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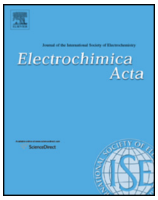

Comparison of Carbon Corrosion Test Methods for Polymer Electrolyte Fuel Cell

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ABSTRACT

The membrane electrode assembly (MEA) durability test protocols proposed by the FCCJ, USFCC and DOE in 2007 for estimating the carbon support corrosion of Pt/C catalyst were compared. The MEA durability tests were performed using JARI's standard single cell. From the results, ECA of the cathode decreased most rapidly by the FCCJ protocol because of the highest potential applied to the cathode. In order to understand the difference in degradation rate of each protocol, we investigated the effects of the dew point of the gas supplied to the cathode and the cycled potential on the carbon corrosion rate. It was shown that the carbon corrosion rate became large when the cathode potential was cycled and the gas supplied to the cathode had a high dew point. These results support the effectiveness of the revision of the FCCJ protocol in 2011.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) for both stationary and mobile applications have attracted much research interest owing to their high energy efficiency and environment-friendly nature. To enable the widespread use of PEFCs, it is important to improve the durability and reduce the cost of fuel cell stacks. Polymer electrolyte membrane fuel cells, especially for automotive applications, must operate over a wide range of conditions for more than 5000 hours in practical use. To investigate the durability of materials developed for the PEFC stack, it is generally impractical and inefficient to estimate the durability of the fuel cell stack under practical conditions because this would require huge testing time and cost. Moreover, the obtained test results would include the decrease in performance resulting from degradation of all the materials in the stack, and so it is difficult to separate a degradation factor. It is important to understand the degradation phenomena and performance degradation behavior of each material for the PEFC stack. Therefore, two or more protocols for evaluating the durability of materials used for the PEFC stack have been proposed as a function of the preliminary screening [1–6], but with different test conditions. If those testing conditions could be unified, the test results would become easy to estimate equally.

The US Department of Energy (DOE), US Fuel Cell Council (USFCC), and The Fuel Cell Commercialization Conference of Japan (FCCJ) proposed several methodologies for testing MEAs and their materials [1–6]. We have applied the protocols of the FCCJ to standard materials and verified their applicability or investigated the degradation phenomena using a JARI standard single cell [7–9]. The JARI standard single cell has an electrode surface area of 25 cm^2 and one serpentine flow channel in each separator of the anode and cathode [7]. This cell has a large gas flow rate in a channel, and can easily produce a pressure distribution. The JARI standard single cell is suitable for simulating the phenomena that may actually occur in a PEFC stack, and so is suitable for evaluating materials under conditions similar to the operating conditions of an actual stack.

The catalyst layer is normally composed of a platinum catalyst supported on high-surface-area carbon. Corrosion of the cathode carbon support, which can occur under certain automobile operating conditions, causes structural changes of the catalyst layer and the degradation of cell performance. Various experiments and analyses have been made to clarify the mechanisms of carbon corrosion [10–15]. In an actual PEFC stack in an automobile, corrosion of the cathode carbon support can occur due to the so-called hydrogen/air front mechanism [10]. The same effects occur by local hydrogen starvation if the supply of hydrogen is locally blocked in the anode [11]. When hydrogen is introduced to the anode flow field, the behavior of cathode potential shows a triangular change and the maximum cathode potential reaches around 1.5 V vs. RHE when the hydrogen flow rate is small [6]. Corrosion of the carbon support at high electrode potentials greatly affects the performance of PEFC, so

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the start/stop test that simulates the operation of a fuel cell vehicle is widely used to test the carbon corrosion durability of an MEA. Start/stop protocols proposed by the USFCC, DOE, and FCCJ in 2007 used different potential wave forms, but the difference in test results among these protocols has not been sufficiently discussed. If there is no great difference in the test results from these protocols, harmonizing these test conditions will make it easier to compare durability of developed materials and to speed up development time. In this study, we experimentally investigated the difference in durability test results from these protocols. Furthermore, the applicability as an accelerated test was considered based on test results for the required testing time, selectivity of carbon degradation, and degradation behavior of power generation performance. The influential factors causing the difference in test results by each protocol were considered. The FCCJ revised their start/stop protocol in 2011 [6], and the DOE revised their protocol with the same potential waveform as the FCCJ in 2013 [16]. The recommendation of the protocol revisions of the FCCJ and DOE was verified.

