

# A Novel Approach to Polymer Electrolyte Fuel Cell Electrode Slurries

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**ABSTRACT:** This study presents a novel approach to evaluating the fabrication process of the catalyst layer. In a polymer electrolyte fuel cell, the catalyst layer represents a reaction field where reactions and mass transport are coupled. The distribution of materials within the catalyst layer and the porous structure of the catalyst layer have an important effect on cell performance. The catalyst layer is fabricated from an electrode slurry, which is prepared by dispersing platinum-supported carbon and ionomers. The structure of the catalyst layer is formed by applying and drying the electrode slurry, but this process is complexly coupled with material composition and process conditions. Furthermore, it is necessary to capture the state of the non-steady-state process of the applied film, which has made it challenging to evaluate in the past. In this study, we investigated the electrode slurry drying process by combining optical methods using a confocal microscope and micro-AC impedance measurement for understanding of the structure formation mechanisms of the catalyst layer.

**KEY WORDS:** Polymer electrolyte fuel cells, catalyst layers, Electrode slurry, Drying process, Measurement

## 1. INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) are prospective energy devices for automotive use and distributed power supply. The PEFC is assembled by putting a membrane electrode assembly (MEA), which consists of the polymer electrolyte membrane (PEM) with the catalyst layers (CLs) and the gas diffusion layers (GDLs) on both sides, between separators. The catalyst layer is the reaction field of the polymer electrolyte fuel cell, and it is necessary for protons, electrons, and reaction gases to be transported to the catalyst. In addition, it is necessary for the generated water to be effectively discharged from the system. Therefore, the porous structure and material distribution of the catalyst layer are important, and these are determined during the fabrication process of the catalyst layer from the electrode slurry (Fig. 1). Therefore, in order to control the structure of the catalyst layer, it is necessary to elucidate the mechanism by which the catalyst layer structure is formed from the electrode slurry. However, the slurry is challenging to assess due to its black, high-viscosity liquid composition, which is a consequence of the dispersed materials. Moreover, the drying process required to form the catalyst layer must be taken into account. As a consequence of these difficulties, the trial-and-error approaches represent the principal method for the development of the catalyst layer. The objective of this study is to demonstrate an evaluation method for

the drying process of the electrode slurry, with a view to understanding the mechanisms of formation of the porous structure. The authors have previously evaluated various properties of electrode slurries<sup>(1,2)</sup>, including their rheology, and have also measured the drying process of slurries using their own impedance measurement system with a microelectrode chip<sup>(3,4)</sup>. In this study, we propose and demonstrate a measurement and evaluation method for the drying process of slurries that combines visualization and drying tracking of the drying surface of slurries

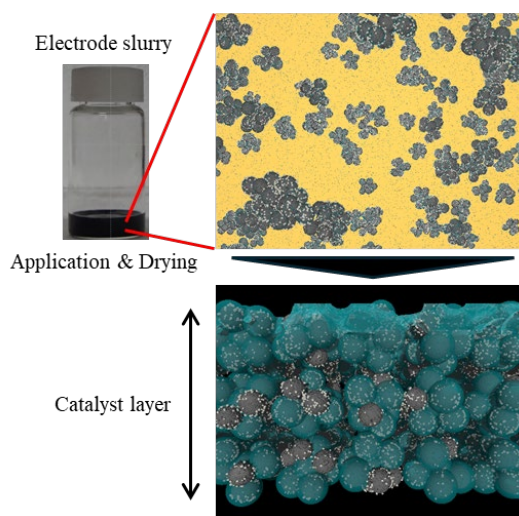


Fig. 1. Electrode slurry and fabrication of the catalyst layer.

using a confocal microscope with evaluation of the particle aggregation process using impedance measurement.

