade-off study between performance requirement and lifespan of the cell. Results showed that the temperature effect on the cell performance and CO tolerance were less obvious in high temperature range (above 180 °C) compared to the low temperature range (below 160 °C). However, the degradation of cell performance is faster in the high temperature range. Analysis of experimental results revealed that the optimal operating temperature window is between 160 and 180 °C by compromising among the cell performance, CO tolerance and durability, and where the low temperature end of the range is preferred depending on the feeding fuel.

1. Introduction

Fuel cells are considered as clean and high efficiency power equipment [1]. Pure hydrogen is considered as an ideal fuel for fuel cells, because fuel cell can achieve the best performance with zero pollution emissions [2]. However, the production, storage and distribution of pure hydrogen are challenges in commercialization of the fuel cell, which result in on-board fuel reforming to produce hydrogen-rich gases from methanol, ethanol or other renewable hydrocarbons offering the fuel flexibility solution for fuel cell applications [3,4]. High temperature PEM fuel cell (HT-PEMFC) with much higher CO tolerance has attracted a lot of attention in recent years, which compares to the traditional low-temperature PEM fuel cell (LT-PEMFC) [5–7]. The HT-PEMFC is much suitable for operating with hydrogen-rich reformate (contents several percent of CO) obtained from onboard reforming of methanol, ethanol or bio-mass [8–10]. However, the performance and durability of HT-PEMFC operating on hydrogen-rich reformate are the major batteries of the onboard reforming system in technical field, which need deep analysis [11].

Several experimental and numerical investigations reported that increasing the operating temperature would increase the performance and improve the CO tolerance of HT-PEMFC [12–20]. The performance improvement with increasing operating temperature is explained by the decrease of the membrane resistance, charge transfer and mass transfer resistance, furthermore, enhancement of reaction kinetics [21,22]. Zhang et al. [20] reported that both the anode and cathode exchange current densities are improved with increasing temperature. For the CO poisoning tolerance of HT-PEMFC, it is dramatically increased with increasing the operating temperature. CO poisoning occurs since CO molecules strongly adsorb onto the surface of platinum (Pt) nanocatalysts, thus blocking hydrogen oxidation reaction. The CO adsorption on Pt particles is related to negative entropy change, which means that CO molecules are adsorbed less strongly at higher temperatures [23]. Hence

* Corresponding authors at: School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.

E-mail addresses: M110050@e.ntu.edu.sg (C. Zhang), mshchan@ntu.edu.sg (S.H. Chan).

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Nomenclature

LT-PEMFC	low-temperature PEM fuel cell
HT-PEMFC	high-temperature PEM fuel cell
MEA	membrane-electrode-assembly
PBI	polybenzimidazole
CO	carbon monoxide
sccm	standard cubic centimeters per minute
T_{PH2}	temperature range when fuel cell operated on pure H_2
T_{PCO1}	temperature range when fuel cell operated on 1% CO in H_2
T_{PCO3}	temperature range when fuel cell operated on 3% CO in H_2
T_{RCOT}	temperature range considering the CO tolerance under different temperatures
T_{RCOCO}	temperature range considering the CO tolerance under different CO concentrations
T_{Pdegra}	temperature range considering the performance degradation

increasing the operating temperature would result in higher H_2 coverage [15]. Li et al. [13] studied CO poisoning effect with CO contents of up to 16 vol% in the temperature range of 125–200 °C. They observed that the presence of 0.5% CO leads to significant performance drop at 125 °C, but less so at elevated temperatures. Das et al. [15] investigated the CO poisoning effect in the temperature range of 120–180 °C. They concluded that the presence of 5% CO can be tolerated at high temperatures with acceptable performance losses and, therefore, suggested that the HT-PEMFC should operate at 180 °C or above. On the other hand, it was noted that increasing the operating temperature of HT-PEMFC would lead to degradation of cell components, such as catalyst, membrane, the electrode and bi-polar plate [24–29], because operating HT-PEMFC at high temperature, high electrochemical potential and high water partial pressure would accelerate the electrochemical carbon corrosion rate and decreases the mechanical strength of the membrane [11,30,31].

