Degradation of polymer electrolyte membrane fuel cells repetitively exposed to reverse current condition under different temperature

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ABSTRACT

Effects of operating temperature on performance degradation of polymer electrolyte membrane fuel cells (PEMFCs) were investigated under the repetitive startup/shutdown cycling operation that induced the so-called 'reverse current condition'. With repeating the startup/shutdown cycle, polarization curves, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), linear sweep voltammetry (LSV) were measured to examine in situ electrochemical degradation of the MEAs. To investigate physico-chemical degradation of the MEAs, scanning electron microscopy (SEM), electron probe micro analysis (EPMA), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR) were employed before and after the startup/shutdown cycling operation. With increasing operating temperature from 40 to 65 and 80 °C under the repetitive reverse-current condition, the cell performance decayed faster since corrosion of the carbon support and dissolution/migration/agglomeration of Pt catalyst were accelerated resulting in increases in ohmic and charge transfer resistance and loss of EAS.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been paid attention as alternative power sources for automobile systems due to high power density and efficiency, rapid startup and low emission of side reaction products. For commercialization of PEMFCs, there are technical problems to be solved; cost and lifetime. For fuel cell vehicles, lifespan of 5000 h is required. However, current technology cannot achieve the target yet. In fuel cell vehicles, PEMFCs are exposed to dynamic operating conditions including load cycle, freeze/thaw cycle, variation in temperature and relative humidity and startup/shutdown cycle [1–3]. These dynamic conditions accelerate degradation of fuel cell components such as catalyst, support, membrane, gas diffusion layer, etc., resulting in irreversible degradation of cell performance. Particularly, startup/shutdown cycle is indispensable in operating fuel cell vehicles so that degradation of those fuel cell components is inevitable during startup/shutdown operation.

It has been reported that during startup/shutdown operation, membrane-electrode assemblies (MEAs) for PEMFCs degraded mainly by corrosion of carbon support and dissolution/

migration/agglomeration of Pt catalyst of the cathode [4–7]. When a fuel cell vehicle is parked for a prolonged time, ambient air diffuses into the stacks since the cathode vent cannot be perfectly sealed and anode and cathode flow fields are eventually filled with air due to diffusion of air from cathode to anode through the membrane. If the fuel cell vehicle restarts under the condition with supplying hydrogen into the anode flow field, a H_2/air boundary is created in the anode flow field and high potential of 1.44 V [8] or twice of open circuit voltage (OCV) [9] is locally present on the cathode facing air in the anode flow field. The high potential that is locally induced on cathode under the so called 'reverse-current condition' can accelerate corrosion of carbon support dissolution/migration/agglomeration of Pt catalyst [4–11].

Operating conditions of PEMFCs such as relative humidity (RH) and stoichiometry of the reactant gases and cell temperature strongly affect the fuel cell performance and durability. With increasing operating temperature up to a certain degree, performance of PEMFCs generally improves primarily due to increases in catalytic activity and ionic conductivity of membrane. However, previous studies have shown that degradation of catalyst was accelerated at higher operating temperature [12,13] Bi and Fuller [12] investigated effects of temperature on durability of Pt/C catalyst with square-wave potential cycling and reported that degradation of the catalyst was faster in order of 80, 60, 40 °C. Lim et al. [13]

examined effects of operating conditions on carbon corrosion using on-line mass spectrometry. According to their results, emission of CO_2 caused by carbon corrosion increased with increasing the operating temperature and RH of reactant gases. In previous studies [4–7] we found that degradation of cathode exposed to the reverse current condition was accelerated at higher RH of the reactant gases since water facilitated corrosion of carbon support and oxidation of Pt catalyst. However, effects of cell temperature on performance degradation of PEMFCs repetitively exposed to the reverse current condition were little investigated.

In this study, we investigated effects of operating temperature on durability of PEMFCs under repetitive formation of the reverse current condition. To investigate in situ electrochemical degradation of membrane-electrode assemblies (MEAs), polarization curves, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were measured before and after 200, 400, 600, and 1200 cycles. After 1200 startup/shutdown cycles, scanning electron microscopy (SEM), electron probe micro analysis (EPMA), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR) were carried out to examine physical and chemical degradation mechanisms of the MEAs.

2. Experimental

2.1. Preparation of a single cell

A single cell was assembled with a commercial MEA which has $25\,cm^2$ active area and $0.4\,mg\,Pt/cm^2$, graphite bipolar plates with serpentine flow pattern, gaskets, gas diffusion layers and endplates. After assembly, the single cell was activated at 0.42 V for 48 h. After the activation, cell temperature of single cell was controlled by a cartridge-type heater to be 40, 65 and 80 °C.