## 2. EXPERIMENTAL

### 2.1. Fabrication of electrode slurry

A platinum-supported carbon (Pt/C, TEC10E50E, Tanaka Kikinzoku Kogyo) and an ionomer (D2020, Chemours) were dispersed in a 1-propanol aqueous solution to make the electrode slurry. The specific conditions and details of the dispersion process are described in the previous study<sup>(5)</sup>. The ionomer to carbon (I/C) ratio was 0.8, 1.0 and 3.0. The drying process was conducted at room temperature and humidity, which are approximately 25°C and 40%RH.

### 2.2. Confocal imaging

A white light confocal microscope was used to visualize the surface of the electrode slurry during drying and to measure the surface displacement. The objective lens magnification was set to 10x, and surface images were captured at a frame rate of 15fps. The surface displacement that occurred during the drying process was measured by tracking the focus during the drying process and measuring the stage displacement at that time. The displacement measurement interval was set to approximately 30 seconds.

### 2.3. Impedance and dielectric spectroscopy

The impedance in the low-frequency range up to 8 MHz was measured using an LCR meter (IM3536, Hioki). The electrode slurry was applied to the microelectrode terminal chip connected to the LCR meter, and the impedance variation during the drying process was measured. Details of the microelectrode terminal chip and measurement method are described in a previous study<sup>(4)</sup>.

A vector network analyzer was employed for the purpose of conducting dielectric spectroscopy in the high-frequency range up to 40 GHz. S-parameters were obtained in order to determine the dielectric constant and dielectric loss. This method can be used to investigate the dielectric constant and dielectric relaxation of materials. In this study, the measurement of water and 1-propanol, which serve as dispersion media for the electrode slurry, was performed.

## 3. RESULTS AND DISCUSSION

### 3.1. Surface observation

Fig. 2 shows the results of visualizing the surface immediately after applying the electrode slurry using a white light confocal microscope. The results for I/C 0.8 and 3.0 are shown, and there is

a clear difference in these two cases. In other words, at I/C 0.8, a rough structure was observed on the surface, suggesting that the agglomerates of particles were distributed on the surface layer. On the other hand, at I/C 3.0, the surface appeared extremely smooth, despite the same amount of Pt/C being included. Ionomer content may affect the dispersibility of Pt/C.

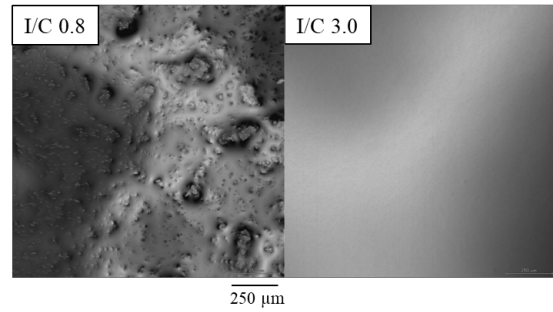


Fig. 2. Surface images of the electrode slurries.

### 3.2. Impedance measurement

Fig. 3 shows the results of impedance measurements during the drying process of the I/C 1.0 electrode slurry. From the measurement results, it can be seen that the phase is 0 for frequencies of approximately 10 Hz or less over the entire

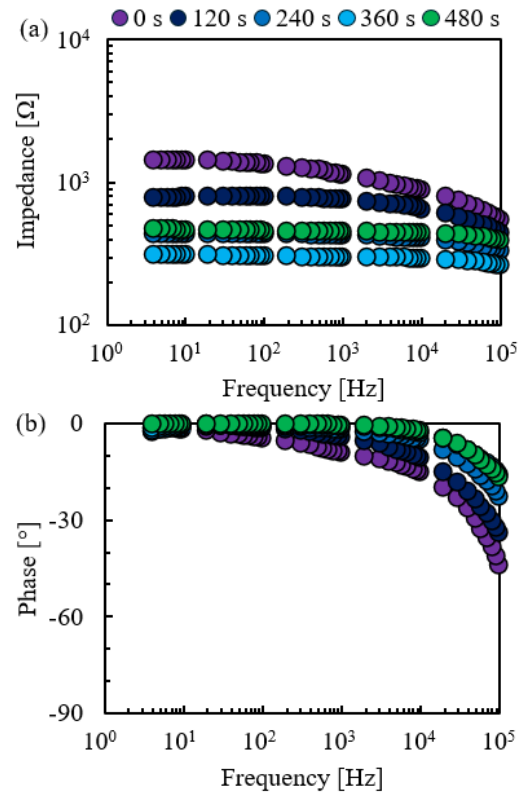


Fig. 3. (a) Impedance and (b) phase during the drying process of the electrode slurry.

