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Physical degradation of cathode catalyst layer: A major contributor to accelerated water flooding in long-term operation of DMFCs

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HIGHLIGHTS

- Acceleration of cathode flooding in long-term DMFC test is thoroughly investigated.
- Both flooding and non-flooding degradations contribute to DMFC voltage losses.
- The rate of flooding degradation is accelerated with the MEA aging process.
- Cathode catalyst layer is severely deformed due to surface wrinkling and cracking.
- Cathode layer cracking is mainly responsible for acceleration of water flooding.

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ABSTRACT

This study presents a comprehensive investigation on the water flooding of direct methanol fuel cells (DMFCs) during long-term testing with regard to the structural changes of the catalyst layer and gas diffusion layer (GDL) of the cathode. Two separate durability operations of DMFCs are conducted for 1000 and 1261 h in order to determine the relative contributions of the cathode catalyst layer and the GDL to time-dependent water flooding during the aging process. The voltage decay rates caused by flooding and non-flooding degradation phenomena are calculated and compared. DMFCs undergo serious voltage decay due to water accumulation in the cathode, and the rate of flooding degradation multiplies approximately every 500 h during the duration of testing. The cathode catalyst layer is found to be severely deformed due to surface wrinkling and cracking during the aging of the membrane electrode assembly (MEA). The morphological alteration of the cathode catalyst layer, particularly the formation of wide and deep cracks is identified as the main reason for the acceleration of water flooding, while degradation of the cathode GDL is minor. This demonstrates that during the long-term operation of DMFCs, the physical disintegration of the cathode catalyst layer is a crucial issue affecting water management, which should be carefully addressed.

1. Introduction

Despite an early market introduction, the widespread commercialization of direct methanol fuel cell (DMFC) technology has yet to materialize mainly because of unresolved challenges that include high cost and inferior lifetime endurance. One of the major reasons for high production cost is the use of noble metal catalysts in large quantities for both electrodes in order to acquire an acceptable level of initial performance and fuel efficiency, both of which are otherwise considerably low due to the problems of sluggish methanol oxidation in the anode and catalyst poisoning in the cathode by permeated methanol [1–3]. Numerous research efforts have been devoted to solving the issue of high cost by either replacing the expensive precious metals with alternative inexpensive materials or by minimizing the loading amounts of the noble catalysts through their enhanced utilization. The challenge of a durable and reliable DMFC lifetime has been addressed with intensive R&D efforts aimed at strategies that include multi-directional pathways encompassing materials science, electrode structure engineering, and the optimization of operation strategies [4–6].

DMFCs encounter both recoverable and irrecoverable performance losses during long-term operation. Irrecoverable performance losses are mainly caused by permanent/irreversible

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degradation of the component materials and by physical degradation of the membrane electrode assembly (MEA) structure, whereas recoverable losses are caused by temporary/reversible changes such as the formation of catalyst surface oxides and water flooding in the cathode [7–11]. Cathode flooding is a major contributor to the recoverable performance losses in low-temperature fuel cells. In a DMFC, the impact of cathode flooding is far harsher than it is in a proton exchange membrane fuel cell (PEMFC) due to the aqueous methanol feed in the anode. Approximately 80% of total water content of a DMFC cathode comes from the anode side mainly by diffusion and electro-osmotic drag mechanisms [12]. This not only deteriorates the initial fuel cell performance but also results in high voltage decay rates during continuous operation.

Generally, DMFCs deliver a stable performance in the initial stage of a durability test. As the operation period is extended, however, voltage degradation accelerates largely due to the water accumulation in the cathode. Water flooding gradually worsens over time and is known to literally halt the operation of a DMFC only after a few hundred hours of operation—in particular, when catalyst-coated membrane (CCM)-type MEAs are used [13,14]. The subsequent performance recovery of a DMFC can be realized by cathode drying for extended durations, which can be prolonged by as much as a few days [14]. This aggravation of water flooding in a DMFC is frequently attributed to a loss of hydrophobicity in the cathode gas diffusion layer/microporous layer (GDL/MPL) resulting from a stripping away of the poly-tetrafluoroethylene (PTFE) additive. One considerable point, however, is that emphasizing the loss of GDL hydrophobic character as the solitary reason for such an early stage acceleration of cathode flooding may lead to a misapprehension of the actual pace of the GDL structural changes and cause an overlooking of the potential contribution by the morphological alterations of the cathode catalyst layer.

