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Fabrication Process Simulation of a PEM Fuel Cell Catalyst Layer and Its Microscopic Structure Characteristics

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Abstract

The catalyst layers (CLs) in proton exchange membrane fuel cells (PEMFCs) are porous composites of complex microstructures of the building blocks, i.e., Pt nano-particles, carbonaceous substrates and Nafion ionomers. It is important to understand the factors that control the microstructure formation in the fabrication process. A coarse-grained molecular dynamics (CG-MD) method is employed to investigate the fabrication process of CLs, which depends on the type and amount of components and also the type of the dispersion medium (ethylene glycol, isopropanol or hexanol) used during ink preparation of the catalyst-coated membranes (CCMs). The dynamical behaviors of all the components are outlined and analyzed following the fabrication steps. In addition, the Pt nano-particle size distribution is evaluated and compared with the labor testing. Furthermore, the primary pore size distributions in

the final formations of three cases are shown and compared with the experiments. The

sizes of the reconstructed agglomerates are also considered on the effect of solvent

polarity.

1. Introduction

The polymer electrolyte membrane fuel cells (PEMFCs) fueled by hydrogen are

considered to be most suitable for automotive applications owing to their fast

dynamics and high power densities. However, the performances are limited primarily

by processes at the catalyst layers (CLs), which highly depend on the microscopic

structure-related properties.[1] The CLs in PEM fuel cells have a complex and

multiphase porous structure, as shown in Fig. 1. Platinum (Pt) nano-particles are

supported on larger carbonaceous substrates, constructing the framework of the

agglomerate with the primary pores of 3-10 nm. The Pt clusters range 2-5 nm and the

most commonly employed carbon support, Vulcan XC-72, has a diameter of 20-30

nm. The spaces between the agglomerates are the secondary pores with sizes in the

range of 10-50 nm.[2] The ionomer in the CLs serves both as a binder and the pathway

for the protons generated/consumed in the electrochemical reactions. In order to

reduce the risk of water flooding, polytetrafluoroethylene (PTFE) is commonly used

to bind the catalyst particles and form a hydrophobic path.[3] The typical thickness of a

CL ranges from 10 to 30 microns and is a function of the material composition and

the fabrication processing.

Due to the limitations of experimental studies at the extreme small scales, mathematical modeling is widely used to investigate the transport and electrochemical phenomena in the CLs. Atomic-scale models (e.g., molecular dynamics, MD) can predict physical properties of materials with ideal, theoretical or proposed microstructures under clearly defined conditions within the size of several nanometers. However, they are not able to probe the random morphology of the complete CLs due to computational limitations. The approaches beyond the atomic-scale and below the conventional continuum scale use coarse-grained pseudo-particles which can either move on a fixed lattice (lattice-based pseudo-particle models) or continuously in space (off-lattice pseudo-particle models).[4] The lattice Boltzmann method (LBM) has been developed to describe the diffusion process in complex pore structures[5] and to study the structure-wettability influence on the underlying two-phase dynamics.[6] The off-lattice pseudo-particle models, such as dissipative particle dynamics (DPD),[7, 8] smoothed particle hydrodynamics (SPH) [9, 10] and coarse-grained molecular dynamics (CG-MD) method, have been applied for exploring the microstructure of the CLs. The DPD can be regarded as coarse-grained nonequilibrium molecular dynamics. It is on the order of 10^5 times faster than MD, but this impressive increase in computational efficiency comes at the expense of loss of details at the atomic/molecular scale. More systematic and reliable ways of coarse graining molecular dynamics to construct DPD models would be an important advance.[11] The SPH was introduced ~30 years ago to simulate astrophysical fluid dynamics,[12] and now can be used to simulate all of the

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complex phenomenology associated with contact line and contact angle dynamics.[13] However, the full range of scales (from the atomistic to the pore scale) cannot be investigated in a single simulation. The deficiency may be mitigated by simulations based on hybrid multiscale particle-based models.[11] In the CG-MD method,[14, 15] super-atoms are used to represent groups of atoms, and interactions are only defined between these super-atoms. Thus, a reduction of the number of degrees of freedom is achieved. At the same time it can consolidate the major features of microstructure formation in CLs of PEMFCs. Through the controlled random algorithm, it can also mimic the experimental fabrication process, which provides an insight into the self-organized phenomena and the microscopic structure of the CLs.[16]

In this study, a CG-MD simulation method is developed as a CL reconstruction technique to reflect the fabricating processes with controlled microstructures. Instead of experiments, a composite network of Pt, carbon, ionomer and PTFE is formed by colloidal dispersion in three different solvents. The step formation of a CL simulates the fabrication process to understand how the dynamic-structural properties of CLs evolve and what are the sizes and distributions of the primary pores. The nano-particle size distribution of Pt is also evaluated and compared with the experiments in this paper.

2 Methodology

2.1 CG beads and their properties

In this study, the CG method is employed to reconstruct the microscopic structure of the CLs in two major steps: ① Introduce and construct the Nafion ionomers,

PTFE, carbon and Pt particles, as well as solvent molecules with specific spherical beads at a predefined length scale; ② Specify the parameters of renormalized interaction energies between the distinct beads as the MARTINI force field,[17, 18] which is a coarse grained force field applied for molecular dynamics simulations of biomolecular systems. For the defined beads in step ①, four main types of interaction sites are considered in step ②: polar (P), nonpolar (N), apolar (C) and charged (Q). The polar sites represent neutral groups of atoms, the apolar sites are hydrophobic moieties, and the nonpolar groups are used for mixed groups, which are partly polar and partly apolar. The charged sites are reserved for ionized groups. For particles of type N and Q, subtypes are further distinguished by a letter denoting the hydrogen-bonding capabilities (d=donor, a=acceptor, 0=not exist). Within the main type of P and C, the subtypes are distinguished by a number indicating the degree of polarity (from 1, low polarity, to 5, high polarity). The mapping of all the components studied in this paper is presented in table 1.