measurement period, indicating a resistive response. In addition, since the impedance decreases as the drying progresses in this frequency band, it is thought that the Pt/C dispersed in the slurry forms a network as it dries, and the electronic conductivity improves. In other words, by examining the impedance in this frequency band, it is possible to evaluate the network formation of Pt/C as it dries.

### 3.3. Evaluation of drying process

The results of the simultaneous confocal microscopic observation and impedance measurement of the electrode slurry drying process are shown in Fig. 4. Based on the results of the previous section, the impedance measurement was used to extract the change in impedance over time at 10 Hz. The results of the surface displacement measurement using the confocal microscope are also shown. The thickness of the slurry immediately after application was approximately 90  $\mu\text{m}$ , and as the drying progressed, the height of the slurry surface and the impedance decreased. The change in the height of the slurry surface was particularly large in the early stages of drying, and then gradually decreased. This trend is the same as in previous studies using other measurement methods<sup>(4,5)</sup>, and is thought to be due to the effective drying surface area decreasing as particles accumulate on the

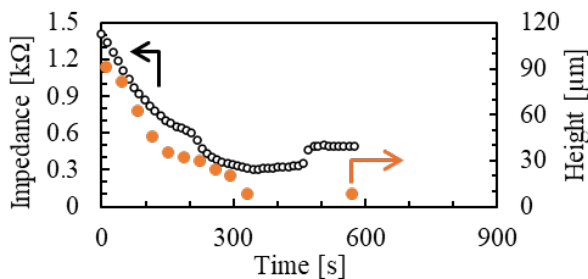


Fig. 4. Simultaneous measurement of impedance and surface displacement during the drying process of the electrode slurry.

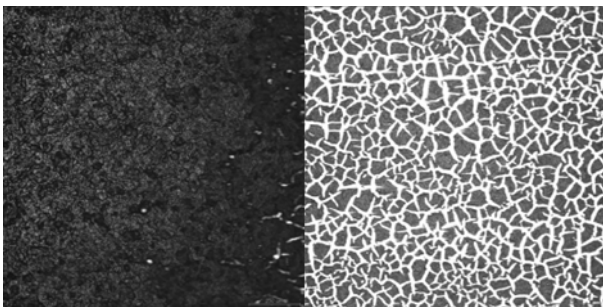


Fig. 5. Surface images of the electrode slurry during the drying process. Just before the formation of microcracks (left) and after the formation of the microcracks (right).

surface as drying progresses. As the surface displacement increased around 300 seconds after drying began, it is possible that shrinkage due to capillary force occurred when the particle concentration was high. After that, at around 330 seconds, the surface image on the left in Fig. 5 shows the state just before microcracks occurred in the observation area. At this point, the impedance also showed a general minimum value, and after that, the impedance began to increase as cracks formed. The state where cracks had formed and reached a steady state was at around 570 seconds. It can be seen that the surface height had hardly changed from just before the cracks occurred. The surface image at this time is shown on the right in Fig. 5. Under the conditions of this study, cracks eventually occurred throughout the entire range of the visualized area, and the catalyst layer was distributed in an island-like pattern. From this, it can be considered that the effect of the fragmentation of the particle deposition layer due to the occurrence of cracks was significant in the final stages of drying, and this appeared in the form of an increase in impedance in the measurement.

