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Experimental study on the start-up with dry gases from normal cell temperatures in self-humidified proton exchange membrane fuel cells

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ABSTRACT

In this study, the start-up characteristics of PEMFCs (proton exchange membrane fuel cells) was investigated with dry gases from normal cell temperatures above 0 °C. Firstly, the effects of flow arrangements (co-flow and counter-flow) were evaluated at a starting cell temperature of 25 °C. Then, the start-up was successful in both arrangements, but it showed better performance with counter-flow. In addition, the hydrogen concentration was measured and it showed that hydrogen crossover contributes to the membrane hydration and the first phase of dry start-up. However, although the cell temperature rose above 45 °C after start-up form 25 °C with counter-flow arrangement, the restart-up after shut-down failed at a starting cell temperature of 45 °C regardless of flow arrangements. Considering the needs of restart-up, the available starting cell temperature should be improved. For this, after first sub-step of start-up process, relatively low flow rates were maintained to retain produced water without purge so that the membrane can be hydrated sufficiently. With this modified process, denominated as WSP (water storage process) in this study, the dry start-up became successful at a starting cell temperature of 45 °C and the cell performance was remarkably improved especially with counter-flow arrangement.

1. Introduction

As a hydrogen energy technology, fuel cells will play an important role on a future energy economy due to its high electrical efficiency and clean exhaust energy conversion [1,2]. Among the various types of fuel cells, a PEMFC (proton exchange membrane fuel cell) is expected to be used widely in portable, stationary, and transportation systems [3]. In PEMFCs, the proton conductivity of the membrane is a crucial factor that determines the cell performance and it depends on the hydration level of the membrane [4]. Therefore, effective water management is one of the key strategies for improving the cell performance water [5]. In most conventional systems, external humidification systems such as membrane humidifiers, bubblers, and injectors are used to hydrate the membrane. However, using an external humidification system introduces disadvantages such as parasitic power loss, increased manufacturing cost, and system complexity. Moreover, although external humidifiers are not used, the amount of water produced by fuel cell reaction is sufficient to humidify the supplied gas up to an operating temperature of 60 °C [6]. Therefore, operating self-humidified PEMFCs would be advantageous, since it would dispense with the need for an additional humidification system.

In self-humidified PEMFCs, ambient air is supplied to the fuel cell without additional humidification. Since ambient air is not always sufficiently humidified, many researchers have attempted to operate PEMFCs with dry gases and have evaluated the effects of operating temperatures, flow arrangements, and gas flow rates in such systems [6–11]. In addition, the in-plane distribution of water on the membrane has been investigated under dry conditions [12,13]. As a result of these efforts, it has been demonstrated that the fuel cells can be stably operated without external installation for humidification. However, most of the previous studies were only focused on the steady-state performance of self-humidified PEMFCs for stable operation without considering the dynamic behavior of cell performance during start-up.