2.2. Startup/shutdown cycle

Fig. 1 shows a schematic voltage profile for the startup/shutdown cycle employed in this study. As an operating step, H_2 and air were supplied to a single cell for 17 s. Then, supply of air was stopped with connecting a dummy load between anode and cathode. In 10 s for the residual oxygen in cathode flow field to be exhausted, supply of H_2 was stopped. After 10 s, both flow fields of anode and cathode were purged with air for 20 s to simulate a prolonged parking condition. After the air purging step, H_2 was supplied to anode with disconnecting the dummy load and then in 3 s air was supplied to cathode. During the startup/shutdown cycle, gas flows were controlled by LabView software (National Instruments, Version 6.1), which controlled direction of 3-way solenoid valves. Flow rate of H_2 and air were 330 and 995 sccm, respectively, with relative humidity of 100%. The startup/shutdown cycling and electrochemical measurements were performed at cell temperatures of 40, 65 and 80 °C.

2.3. Electrochemical analyses

To examine electrochemical characteristics of single cells with the repetitive startup/shutdown cycles, polarization curves, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), linear sweep voltammetry (LSV) were measured before and after repeating 200, 600, 800 and 1200 cycles.

Polarization curves were measured using an electrical load (Daegil, ELT DC Electronic load ESL-300Z). Fully humidified H_2 and air passing through a bubbler-type humidifier were supplied to anode and cathode, respectively. Stoichiometric ration of H_2 and air were 1.5 and 2.0, respectively. EIS was performed with
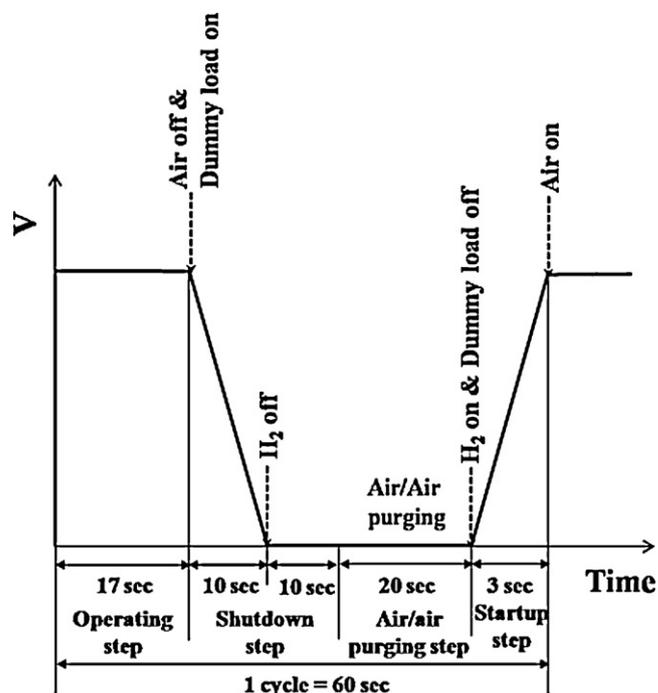
Fig. 1. A schematic voltage profile for the startup/shutdown cycle employed in this study.

an IM6 model (Zahner) to obtain ohmic and charge transfer resistance. Fully humidified hydrogen and air were supplied for anode (counter/reference electrode) and cathode (working electrode). Voltage signal with a frequency range of 50 mHz–10 kHz and an excitation voltage of 5 mV were applied at a DC potential of 0.85 V. To calculate electrochemical active surface area (EAS), CV was performed with an IM6 model. A potential range was from 0.05 to 1.2 V at a scan rate of $0.05\,V\,s^{-1}$. To evaluate H_2 crossover current density, LSV was carried out in a potential range from 0.05 to 0.6 V at a scan rate of $1\,mV\,s^{-1}$. During the measurement of CV and LSV, fully humidified hydrogen and nitrogen were supplied to the anode and cathode, respectively [14].

2.4. Post-mortem analyses

To examine physical and chemical degradation mechanism of the MEAs, scanning electron microscopy (SEM), electron probe micro analysis (EPMA), X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR) were carried out for the MEAs before and after 1200 startup/shutdown cycling.

Thickness of electrodes and distribution of Pt catalysts were observed by SEM (XL-30 FEG) and EPMA (JXA-8500F) equipped with wavelength dispersive spectrometer (WDS). MEA samples were prepared in a form of small strip, which was cut in liquid nitrogen to get clear cross-sectional image.

FETEM was performed by TECNAI F30 at accelerating voltage of 200 kV to determine the average Pt particle size and distribution. The Pt catalysts were scrapped from the MEAs and dispersed in isopropyl alcohol (IPA) solvent using ultra sonication. A drop of the dispersion solution was placed onto a 200 mesh Cu grid, which was coated by carbon film using a micropipette. The Cu grid with the dispersion solution was dried in the oven at least 1 h to evaporate IPA solvent.

To examine chemical structure of membrane, FT-IR was performed by using Thermo Mattson Infinity gold FT-IR with an attenuated total reflectance (ATR) accessory. For sample preparation, MEAs were immersed in IPA solution for 20 min to remove