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Effects of anode flooding on the performance degradation of polymer electrolyte membrane fuel cells

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HIGHLIGHTS

- Anode flooding can occur by direct flow of condensed water in humidified fuel.
- Anode flooding induces local fuel starvation and high potential in the anode.
- High potential locally present in the anode results in anode carbon corrosion.
- Anode carbon corrosion plays a key role in MEA degradation by anode flooding.

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ABSTRACT

Polymer electrolyte membrane fuel cell (PEMFC) stacks in a fuel cell vehicle can be inevitably exposed to harsh environments such as cold weather in winter, causing water flooding by the direct flow of condensed water to the electrodes. In this study, anode flooding was experimentally investigated with condensed water generated by cooling the anode gas line during a long-term operation (~1600 h). The results showed that the performance of the PEMFC was considerably degraded. After the long-term experiment, the thickness of the anode decreased, and the ratio of Pt to carbon in the anode increased. Moreover, repeated fuel starvation of the half-cell severely oxidized the carbon surface due to the high induced potential (>1.5 V_{RHE}). The cyclic voltammogram of the anode in the half-cell experiments indicated that the characteristic feature of the oxidized carbon surface was similar to that of the anode in the single cell under anode flooding conditions during the long-term experiment. Therefore, repeated fuel starvation by anode flooding caused severe carbon corrosion in the anode because the electrode potential locally increased to >1.0 V_{RHE}. Consequently, the density of the tri-phase boundary decreased due to the corrosion of carbons supporting the Pt nanoparticles in the anode.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) have been extensively developed as an electrochemical energy conversion device and the main power source for hydrogen vehicles because of their high efficiency and environment-friendly operation [1]. PEMFCs consist of many components developed by various technologies related to electrochemistry, materials science, and chemical and mechanical engineering; membrane electrode assemblies (MEAs), gas diffusion layers (GDLs), and bipolar plates with gas flow channels. Global automakers have achieved significant accomplishments to commercialize fuel cell vehicles (FCVs) over the past decade. Recently, Hyundai motor company started the commercial production of the Tucson ix35 FCV with a well-designed fuel cell stack, which can cover ~594 km under new European driving cycle conditions without hydrogen refueling. However, to be more commercially viable, the fuel cell stacks should be improved further by overcoming technical issues such as high Pt loadings [2,3], difficulty in water management [4,5], corrosion of bipolar plates [6,7], and low hydrogen storage capacity of the fuel tank [8,9].

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Among these obstacles, water management in the MEAs is one of the most crucial issues affecting the performance of the fuel cell stack [10]. The cathode of a PEMFC electrochemically produces water by the oxygen reduction reaction (ORR), and some of the water thus generated can be transferred to the anode by the back-diffusion mechanism [11]. In contrast, the protons generated at the anode are transferred with water to the cathode by electroosmotic drag [12]. Furthermore, under normal fuel cell operation, H_2 and air with high relative humidity (RH) are supplied to the anode and cathode of fuel cell stacks, respectively [2,4,13]. Therefore, if the water present in the catalyst layers is not properly managed, it severely inhibits the transport of H_2 and O_2 to the catalyst surface through the electrodes with a thickness of several micrometers.

The effects of cathode flooding on fuel cell performance have been already studied [10,14,15]. It has been reported that liquid water blocks the catalytic active sites in the cathode, resulting in extremely low performance of the fuel cell because of the high mass-transfer resistances in the high current density region and the high overpotential of the ORR itself. To remove water from the cathode efficiently, hydrophobic additives, such as polytetrafluoroethylene (PTFE), have been added to the cathode catalyst layers [14,15], or the surface of carbon support materials has been selectively functionalized with a temperature-directed switchable polymer to thermally change the hydrophilicity of the catalyst layers [10].

Despite the technical importance, anode flooding has been rarely investigated since the anodic reaction, hydrogen oxidation reaction (HOR), has a low overpotential compared to the ORR. Under practical operating conditions such as cold weather during winter, anode flooding in the MEAs can be accelerated due to the direct flow of condensed water to the anode; humidified hydrogen can be cooled down during passing through the gas lines connecting the humidifier to the stack. Moreover, during long-term operation, excess water can be transferred from the cathode to the anode by back diffusion. Continuous water accumulation in the anode may cause severe anode flooding and localized fuel starvation in the fuel cell stacks. This may become an important factor for anode degradation, and severe problems such as carbon corrosion can be electrochemically observed in the anode.