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As well as stable operation, successful start-up is of great importance for commercialization of PEMFCs and Singdeo et al. [14] studied start-up time for high temperature polymer electrolyte fuel cells In their research, different warm-up methodologies were analyzed for phosphoric acid doped PBI membrane based fuel cells. Start-up from subzero temperatures, often referred to as cold start, is one of the most significant challenges in PEMFCs [15]. In the winter, the outdoor temperature goes down below zero and residual water freezes after shut-down. Therefore, the water remaining inside the fuel cell should be purged during the shut-down process to prevent or minimize the problems such as degradation, freezing, and so on [16,17]. Nevertheless, as a result of fuel cell reaction during start-up, the water is produced and freezes when the temperature inside the PEMFC is lower than the freezing point of water. If the catalyst layer is fully covered by ice before the cell temperature rises above the freezing point, the electrochemical reaction may be stopped due to the blockage of the reaction site. For this reason, the ice formation/growth characteristics inside PEMFCs under different cold-start conditions have been investigated [18–26]. In addition to cold start-up, start-up from normal cell temperatures above 0 °C is also an inevitable situation since the cell temperature rises during operation and restart-up should be possible in a short time after shut-down. For this reason, the dynamic characteristics of start up in PEMFCs from normal temperature have been studied by several groups [27–29]. Shen et al. [27] investigated several different start-up and shut-down processes and suggested appropriate processes to avoid the formation of hydrogen/air boundary. For this, the fuel cell was operated at ambient temperature and pressure, and kept at open circuit conditions in all tests. Hydrogen and air were humidified at ambient temperature, and fed into the anode and the cathode respectively at constant flow rates. Mishra and Wu [28] studied the start-up characteristics of PEMFCs with unsteady two phase non-isothermal model at an operating cell temperature of 353 K fed by fully humidified hydrogen and air. However, in their research, humidified gas was supplied to the fuel cell for start-up and self-humidified mode was not considered. In self-humidified PEMFCs, if the starting cell temperature is below zero, the situation is the same with cold start-up in external-humidified PEMFCs and ice formation is the limiting factor of successful start-up. On the other hand, if the starting cell temperature is sufficiently high, dehydration of the membrane may be the limiting factor of successful start-up in self-humidified PEMFCs. Although the membrane is dehydrated after purge process, if external humidifiers are available, start-up at high cell temperature may be successful since the supplied air can be humidified passing through the external humidifier. However, in self-humidified PEMFCs, no external humidifiers are available and dry gases are supplied directly to dehydrated membrane. Therefore, in self-humidified PEMFCs, start-up from normal cell temperature may be difficult. Since start-up was conducted with dehydrated membrane fed by dry gases, this situation is termed as dry start-up in this study. Considering the temperature rise of fuel cell during operation and the needs of restart-up in a short time after shut-down, quick and stable start-up from normal cell temperature is an important issue, especially in self humidified PEMFCs. Despite the importance of dry start-up in self-humidified PEMFCs, there have been little discussions on the start-up with dry gases from normal cell temperatures above 0 °C except an experimental result by Didierjean et al. [29]. They evaluated the transient response of a fuel cell stack during the start-up procedure with pure and dry hydrogen and oxygen to determine the operating parameters corresponding to achieve fast and stable dynamic response to the power requirement. However, pure oxygen is not a practical gas for conventional applications. Furthermore, in their research, the stack temperature was set to 20 °C by means of a cooling circuit so that start-up was conducted only from 20 °C that was close to the room temperature. Since the cell temperature rises during operation without additional cooling system, start-up with dry gases from higher cell temperatures should be explored with dry hydrogen and air. Although Yu and Ziegler [30] studied dynamic behavior of cell performance with dry air and hydrogen at 40 °C, the fuel cell was conditioned with humidified gas before the measurement. Then, the gas was switched to dry gases for the designed ramp sweep measurement. Since the membrane was hydrated before dry gases were supplied, it is somewhat different situation compared with dry start-up.

In this study, the start-up characteristic was investigated under dry condition (fed by dry gases after purge process). In order to evaluate the effects of reactant flow arrangements and starting cell temperatures, the experiments were conducted with counter-flow arrangements and co-flow arrangements at starting cell temperatures of 25 °C and 45 °C. In addition, in order to explain the reason for possibility of dry start-up, the amount of produced water result from hydrogen crossover and its direct reaction with oxygen was obtained by measuring hydrogen concentration at cathode side using a mass spectrometer. Lastly, as a possible operating strategy for successful start-up at a starting cell temperature of 45 °C, a WSP (water storage process) was introduced to start-up process and the effects were evaluated.

2. Experimental

2.1. Experimental apparatus

Fig. 1 shows a schematic diagram of the experimental setup used in this study. A single cell, composed of electrically insulated end plates, graphite bipolar plates with flow channels, PTFE (polytetrafluorethylene)-type gaskets, commercial gas diffusion layers (GDLs; 35BC, SGL Carbon Weisbaden, Germany), and a MEA (membrane electrode assembly) were prepared. The active area of the cell was 9 cm^2. The MEA (CNL Energy, Korea) was composed of Nafion-211 and a catalyst layer (0.4 $mgPt/cm^2$) on both the anode and the cathode sides.

For the electrochemical measurements, an electric loader (PLZ 664WA, Kikusui Electronics, Japan) was installed in the system. In addition, an online quadrupole mass spectrometer (HPR-20 QIC, Hiden Analytical, UK) and a dew point hygrometer (Finedew, Yamatake, Japan) were installed for advanced analysis on the dry start-up.

The flow rates of the reactants were adjusted using mass flow controllers (HI-TEC MFC, Bronkhorst, Netherlands), which were

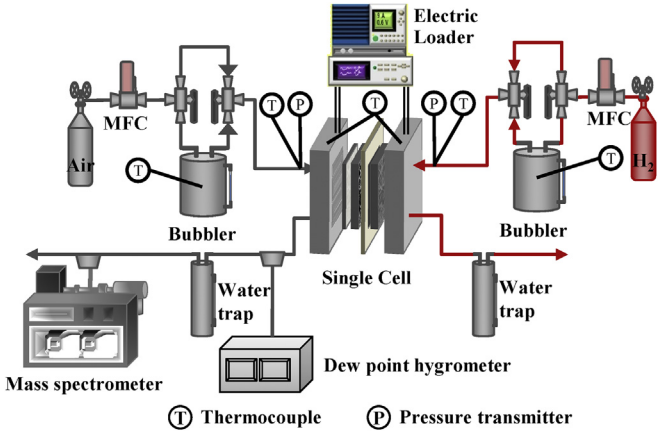

Fig. 1. Schematic diagram of the experimental setup.