



Observation of ionomer in catalyst ink of polymer electrolyte fuel cell using cryogenic transmission electron microscopy



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ABSTRACT

Optimizing the catalyst layer structure is one of the key issues for improving performance despite lower platinum loading. The catalyst ink, consisting of platinum-loaded carbon particles and ionomer dispersed in an aqueous solvent, is a key factor for controlling the structure of the catalyst layer because the catalyst layer is prepared in a wet coating process. For that purpose, we visualized the nanostructure of the ionomer in the catalyst ink by cryogenic electron microscopy, especially cryogenic transmission electron microscopy (cryo-TEM). By cryo-TEM, it was revealed that ionomer molecules formed rod-like aggregates macro-homogeneously in the solvent, and a similar morphology was observed in a carbon-particle-containing solvent. In contrast, ionomer aggregates in the catalyst ink containing platinum nanoparticles loaded on carbon particles were denser in the vicinity of the platinum-loaded carbon particles. That can be attributed to strong interaction between platinum nanoparticles and sulfonic acid groups in the ionomer. It also implies that a good understanding of ionomer morphology in the catalyst ink can play an important role in controlling the catalyst layer microstructure for reducing platinum loading.

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1. Introduction

Fuel cell electric vehicles (FCEVs) are an effective solution for reducing carbon dioxide (CO₂) emissions and the consumption of petroleum fuel. The biggest issues to be addressed in popularizing FCEVs are cost reduction of polymer electrolyte fuel cell (PEFC) power systems and the development of the market infrastructure for supplying hydrogen. It is estimated that the cost of the catalyst and application accounts for 49% of the total PEFC stack development cost for automotive application at 500,000 units per year [1]. This estimation indicates that reducing platinum loading is essential for cutting the PEFC stack cost. However, lower platinum loading increases activity and mass transport losses and reduces the performance of the PEFC stack [2,3].

Improving the electrocatalysts is an effective way of reducing activity loss. Various research activities on PEFC electrocatalysts

have been reported so far concerning high oxygen reduction reaction (ORR) activity and durability mainly measured in aqueous electrolyte systems such as by the rotating disk electrode method [4–11]. The catalyst layer of a PEFC is a multiscale component consisting of the catalyst material and ionomer. This means that the structure of the catalyst layer is also important for improving the performance of a membrane electrode assembly (MEA), especially for reducing the mass transport loss.

We have so far been conducting research on catalyst layers for the purpose of understanding the correlation between the performance of the catalyst layer and constituent materials by examining their apparent properties and structure via key mechanisms [2]. Gas transport resistance in the catalyst layer has been analytically measured and reasonably interpreted [12–14] consistent with the results of other research activities [15,16]. Proton transport resistance in the catalyst layer has been analyzed so far by electrochemical impedance spectroscopy [17,18] and a unique method using a hydrogen pump technique [19,20]. We have found that ionomer coverage on the electrocatalyst is one of the key parameters governing the properties of the catalyst layer [21,22].

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In order to optimize the structure of the catalyst layer, it is necessary to have a good understanding of the catalyst layer preparation process. As shown in Fig. 1, a wet coating process is generally used for forming the catalyst layer of PEFCs. The electrocatalyst-dispersed catalyst ink and ionomer in an aqueous solvent are coated on a substrate or polymer electrolyte membrane. The catalyst-ink-coated substrate is then dried to obtain the catalyst layer. In our analyses of the catalyst layer preparation process, we have so far studied the influence of materials and/or process parameters such as the solvent used or the mixing condition [23–30]. The results of previous studies showed a correlation between the materials and the preparation process as the inputs and I–V performance as the output, but what happens during the preparation process has not been evaluated in detail. Other research activities have focused on structure formation in the catalyst ink and have provided new insights concerning ionomer adsorption/desorption behavior of catalyst materials [31–33], but the relationship with catalyst layer performance was not discussed.

We consider that visualizing the dispersion of materials in the catalyst ink is useful for understanding and controlling the structure of the catalyst ink. The dispersion of platinum nanoparticles on carbon supports (Pt/C) in the catalyst ink has been observed by cryogenic scanning electron microscopy (cryo-SEM) [34]. In our previous study, we chose a metal contact, by which specimens were pressed on a mirrored copper block cooled in liquid nitrogen, in order to achieve a high freezing velocity and avoid structural change due to the growth of ice crystals. The results revealed that the dispersion of Pt/C aggregates was governed by the composition of the solvents of the catalyst inks and correlated with the structure and performance of the catalyst layer. That study also showed that the freezing velocity has a large impact on the dispersion of catalyst materials in catalyst inks. A low freezing velocity caused the growth of ice crystals that changed the structure of the frozen specimen. The resolution of cryo-SEM is insufficient to observe the ionomer nanostructure in the catalyst ink because the molecular size of the ionomer is less than 10 nm [35]. In terms of resolution, transmission electron microscopy (TEM) is a powerful tool for observing the nanoscale structure of the ionomer in the catalyst ink. Previously, TEM was used for visualizing the ionomer morphology in the solvent or the catalyst ink [29,32]. However, the real ionomer morphology in the catalyst ink has probably not been observed yet by conventional TEM due to the artifact caused by the specimen preparation process mentioned above.