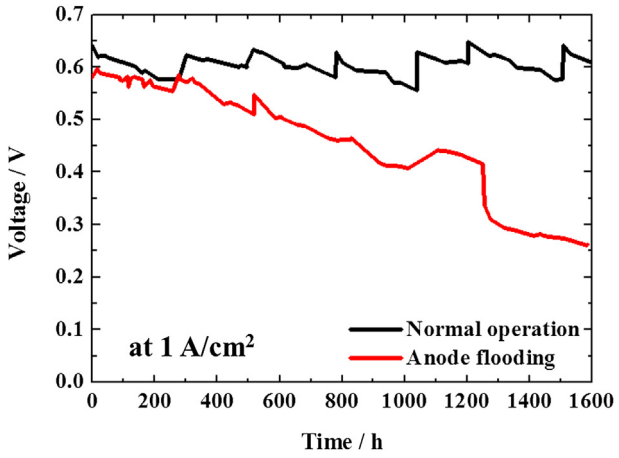

Fig. 2. The voltage decay profiles of the single cells for 1600 h at the constant current density of 1 A cm^{-2}.

As shown in previous studies on fuel starvation at the anode, the oxidation reaction of carbon supports (carbon corrosion) predominated over the HOR at the anode due to the abnormally increased electrode potential of >1.0 V_{RHE} when H_2 gas was not sufficiently supplied to the anode [16–19]. The carbon corrosion mechanism can be expressed as follows:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- (0.207\ V_{RHE})$$

$$C + H_2O \rightarrow CO + 2H^+ + 2e^- (0.518\ V_{RHE})$$

where RHE is the reversible hydrogen electrode.

Although carbon corrosion reactions in the anode are generally not thermodynamically or kinetically favored under normal operating conditions, those reactions can be accelerated when the electrode potential increases to >1.0 V_{RHE} due to hydrogen fuel starvation [20–26]. Therefore, anode flooding is very similar to fuel starvation, in that severe concentration overpotential is induced

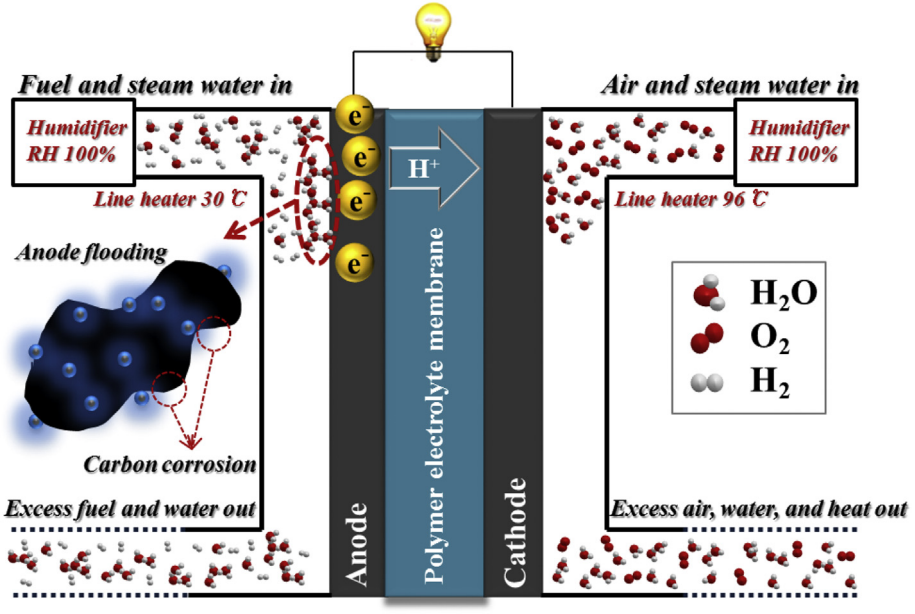

Fig. 1. A schematic diagram of the experimental set-up to simulate the anode flooding status during long-term performance test of single cell.