



Overpotential analysis of the Direct Formic Acid Fuel Cell



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ABSTRACT

An overpotential analysis is carried out in the range of 298 K–353 K to clarify the dominant overpotential factor above 333 K of the direct formic acid fuel cell, DFAFC using 2 mg cm^{-2} of Pd-black catalyst for the anode. It is found that the mass transport overpotential at the anode which is estimated at a specific current density showing the maximum current density increases from 45 mV to 196 mV when the cell temperature increased from 298 K to 353 K although the formic acid crossover flux through the membrane also increases. Moreover, the effect of the loading of microporous layer, MPL, in the range of $1\text{--}4 \text{ mg cm}^{-2}$ at the anode fabricated using Nafion as a binder, which affects the mass transport, on the overpotential behavior is also investigated. It is found that the lower MPL loading is appropriate for the DFAFC operation due to the poor mass transport of the formic acid although the higher MPL loading is appropriate for the hydrogen-oxygen, PEFC, operation. Based on the comparisons of the overpotential distributions between the DFAFC and the PEFC, it is suggested that both the poor mass transport in the anode and the formic acid crossover should be simultaneously improved in order to obtain the higher power density of the DFAFC above 333 K.

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1. Introduction

Recently, DFAFCs have attracted much attention due to their higher power density [1] and lower crossover flux [2] compared to those of the direct methanol fuel cells (DMFCs), and they have been considered to be a promising power source for portable devices. Especially, Chang et al. demonstrated that a 550 mW cm^{-2} power density, which is the highest power density for a DFAFC to the best of our knowledge, was obtained using the Pd-Ni₂P/C catalyst for the anode of the DFAFC at 303 K [3]. This performance is excellent as a direct liquid fuel cell, DLFC, however, it has not reached to the performance of the PEFC.

Generally, PEFCs have been operated at 333–363 K and their power density has exceeded 1 W cm^{-2} . Typically, the power density of the fuel cell, such as the PEFC and DMFC, increases with the increasing operating temperature [4,5]. Taking into account this fact, it is expected that the power density of the DFAFC approaches that of the PEFC by increasing the operating temperature. However, it has been reported that the power density of the DFAFC has gradually increased with increasing the operating temperature up to 323 K, but did not increase above 323 K [1,6–8]. As a reason for this phenomenon, it has been reported that the high temperatures lead to an increase water vaporization at the cathode

which reduces, e.g., the partial pressure of the oxygen and the mass transport limitation of the anode [1,8]. However, these have not been experimentally investigated. Moreover, it has been also reported that the anode kinetic was not improved when the cell temperature increased from 318 K to 333 K by the result of the electrochemical impedance spectra, and this is the reason for the cell performance showed plateau when the cell temperature increased from 318 K to 333 K [7]. These findings were derived based on the experimental results, however, the electrochemical impedance spectra was not obtained at the condition showing the maximum power output. Therefore, the effect of the cell temperature on the electrode potentials of the anode and the cathode and the overpotential distributions at the various cell temperature should be experimentally investigated at the specific current density showing the maximum power density to specify the factors of power density showing plateau above 323 K.

In this study, an overpotential analysis of the DFAFC was conducted in the range of 298–353 K by individually measuring the electrode potentials of the anode and the cathode to experimentally clarify the main factors of the overpotential above 323 K. Since an increase in the operating temperature caused the variation in the mass transport, such as the formic acid crossover [2,9], the effect of the mass transport on the overpotential distributions of the DFAFC was also investigated using different types of membrane electrode assemblies having various amounts of a microporous layer, MPL, for the anode. They were then compared the PEFC which had the same construction as the DFAFC, but it operated

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with hydrogen and oxygen to clarify the difference in the overpotential behavior in the high temperature regions above 323 K between the DFAFC and PEFC.

2. Experimental

2.1. Membrane electrode assembly (MEA) preparation

NR212 was used as the polymer electrolyte membrane. Palladium black (Alfa Aesar) was used as the catalyst for the anode. The catalyst ink was prepared by dispersing the appropriate amount of the catalyst in a solution of deionized water, isopropyl alcohol, and 5 wt% Nafion solution (Wako Pure Chemical Industries, Ltd.). For the electrodes preparation, the Pd ink was coated on the microporous layer, MPL, which was prepared with 0.5–4 mg cm⁻² of a carbon black containing 10 wt% Nafion on the carbon papers (TGP-H-60H, ElectroChem, Inc.). The catalyst loading was 2 mg cm⁻², and the ionomer loading of the catalyst layer was 10 wt%. For the cathode electrodes, commercial Pt/C (2 mg-Pt cm⁻², Pt:50 wt%, GDL; TGP-H-60H, ElectroChem, Inc.) electrodes were purchased from Chemix Co., Ltd. The MEA was then fabricated by sandwiching the membrane between the anode and the cathode and hot pressing them at 408 K and 5 MPa for 3 min. The projected area of the electrode was 4.84 cm² (2.20 × 2.20 cm).

2.2. Cell structure

The cell (FC-05-02H2R, ElectroChem, Inc.) consisted of current collectors, separators, rubber sheets and the MEA. The MEA was sandwiched between the separators made of graphite blocks having serpentine flow channels with a rubber sheet. The formic acid was directly supplied to the graphite flow field without the contact of the metal end plate or tube to avoid the contamination. The Pt wire reference electrode was located in an open compartment independent of the flow field of the anode. It contacted the Pt/C electrode which was the same as the cathode electrode and contacted the NR 212.