### 3.4. Dielectric spectroscopy of liquids

In order to obtain detailed information on the electrode slurry through further expansion of electrical measurements, dielectric spectroscopy measurements were carried out in the GHz band. Here, as basic data, the results of measurements on water, NPA, and mixtures of these substances used as dispersion media for

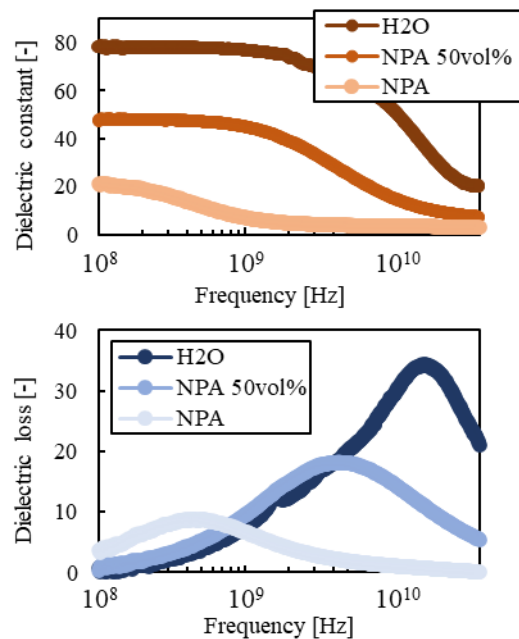


Fig. 6. Dielectric spectroscopy of dispersion media for electrode slurries.

electrode slurry are shown in Fig. 6. In all cases, the dielectric constant shows a constant value around  $10^8$  Hz, which is consistent with the values generally known as the dielectric constants of each substance. On the other hand, in the region above  $10^9$  Hz, the dielectric constant decreases as the frequency increases, and a peak in dielectric loss is seen. This is a phenomenon known as dielectric relaxation, which occurs when the rotational orientation of the molecules in the dispersion medium cannot keep up with the frequency. The dielectric relaxation is influenced by the constituent molecules and the interactions between the constituent molecules and their surroundings. Accordingly, this approach offers considerable promise for elucidating the specifics of the electrode slurry's state. In the presentation, the results of measurements of electrode slurry will be presented as a more practical example.

#### 4. CONCLUSIONS

In this study, we proposed and demonstrated a novel evaluation method for the drying process of electrode slurry using a confocal microscope and impedance measurement. The use of a confocal microscope enabled the visualization of the surface properties of the slurry and the measurement of surface displacement. Moreover, employing a low frequency range of approximately 10 Hz in impedance measurement enabled the observation of particle network formation within the slurry. Furthermore, it was demonstrated that dielectric spectroscopy in the high-frequency range enables the acquisition of comprehensive insights into the internal dynamics of the slurry.

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#### REFERENCES

- (1) T. Suzuki, S. Okada, S. Tsushima, "Characterization of Catalyst Inks by Rheology and Microscopic Particle Properties," *ECS Transactions*, vol. 86, no. 13, pp. 193–198, 2018.
- (2) Y. Tokunaga, T. Suzuki, S. Tsushima, "Characterization of Agglomerated Particles in a PEFC Electrode Slurry by Soft X-ray Radiography," *ECS Transactions*, vol. 104, no. 8, pp. 197–202, 2021.
- (3) T. Suzuki, M. Kobayashi, H. Tanaka, M. Hayase, S. Tsushima, "Investigation of Solvent and Carbon Particles Behavior during Drying Process from Catalyst Ink to Catalyst Layer," *ECS Transactions*, vol. 69, no. 17, pp. 465–470, 2015.
- (4) T. Suzuki, T. Nagai, S. Tsushima, "Simultaneous in situ measurements and numerical analysis of mass transfer in polymer electrolyte fuel cell electrode slurries during drying," *Journal of Thermal Science and Technology*, vol. 16, no. 1, pp. 20-00259, 2021.
- (5) T. Suzuki, H. Tanaka, M. Hayase, S. Tsushima, S. Hirai, "Investigation of porous structure formation of catalyst layers for proton exchange membrane fuel cells and their effect on cell performance," *International Journal of Hydrogen Energy*, vol. 41, no. 44, pp. 20326–20335, 2016.