



Effect of blending carbon nanoparticles and nanotubes on the formation of porous structure and the performance of proton exchange membrane fuel cell catalyst layers



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H I G H L I G H T S

- Catalyst layers were fabricated, by blending with differing carbon materials.
- Carbon black (CB) and two types of multi-walled carbon nanotube (MWCNT) were used.
- Catalyst layers blended with MWCNT have lower porosity and fewer micro-cracks.
- Catalyst layers blended with thin MWCNT have smaller pore size.
- The pore size of the catalyst layers affects cell performance as well as porosity.

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Different kinds of sub-micron structured carbon, namely carbon black and multi-walled carbon nanotubes (MWCNTs), were blended in catalyst ink in order to fabricate catalyst layers having differing porous structures. Carbon black is used as catalyst support in the conventional catalyst layers; the pore structure depends strongly on its aggregate structure. MWCNTs have a structure completely different from the carbon black at sub-micron scale. Two kinds of MWCNT, of differing diameters, were used as blending materials in the catalyst ink with the platinum-supported carbon, and their effects on the porous structure and cell performance were investigated. The catalyst layer containing thick MWCNT had lower porosity, fewer micro-cracks and larger pores than the conventional catalyst layer blended with carbon black. The MWCNT diameter influenced the distribution of pore sizes in the catalyst layers. The catalyst layer containing the smaller diameter MWCNTs displayed a shift in the peak of the pore size distribution, toward smaller size. These characteristic porous structures affected the performance of the resulting cell and caused a large voltage drop at high current densities in the polarization curve. This is because of the porosity and also the pore size.

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1. Introduction

The mass transport properties of catalyst layers (CLs) for use in proton exchange membrane fuel cells (PEMFCs) depend strongly on the structure involved [1–3]. Typical CLs consist of platinum-supported carbon (Pt/C), ionomer and pores. They have nano-scale and micro-scale porous structure and their components are responsible for transport of electron, proton, reactant gas and the

water generated. CLs are electrodes and indispensable components in the PEMFCs. Especially in operating condition, correlation between reactant transport and water generation should be considered. Water should be discharged from the CLs to avoid condensation and prevention of oxygen transport. Then capillary condensation [4] should be considered in the nano-scale pores. However, mass transport dynamics in such complex structure have been regarded as kind of a black box. The mass transport has strongly correlated with the porous structure. Performance evaluation of structurally-controlled CLs can help to consider these phenomena. Control of structure is therefore important in understanding transport phenomena in the CLs and achieving better cell

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performance. Several methods of fabricating CLs are in common use [1,5–7]. The fundamental process involves blending of the materials to produce a slurry called catalyst ink, which is then applied so as to form a thin layer, followed by drying to evaporate the solvents and leave a porous structure. The CLs have been fabricated using a trial and error approach, because they have both nano-scale and micro-scale complex structure, and many parameters are involved in the fabrication process. An understanding of the mechanism and key parameters of structure formation is necessary to the development of high-performance CLs.

The structure of the catalyst and its effect on cell performance have been studied. The ionomer to carbon weight ratio (I/C) and the porosity have been identified as key structural parameters. The I/C ratio has a marked effect on the performance of the fuel cell [8–13]. It has been found that the porosity also changes as I/C varies. The porosity of the CLs is a further important macroscopic structural parameter. It affects the transport of reactant gas and of the water generated. Many detailed studies of the porous structure have been made because of its importance for PEMFC performance. Several well-known techniques exist for determining the nano-scale and micro-scale porous structure. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) facilitate the visualization of two-dimensional porous structures. Mercury intrusion porosimetry and nitrogen physisorption measurements can determine the pore-size distributions. Soboleva et al. determined the volumes of primary and secondary pores in CLs having various ionomer content, using nitrogen physisorption measurements [14]. They found that the volume of the primary pores decreased with increasing ionomer content, suggesting that the primary pores are coated with ionomer. They also determined the performance of the cell with these CLs [15]. New ways of determining the porous structure of CLs are also being developed and applied. For example, focused ion beam/scanning electron microscopy (FIB/SEM) has been developed and applied to the CLs of PEMFCs [16]. With this method it is possible to observe three dimensional structures with SEM resolution, although the observation destroys the sample. Nanometer-scale X-ray computed tomography (nano-CT) also can visualize the three-dimensional structure of the CLs [17]. Although resolution is several tens of nanometers, the method is non-destructive. Another approach is in-situ visualization of the water content distribution in the CLs, which is affected by the porous structure and directly affects cell performance; this has been demonstrated by Deevanhxay et al. [18]. Although there are a number of studies for structure and transport phenomena in the CLs, a method of generating a porous structure with a given I/C value has not yet been established, and the relation between microscopic porous structure and macroscopic cell performance remain unclear.

