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Analysis of Water Adsorption and Condensation in Catalyst Layers for Polymer Electrolyte Fuel Cells

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ABSTRACT

Water sorption isotherm of catalyst layers in polymer electrolyte fuel cells is analyzed by a mathematical model. The model takes into account multi-layer water adsorption on adsorption sites and capillary condensation in hydrophilic pores. The detailed structures of CLs including the pore size distribution, volume fraction of hydrophilic pores, and ionomer coverage over carbon supports and Pt surface are thoroughly considered. Quantitative estimation of water uptake at different locations in CLs as a function of vapor activity is successfully achieved. The model reveals that water adsorption in CLs firstly takes place on the adsorption sites such as side chains in Nafion® ionomer, Pt surface, and surface groups on carbon supports at low vapor activity. The primary pores are filled with capillary condensed water at activity of 0.4. The condensation of water in the secondary pores is observed at activity from 0.9 to 1. The wetting property of the primary pores strongly depends on carbon materials, while surface of the secondary pores is found to show the hydrophobic nature irrespective of carbon materials. The amount and location of water in CLs are correlated with electrochemical double layer and effective proton conductivity.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising power sources for automotive use. From an industrial point of view, the cost is the most significant issue for the commercialization of fuel cell electric vehicles (FCEVs). Catalyst layers (CLs), where multicomponent transport phenomena and electrochemical conversion take place, are the central component to solve this issue [1–4]. Pt used in CLs incur a large portion of the material cost in PEFC. Lowering Pt loading without sacrificing power density as a result of improving Pt utilization is a major challenge for the cost reduction of FCEV.

CLs typically consist of Pt nanoparticles, dispersed on highly porous and electron-conducting support materials, and proton conducting electrolyte. Carbon materials are usually used for catalyst support materials because of their high electronic conductivity and stability in acid environment [5–10]. Nafion®, a sulfonated tetrafluoroethylene copolymer, is the primary choice as the proton-conducting electrolyte in CLs.

In order to improve the Pt utilization in CLs, it is of vital importance to understand the complex interplay between reactant gas, water, and proton transport phenomena and electrochemical reaction [11–19]. Water in CLs plays a crucial role in promoting mass transport and electrochemical reaction. Water is essential for the proton transport and formation electrochemically active interface, while excessive amount of water significantly diminish the gas transport. Optimization of water amount in CLs is vital for realizing high Pt utilization [20–24].

Despite the importance of controlling water, structure and distribution of water in CLs is still elusive. Neutron radiography or Magnetic resonance imaging achieved considerable success in understanding water distribution across a membrane electrode assembly [25,26]. However, the resolution is still not enough to quantify the liquid water amount in CLs. Theoretical models from simple diffusion based model to complex structural based model have been proposed to understand the interplay among composition, porous structure, electrochemical reaction, and water distribution in CLs. The pore size distribution (PSD) is correlated with capillary pressure and liquid water saturation by Kelvin equation [20–22]. The interplay between CL structure and water flooding is well captured by the structural based model. The consideration of PSD with different wettability of pores provides better description on water saturation and its influence on permeability of gas and water through CL [27]. The reasonable estimation for liquid water pressure and wetting angle is vital for the accurate prediction.

In the PSD based structural model, the consideration of relatively dry conditions is problematic, since the water adsorption

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becomes dominant rather than capillary condensation in pores. Water adsorption in CLs is considered in a diffusion based model by applying the same water adsorption and transport property as in a bulk Nafion® membrane for the estimation of proton conductivity, water diffusivity, and gas diffusivity through ionomer in CL [12–15]. This assumption is not necessarily correct because of the presence of the other materials such as carbon supports or Pt particles. Thorough study on the proton conductivity with different carbon materials in CLs by Iden et al. revealed the difference in proton conductivity with two carbon supports, ketjen black (KB) and graphitized ketjen black (GKB), could be attributed to the influence of the surface properties of carbon support materials on water uptake ability of ionomer [28]. For the further improvement of the performance models, it is of vital importance to consider both water adsorption and capillary condensation simultaneously, in order to reasonably describe the transition from dry to flooding phase in CLs.

Water sorption isotherm is one of the basic characteristics of wettability in random porous media. The other way to characterize wettability of pore is the use of the capillary pressure curve. [27,29] Mulone et al. estimated the PSDs of hydrophilic and hydrophobic pores from the capillary pressure curve. Although their approach provided reasonable estimation for relatively large pores, small pores existing inside carbon aggregates or primary pores, where most of Pt catalysts distribute, were not correctly captured. The Pt utilization is significantly influenced by the amount of water in the small pores which is essential for the formation of electrochemically active surface [30]. The better understanding of water adsorption and condensation in small pores based on the analysis of the water sorption isotherm is beneficial for the improvement of Pt utilization.