Literature survey revealed that even though the performance and CO tolerance are improved by increasing the operating temperature, the performance degradation of HT-PEMFC should be considered when choosing an optimum operating temperature. Hence, the objective of this study is to determine the optimal operating temperature range for HT-PEMFC by considering the overall performance improvement, CO tolerance and durability. To avoid the acid leakage at operating temperature less than water boiling point and to avoid serious dehydration of membrane at high operating temperature, the temperature range of 120–200 °C have been chosen in this study [32]. In addition, electrochemical impedance spectroscopy (EIS) measurements were conducted to understand the temperature effect on cell performance. Furthermore, amperometric tests were conducted to investigate the durability of the cells operating at high temperatures.

2. Experimental

2.1. Experimental setup

Fig. 1(a) shows the schematic of a HT-PEMFC in the test fixture. It includes a membrane-electrode-assembly (MEA), two bipolar plates, two gaskets and two end-plates. The MEA (Celtec® P1000) with a phosphoric acid content up to 70 phosphoric acid molecules per PBI repeat unit in the PBI matrix and an active area of 45 cm^2 was bought from BASF Fuel Cell GmbH (Frankfurt, Germany). The specifications of this MEA, such as membrane thickness, carbon support and Pt loading, can be found elsewhere [33,34]. The flow-field in graphite plates of anode and cathode are 5-stepserpentine. The geometrical specifications of the cell are presented in Table 1. Two pieces of high temperature resistant gaskets were served as sealant material between the MEA and graphite plates. Two gold-plated metallic end-plates clamped the components to a single cell test fixture. Thin bi-polar plates were directly attached to the end-plates for current collection and to improve the heat exchange in a temperature-controlled oven.

The schematic of the test rig arrangement is shown in Fig. 1(b), which includes fuel supply, temperature control, a load bank and a data acquisition system. Gas streams from respective cylinders were channelled to the test cell via regulators and mass flow controllers (MFC, Alicat). N_2 was used to purge the residual H_2 to reduce the potential difference between anode and cathode (open circuit voltage) after testing and to remove the air in the anode flow field before testing. Mixtures of H_2 and CO with different contents were prepared by online mixing. The CO concentrations are 0%, 1%, 3% and 10%, and denoted as Fuel A, Fuel B, Fuel C and Fuel D, respectively, in Table 2. At the cathode side, the dry and pressurized air was fed to the electrode via another mass flow controller. The test rig was housed in a programmable oven (Memmert GmbH) to control the operating temperature. The metallic end-plates, which serve as heat sinks helped to keep the temperature of the HT-PEMFC the same as that of the oven. The fuel cell impedance meter KFM2150 (KIKUSUI), PLZ-4WA (KIKUSUI) and the application software worked as a fuel cell measurement and data recording system. Another controller was used to control the switching of the solenoid valve for gases mixing and the bleeding resistor [35]. The exhaust gases were properly vented, as the gases were in high temperature and may contain tracer of phosphoric acid leaching from the HT-PEMFC.

2.2. Test procedure

Initially, a break-in process of the MEA was run according to the recommended conditions of the MEA manufacturer (i.e., 0.2 A cm^{-2}, 160 °C, pure H_2 flow rate of 4.5 L/h (anode), air flow rate of 18 L/h (cathode) for 60 h). The break-in process is to redistribute the phosphoric acid within membrane and electrodes, which is enable the fuel cell to reach the stable performance and reproducible results [11,36]. A typical CO content in reformate gases is dependent on the fuel source, type of thermochemical process and catalyst used, and the reforming temperature and pressure, which could be varied from 1% to 4.3% in 230–350 °C and up to 10% at 500 °C [37,38]. To simulate poisoning environment, the cell were fed with different concentrations of CO (1%, 3% and 10%) in H_2 under same conditions as the break-in process prior to measuring polarization curve in the subsequent step.

Four sets of polarization curves were obtained after the fuel cell had reached the steady state at 0.7 V according to the measurement matrix in Table 3, which includes 20 measurement runs. All cell operated at atmospheric pressure and flow-rates of 80 sccm (anode) and 310 sccm (cathode). One set of polarization curves was obtained with pure H_2 denoted as Fuel A. The other three sets of polarization curves were obtained with Fuel B, Fuel C and Fuel D, respectively. The polarization curves were recorded two times under chronoamperometry mode and the test started at current of 0 A up to a protection shut-down at 150 mV and at current