Diagnostic techniques for investigating porous structure and transport phenomena in CLs are under development. Moreover, techniques have not yet been established for the fabrication of structurally-controlled CLs. Two approaches exist for the control of porous structure. The first is via the materials used as substrate for the CLs, and the second involves the fabrication process, which consists of the blending, applying and drying of catalyst ink. Hot-pressing so as to assemble a catalyst-coated membrane (CCM) from PEM and CLs is one way to control the pore structure. Yim et al. found that secondary pores become smaller and fewer as the hot-pressing pressure increases [19]. These authors also found that cell performance is degraded upon using extremely hot-pressed CLs because of the increase in the concentration overpotential. Suzuki et al. compared geometrical and effective porosities for gas transport [20]. They found that these porosities both decrease and their difference increases as the hot-pressing pressure increases. The variation in porosity with the hot-pressing pressure is limited,

however, and the pore diameter also changes. This limitation is due to the material structure. The carbon structure largely determines the porous structure, because carbon is the substrate of the CLs. A better understanding of how this happens is needed to allow for accurate control of porosity and pore diameter over a wide range. By controlling the porosity over a wide range, a greater choice of the structure, including the I/C ratio, can be realized; the range of the I/C ratio has conventionally been limited by the porosity.

Recently, another factor of mass transport resistance in the CLs has been suggested. Oxygen permeation into ionomer coating catalyst in the CLs can be a significant resistance [21–23]. Lee et al. evaluated effectiveness of Pt in the CLs diluted by carbon black and showed better effectiveness in the optimally diluted CL [3]. They suggested that the reason was local oxygen transport in the CL. Suzuki et al. showed large voltage drop in high current density range of polarization curve using low Pt-loaded CL, suggesting local water condensation in the CL [24]. In the actual operating condition, oxygen dynamics taking into account generated water behavior is still unknown. For the further study in this field, precise understanding of porous structure of the CLs and its control are required because ionomer distribution has relationship with porous structure and its morphology.

Carbon black (CB) is usually used as a substrate for platinum in the CLs. The carbon black takes an aggregate structure which consists of primary carbon particles. The porous structure depends on the aggregate structure of the CB. Several studies have used different carbon materials, including carbon nanotubes as a catalyst support [25,26]. Upon comparing their original CLs with a conventional CL, they find variations in performance. There is wide variety of fabrication processes for depositing catalyst on the supports. The shape and catalytic activity of fabricated catalysts is liable to vary according to the process. Both the porous structure and catalyst properties influence cell performance, but the effects of the porous structure on performance are unclear.

Various methods of blending materials so as to control the porous structure have been studied in micro porous layers (MPLs) [27,28]. Multi-walled carbon nanotubes (MWCNTs) have been used as blending materials with carbon black and have enabled controlled variation of the porous structure according to the blending ratio of MWCNTs. The detailed mechanism is not clear, however. MWCNTs can also have widely differing diameters and lengths, and these parameters may affect the resulting porous structure.

The present study focuses on the porous structure of the CLs. To determine the effects of material structure on the porous structure of the CLs, differing kinds of sub-micron structured carbon, namely carbon black and MWCNTs, were blended in catalyst ink, and CLs were fabricated using the same structure and amount of catalyst in order to maintain the catalytic activity. The structure and performance of the resulting CLs were determined.

2. Experimental

2.1. Blending of carbon materials and CCM fabrication

MWCNTs are completely different in structure from carbon black at sub-micron scale. Two types of MWCNT were blended with the platinum-supported carbon in the catalyst ink, and their effect on the resulting structure and performance were studied. One of the MWCNTs was 20–50 nm in external diameter (CNT1), which is almost the same as the primary-particle diameter of the carbon black (ca. 30 nm); the other was 40–70 nm in external diameter (CNT2), which is larger than the primary-particle diameter. Carbon black, known as ketjen black and of the same type as the catalyst support, was also used as the blending material so as to fabricate a

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