2. Experimental

2.1. MEA preparation and measurement of initial performance

A commercially available Pt/C catalyst (TEC10E50E), polymer electrolyte dispersion (DE2020) and polymer electrolyte membrane (Nafion) were used to prepare a catalyst coated membrane (CCM) used in this study. The catalyst paste made of Pt/C catalyst and polymer dispersion was applied onto a Teflon sheet using the doctor-blade method and was heat-treated at 125 °C for 1 h. The Pt metal loading was calculated based on the chemical composition of the catalyst paste. A sheet of Nafion membrane (8 × 8 cm) was sandwiched between catalyst sheets of 25 cm^2 (5 × 5 cm), with the catalyst layer side of the sheets in contact with the Nafion membrane. The sheet-membrane unit was hot-pressed at 135 °C for 10 min, after which the Teflon sheets were removed to obtain the CCM. The CCM specifications as prepared in this study are shown in Table 1.

All measurements in this study were performed using JARI's standard single cell; the specifications of the cell are shown in Table 2. After the CCM was assembled into JARI's standard single cell, the cell was operated at a constant current density of 1000 mA/cm^2 at a temperature of 80 °C until the change in cell voltage was reduced to below 1 mV/hr (more than approx. 16 h). We then measured the I–V performance for the initial power generation test before starting the durability tests. The test conditions used for I–V measurement are shown in Table 3. Cyclic voltammetry for measuring electrochemical surface area (ECA) was carried out following I–V measurement at the same cell temperature of 80 °C as the I–V measurement.

2.2. Comparison of test conditions in 2007 protocols

After the initial diagnostics of MEA before the durability test, the carbon corrosion test was carried out based on the protocol proposed in 2007 by FCCJ, USFCC and DOE. The potential wave profiles of each protocol are shown in Table 4. These potential cycle tests were performed at a predetermined number of cycles or duration, and I–V and CV measurements were performed to diagnose the degradation status. These durability tests and diagnosis were terminated when the ECA became approximately 40–50% of the initial value. During the carbon corrosion durability test, the concentration of CO_2 in the nitrogen gas exhausted from the cathode outlet was measured with a non-dispersive infrared analyzer in order to calculate the amount of carbon support corrosion. All the experiments were conducted at the cell temperature of 80 °C.

In general, the degree of Pt/C catalyst degradation is estimated by the normalized ECA ratio as an initial value. Any degradation of carbon or Pt in the Pt/C catalyst causes decrease of the ECA. The durability of the Pt/C catalyst is dependent on the durability of both carbon and Pt in the catalyst. When the selectivity of the carbon degradation by a start/stop test is high, carbon corrosion could be compared easily in ECA. High selectivity of the carbon degradation by a start/stop test is effective for the comparison of the carbon durability of Pt/C catalysts. Since the selectivity of carbon degradation should be taken into consideration, we defined a criterion to compare the selectivity of carbon corrosion by each protocol. The relation between the amount of ECA decrease and the amount of oxidized carbon support was considered for the criteria.
where,

ΔECA is the decline of normalized ECA ratio/%,
ΔMc is the corroded amount of carbon/mol,
ΔMc/ΔECA is the selectivity index of carbon corrosion.

Mechanisms for instability of Pt nanoparticles in low temperature fuel cells have been proposed [17]. ECA decreases if coarsening of Pt particles on carbon support by crystal migration and coalescence or Ostwald ripening via Pt dissolution and redeposition, dissolution and precipitation in the ion conductor occurs. These are the degradation phenomena of the Pt/C catalyst which occur even if carbon support does not corrode, and in these cases ΔMc/ΔECA becomes zero. Other than these degradation phenomena, there is detachment of Pt particle from carbon support occurring because of carbon support corrosion [18]. In the case of this phenomenon that ECA drop and carbon corrosion happen, it is unable to evaluate the degradation state of the Pt/C only with the decrease of ECA. Therefore, the degradation state after the examination should be estimated by the ratio of ΔMc/ΔECA.

We compared durability test results by each protocol in terms of the duration necessary for the durability test, selectivity of carbon corrosion and behavior of performance degradation.

2.3. Effects of test conditions on the carbon corrosion rate

In order to understand the difference among test results obtained from each test protocol, the effects of cathode potential,

Table 1
CCM specifications.

Catalyst	Pt/CB (TEC10E50E), TKK
Anode/Cathode Pt loading/mg cm^{-2}	0.3/0.3
Ionomer	D2020, DuPont
Electrolyte membrane	NR211/212, DuPont

Table 2
Specifications of JARI standard single cell.

Electrode area	25 cm^2
Number of flow channels, configuration	1, serpentine
Flow channel, land width	1 mm, 1 mm
Flow channel depth	1 mm
Gas flow direction	Counterflow

Table 3
Measurement conditions of I–V performance.

Cell temperature	80 °C
Fuel/Air utilization ratio	70/40%
Fuel/Air dew point	77/60 °C
Pressure	Atmospheric at cell outlet

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