Against this background, in this study cryogenic transmission electron microscopy (cryo-TEM) was applied to observe the dispersion of the ionomer in a real catalyst ink that can actually be used for the catalyst layers of PEFC stacks. Specimens for cryo-TEM were frozen by immersion freezing into liquid ethane. Cryo-TEM was used to study the effect of the solvent composition and carbon-supported platinum nanoparticles on the ionomer morphology in the catalyst ink.

2. Experimental

2.1. Preparation of ionomer dispersion

The sample specifications are shown in Table 1. Nafion[®] (D2020, DuPont) was used for ionomer dispersions that were in separate aqueous solvents with different compositions. Ionomer concentration was the same as a catalyst ink, as shown in Table 2. The solvents consisted of ultrapure water (Milli-Q, Millipore) and 1-propyl alcohol (NPA), and the weight fractions of NPA were 0.2, 0.4 and 0.8. They were mixed by a magnetic stirrer.

2.2. Preparation of ionomer and carbon particle dispersion and catalyst ink

The specifications of the samples containing particles are shown in Table 2. The same ionomer (Nafion[®]) as mentioned above was used. A typical platinum-based electrocatalyst was used for the catalyst ink, i.e., platinum nanoparticles were deposited on Ketjenblack (KB). For the ionomer and carbon particle dispersion called the reference ink in the following, KB without platinum nanoparticles was used as the carbon particles. Dispersions were in separate aqueous solvents with different compositions to keep their solid content at 7 wt%. The solvents consisted of ultrapure water and NPA, and the weight fraction of NPA was 0.4. They were mixed and degassed with a planetary centrifugal mixer and ground with a bead mill machine (BSG-04, Aimex) in the same condition, respectively, to prepare the reference ink and the catalyst ink. The beads were made of zirconia with a 1.5 mm diameter.

2.3. Cryogenic transmission electron microscopy (cryo-TEM)

Cryo-TEM was used to visualize clearly the ionomer morphology in the dispersion. The ionomer dispersions, the reference ink, and the catalyst ink for cryo-TEM were prepared based on the ice embedding technique used in structural analysis of biomolecules

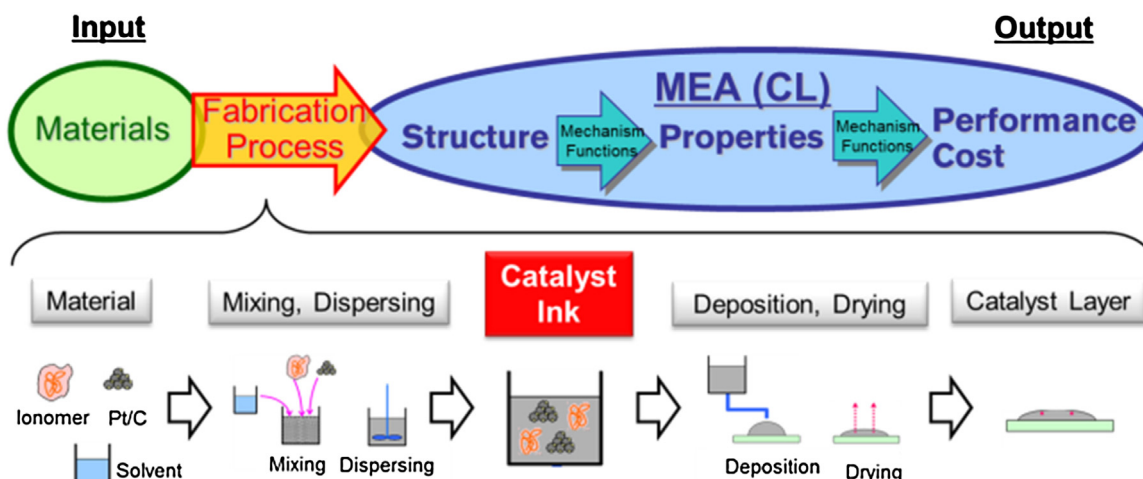


Fig. 1. Design scheme for catalyst layer of PEFC.

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