Water sorption isotherm of carbon materials has been studied for years [31–35]. Wettability of carbon surface depends on surface morphology and presence of hydrophilic surface groups. Several empirical methods to describe the water adsorption phenomena on carbon materials have been proposed [36–40]. According to the empirical model proposed by Do and Do et al. [39], water adsorption on carbon materials initially takes place at primary adsorption sites such as surface functional groups and carbon surface. The primary adsorbed water can work as adsorption sites for secondary multilayered water adsorption. Water adsorption in small pores takes place simultaneously with the water adsorption in the primary and secondary adsorption sites. Adsorption equilibrium constants and numbers of water molecules adsorbed on the adsorption sites are treated as fitting parameters. The porous structure is not explicitly considered in the model by Do and Do et al. Water uptake property of PEM is widely studied by experimental and theoretical approach [41–44]. The same kinds of empirical model for carbon materials are applied to the calculation of water uptake of PEM [44]. Although the empirical model makes a substantial contribution for the basic understanding of water sorption property of porous media, water uptake phenomena in CLs is still elusive since there is no appropriate model for water sorption isotherm of CLs due to their complexity in structure composed of multicomponent materials.

The morphology of ionomer, the primary source for water adsorption, has been controversial due to difficulties of direct measurement. Recently, its structure is gradually revealed through several experimental and theoretical efforts [45–53]. The thin film like structure of ionomer has clearly different water uptake and proton transport properties compared to the bulk membrane [47–49,53–55]. The surface wettability of adhesive thin Nafion® ionomer film is significantly affected by the surface wettability of substrates. Specifically, the hydrophilic substrate leads to hydrophobic surface of Nafion® thin film on the substrate as a result of re-orientation of hydrophilic sulfonic acid groups in the direction towards substrate [47]. The influence of wettability of substrate on ionomer morphology is also proved in the theoretical study by molecular dynamics method [53,54,56]. Consequently, thorough consideration of the detailed structure of ionomer is indispensable for understanding of water uptake in CLs.

Here, we introduce a mathematical model which considers multilayer water adsorption on adsorption sites and capillary condensation in hydrophilic pores in PEFC catalyst layers. Detailed structures of CLs including PSD, surface area of Pt and carbon, number of hydrophilic surface groups, ionomer coverage on Pt/C catalyst, and the orientation of sulfonic acid groups in ionomer are thoroughly taken into account and correlated to water uptake ability. The effect of catalyst materials and compositions of CLs on water adsorption isotherms is investigated. Quantitative estimation of water uptake at different locations in CLs is successfully achieved by the mathematical model. The deconvolution of water sorption isotherms by the presented model reveals useful insights into how the amount and location of water in CLs are correlated with electrochemical double layer and effective proton conductivity.

2. Experimental

2.1. Preparation of samples

Two different carbon materials [ketjen black (KB) or graphitized ketjen black (GKB)] and two catalysts [KB with 46 wt% of Pt (Pt/KB) or GKB with 46 wt% of Pt (Pt/GKB)] were used for water adsorption isotherm measurement in order to decompose water uptake on carbon and Pt. Three CLs with different ionomer contents were fabricated with Pt/KB and Pt/GKB, respectively. The pseudo catalyst layers (PCLs) without Pt with different ionomer contents were also prepared. Nafion® ionomer (DE2020, EW1000, DuPont) was used for proton conducting electrolyte for CLs and PCLs. The ionomer contents were set by controlling weight ratio of ionomer to carbon supports (I/C weight ratio) to be 0.7, 0.9, and 1.3. The CLs and PCLs were formed on polytetrafluoroethylene (PTFE) substrates using a screen-printing technique. After the drying process at 353 K for 15 min to remove solvent, CLs and PCLs were scratched off from PTFE substrates for the water uptake measurement. Recast Nafion® membrane (EW1000, DuPont) were used to characterize water uptake of bulk ionomer.

2.2. Water sorption isotherm measurement

Water sorption isotherms of KB, GKB, Pt/KB, Pt/GKB, recast Nafion® membrane, PCLs, and CLs were measured by an automatic vapor adsorption apparatus (Belsorp 18 Plus-HT, Nihon Bell). 0.03 ∼ 0.05 g of samples were placed in a glass sample tube. The samples were dried at 363 K for 5 hours in vacuum so as to remove pre-adsorbed water. Water vapor with different relative humidity (RH) was introduced and equilibrated at 353 K. The mass of samples at different RH was measured. The isotherm of adsorption process was used for the analysis.

2.3. Structural picture of CL

In the porous materials, pore size is generally classified into three ranges, micropore with diameter of less than 2 nm, mesopore with diameter of 2 nm ∼ 50 nm, and macropore with diameter of more than 50 nm [57]. Because of the typical size (∼40 nm) of the carbon primary particle used in PEFC CL which is comparable to the mesopore size [4,31], the typical definition of pore sizes could not be convenient for characterizing porous structure of CL. In this study, pore sizes in CL were defined by two kinds, primary pores with diameter of less than 10 nm which exist inside