2.3. Measurement of the power generation characteristics

A formic acid solution was prepared by diluting the formic acid (special grade reagent, Wako Pure Chemical Industries, Ltd.) with purified water which was produced by the distillation using deionized water and corresponded to the A4 grade of JIS K055 (Distilled water, Kyoei Pharmaceutical Co., Ltd.). The current-voltage, *i*-*V*, characteristics were measured by linearly sweeping the voltage from the open circuit voltage to zero at the scan rate of 5 mV s⁻¹. The *i*-*V* measurement was conducted at least three times to check the accuracy of the experiment, and it was confirmed that the differences in the cell voltage and the anode/cathode potential among three measurements were less than 5 mV. The electrode potentials versus the hydrogen reference electrode were recorded by a data logger (GL 200, Graphtech) during the *i*-*V* measurement. All the electrochemical measurements were conducted using an electrochemical measurement system (Hz-7000, Hokuto Denko, Co., Ltd.). As a cell conditioning, the current-time, *i*-*t*, measurement at 0.6 V with humidified hydrogen/oxygen under 333 K was conducted for 2 h. In order to check that the cell conditioning was finished or not, three times of *i*-*V* measurements were then conducted. The *i*-*t* measurement and the *i*-*V* measurements were repeated until three *i*-*V* curves were completely fitted.

The cell was operated at temperatures from 298 to 353 K. For the DFAFC operation, 2 ml/min of 3 M formic acid was supplied to the anode and 500 ml/min of oxygen was supplied to the cathode. For the PEFC operation, 500 ml/min of hydrogen was supplied to

the anode, and the 500 ml/min of oxygen was supplied to the cathode. The stoichiometric ratios of the gases were 15 for hydrogen and 30 for oxygen at 1 A cm⁻². During the PEFC operation, the hydrogen and oxygen were fully humidified, i.e., they were bubbled through water heated to the cell temperature. During the both operations, 50 ml/min of fully-humidified hydrogen was also supplied to the reference electrode.

Because the anode performance degraded with the operation due to catalyst poisoning, the following regeneration process (RP) was conducted. After the power generation, the formic acid solution was replaced with fresh water and the cell to wash the anode surface. This washing was continued until the residual cell voltage decreased to 0.1 V according to the previous report by Zhou et al. [10]. The anode performance was completely regenerated by this RP process to the initial condition.

2.4. Measurement and calculation of the crossover flux

Formic acid crossover flux was estimated by the CO₂ gas concentration of the cathode exhaust as following manners [11,12]. The DFAFC was operated at the constant voltage of 0.4 V. At 1 h, the cathode exhaust gas through the cold trap was collected in a sampling bag. The CO₂ gas concentration in the sampled gas was measured by a microgas chromatograph (GC-400, Agilent). Based on the assumption that the permeated formic acid was completely and immediately oxidized to CO₂ by the cathode catalyst, the formic acid crossover flux was estimated from the CO₂ concentration in the exhaust gas from the cathode.

2.5. Overpotential analysis

It has been widely known that overpotential consists of four losses: (1) activation losses, (2) fuel crossover, (3) ohmic (IR) losses, and (4) mass transport losses. Using these four losses, the cell voltage, *V*, can be estimated as follows [13];

$$V = (P_{(c)} - P_{(a)}) - (i + i_n)R \quad (1)$$

$$P_{(c)} = E_{(c)} - A_{(c)} \ln \left(\frac{i + i_n}{i_{o(c)}} \right) + B_{(c)} \ln \left(1 - \frac{i + i_n}{i_{l(c)}} \right) \quad (2)$$

$$P_{(a)} = E_{(a)} + A_{(a)} \ln \left(\frac{i + i_n}{i_{o(a)}} \right) - B_{(a)} \ln \left(1 - \frac{i + i_n}{i_{l(a)}} \right) \quad (3)$$

In Eqs. (1)–(3), *P* is the electrode potential, *E* is the reversible open circuit potential, *i_n* is the fuel crossover equivalent current density, *R* is the specific resistance, *A* is the slope of the Tafel line, *i_o* is the exchange current density, *B* is the mass transfer parameter, and *i_l* is the limiting current density. The subscripts (a) and (c) denote the anode and cathode, respectively. On the right-hand side of Eq. (1), the second term is the ohmic loss. On the right-hand side of Eqs. (2) and (3), the second terms are the activation losses, and the last terms are the mass transport losses of the anode and the cathode, respectively. The potentials of the anode and cathode versus the reversible hydrogen electrodes during the *i*-*V* measurement, resistance of the cell and the crossover flux were obtained from the experiment, hence, the *A*, *B* and *i_o* were estimated as a fitting parameter from Eqs. (2) and (3) by goal seek using an EXCEL spread sheet [13]. Based on these results, we obtained five overpotentials, OP, as shown in Table 1. Here, the IR loss was not divided into that of the anode and the cathode since the ohmic resistance between the anode electrode and cathode electrode was measured as the cell resistance. Comparing the cell voltage, the

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