During long-term operations, catalyst layers are known to undergo morphological changes such as crack formation and propagation due to the dimensional changes of the proton exchange membrane (PEM), and an alteration/collapse of the pore structure due to the agglomeration of catalyst nanoparticles and carbon support corrosion [15–20]. The DMFC electrodes are highly prone to such types of structural changes due to the aggressive nature of a methanol environment. Methanol solution can not only damage the integrity of the anode catalyst layer but can also cause the crack formation in the cathode catalyst layer by permeating through the membrane. The degree of electrode cleavage and the resultant irrecoverable performance losses of DMFCs are escalated with higher methanol concentrations during long-term operations [20]. In addition to the permanent performance decline, there is also a possibility that the physical degradation of electrodes, particularly that of the cathode, may pose detrimental effects on water drainage capabilities during a continuous test and aggravate the water flooding issue. However, we could find no report in the literature correlating the water flooding behavior to morphological changes in the cathode catalyst layer during extended operation of DMFCs.

In the present study, we have thoroughly investigated the impact of structural changes of the GDLs and catalyst layers with respect to cathode flooding behaviors during long-term operations. Two separate DMFC tests have been conducted for 1000 and 1261 h using CCM-type MEAs. Changes in the morphological and electrochemical characteristics of the GDLs and MEAs have been analyzed using various electrochemical and physicochemical tools. The performance decay rates caused by flooding and non-flooding degradations have been calculated and compared. To the best of our knowledge, this is the first report that has specifically demonstrated the detrimental effect of the physical degradation of the cathode catalyst layer on the time-dependent water flooding of a DMFC during long-term operation.

2. Experimental

2.1. Membrane electrode assembly

All the MEAs used in this work were prepared using a previously reported roll-press decal technique [21]. Briefly, the anode and cathode catalyst layers were prepared by spraying colloidal inks containing catalyst powders, de-ionized water, 5 wt.% Nafion ionomer solution (DuPont) and isopropyl alcohol (IPA) on Kapton® sheets (DuPont) that had been pre-coated with thin carbon black layers. PtRu black (HiSPEC™ 6000) was used as the anode catalyst with a total loading of 3.0 mg cm^{-2} whereas Pt black (HiSPEC™ 1000, Johnson–Matthey) was used for the cathode with a total loading of 2.0 mg cm^{-2}. An ionomer content of 10 wt.% (dry ionomer basis with respect to catalyst) was used for each electrode. The geometric area of the electrodes was 10.89 cm^2. After drying, the anode and cathode electrode layers were transferred on each side of a Nafion®115 (DuPont) membrane using the decal technique. The decal-transferring step was carried out using a roll-press machine under an applied pressure of 3 MPa at a temperature of 170 °C with a roller speed of 50 mm min^{-1}. After the hot-pressing step, Kapton sheets were peeled off from both sides of the MEA. Toray TGP-H-060 carbon paper (containing 20 wt.% PTFE) and SGL 25BC were used as the anode and cathode GDLs, respectively.

2.2. Single-cell and long-term DMFC tests

Single-cell polarization curves of DMFC were recorded at 60 °C by supplying a 1.0 M methanol solution to the anode and dry air to the cathode at stoichiometric values of 6 and 9, respectively. A commercial test station (SMART-II, WonA Tech, Korea) was used for the single-cell and durability tests.

Long-term DMFC tests of two identical MEAs were conducted in a galvanostatic mode at 60 °C under an applied current density of 150 mA cm^{-2} using a 1.0 M methanol solution in the anode and dry air in the cathode with a stoichiometry value of 3 for both reactants. The purpose of using such a low airflow stoichiometry value was to enable a close understanding of the cathode retardation by water accumulation over time. The long-term tests were conducted in a continuous mode without applying any intermittent air break or load on–off strategy. However, at certain intervals, the DMFC operation was stopped in order to dry the cathode followed by the measurement of polarization curves. The cathode drying was performed for 15 min by purging dry N_2 at a flow rate of 800 sccm. Periodic cathode drying followed by polarization curve measurements of the DMFC was adopted in order to estimate the voltage losses arising from the flooding and non-flooding degradation mechanisms.

During the long-term tests, the first MEA was run for 1000 h without any change of its initial configuration, while for the second MEA, the cathode GDLs were replaced twice with new ones during the long-term operation in order to evaluate the effect of GDL aging on the water flooding behavior of a DMFC.

2.3. Electrochemical and physicochemical characterization

Changes in the morphological and electrochemical characteristics of the GDLs and MEAs were analyzed using various electrochemical and physicochemical tools. Cyclic voltammograms (CVs) of the electrodes were recorded using a potentiostat (Autolab, Eco Chemie) in order to estimate their electrochemically active surface areas (ECSAs) before and after the long-term test. The values of cathode ECSAs were calculated in a potential range of 0.05–0.4 V vs. a dynamic hydrogen electrode (DHE).