In this CG model, the nonbonded interactions between sites i and j are described by the Lennard-Jones (LJ) potential, which has become a standard procedure in MD simulations

$$V_{LJ}(r) = 4\varepsilon_{ij}\left[(\frac{\sigma_{ij}}{r})^{12} - (\frac{\sigma_{ij}}{r})^{6}\right]$$

[1]

In Eq. 1, ε_{ij} represents the depth of the potential at the minimum ($r_{min} = 2^{1/6}\sigma_{ij}$) and σ_{ij} is the point at which $V_{LJ} = 0$. In analogy to the case in Ref.[17, 18], the interaction strength ε_{ij} within the model is divided into 10 levels, from 2.0 kJ mol^{-1} to 5.6 kJ mol^{-1}. This allows for more fine-tuning in the reproduction of experimental

solubilities. The effective bead diameter (σ_{ij}) is 0.43 nm. The LJ parameters, $4\varepsilon_{ij}\sigma_{ij}^6$ and $4\varepsilon_{ij}\sigma_{ij}^{12}$, can be calculated based on the level of interactions (see Table 2).[19] For example, carbon slabs (N0) are partially hydrophobic, semi-repulsive interaction with water (P4) and Nafion side chains (Qa), but semi-attractive interaction with other carbon and Pt beads (Na) as well as with Nafion backbones (C3).[20] In this work, a cutoff of 1.2 nm is used for the LJ interaction potential.[17, 18]

In addition to the LJ interactions, the other ones between charged groups (type Q) are evaluated via the normal electrostatic Columbic potential:

$$V_{el}(r) = \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r}$$

[2]

with relative dielectric constant ε_r=20 for explicit screening. The potential is shifted smoothly from 0 to 1.2 nm, which has the same cutoff distance as used for the LJ interactions. The standard shift function of GROMACS is used in which both the energy and force vanish at the cutoff distance.[18] Shifting of the electrostatic potential in this manner reflects the effect of a distance-dependent screening.

Bonded interactions between the chemically connected sites are described by a weak harmonic potential V_{bond}(R) with the equilibrium distance (the same as σ_{ij}, 0.43 nm)

$$V_{bond}(R) = \frac{1}{2}K_{bond}(R - R_{bond})^2$$

[3]

The LJ interaction is excluded between the bonded particles, but included between the second nearest neighbors. The force constant of the harmonic bonding potential is K_{bond}=1250 kJ mol^{-1} nm^{-2}. To represent chain stiffness, a weak harmonic potential $V_{angle}(\theta)$ of the cosine type is introduced:

$$V_{angle}(\theta) = \frac{1}{2}K_{angle}\{\cos(\theta) - \cos(\theta_0)\}^2$$

[4]

where the basic equilibrium bond angle θ_0 is 180°, with a force constant of K_{angle}=25

kJ mol^{-1} rad^{-2}. Such a small force constant allows an angle deviation of 30°, which

reproduces the properties of Nafion chains. [18]

2.2 Mapping in the CG model

The MD method above is implemented by the GROMACS package,[21] which is

primarily designed for biochemical molecules like proteins, lipids and nucleic acids

that have a lot of complicated bonded interactions. However, because GROMACS is

extremely fast at calculating the nonbonded interactions, many research groups are

also using it for research on non-biological systems, e.g., polymers.[22, 23] In this work,

the whole CG model of Nafion copolymer, as shown in Fig. 2, includes a part of the

atomistic level configuration of a Nafion chain. According to Ref.[24], a side chain unit

in the Nafion ionomer has a molecular volume of 0.306 nm^3, which is comparable to

the molecular volume of a four-monomer unit of poly(tetrafluoro-ethylene) (PTFE)

(0.325 nm^3). Therefore, one side chain and four-monomer unit ($-(CF_2CF_2)_4-$) are

coarse-grained as spherical beads of volume 0.315 nm^3 (r=0.43 nm). The Nafion

oligomer consists of 20 repeated monomers;[25] therefore, there are 20 side chains, with

the total length of ~30 nm. The repeated monomers are represented by two blue apolar

beads (C3) as the hydrophobic backbone and one yellow charged bead (Qa) as the

hydrophilic side chain, as shown in the shaded rings in Fig. 2.

In Fig. 3a, the carbon slab is firstly constructed by the Atomistic Simulation

Environment (ASE) software at the atomic scale. The ASE is the common part of the

simulation tools and provides python modules for manipulating atoms, analyzing simulations and visualization.[26] When the atomic numbers and positions are given, the density functional theory (DFT) calculations of the carbon slab are performed by the Jacapo calculator, which is an ASE interface for Dacapo and fully compatible with ASE. In the Jacapo, the ultrasoft pseudopotentials are used to describe the interaction between valence and core electron, and the wave functions are expanded in plane waves with the kinetic energy cutoff of 350 eV.[27, 28] To describe electron exchange-correlation interactions, generalized gradient approximation with Perdew-Wang (PW91) function is adopted.[29] Thus, the unit structure of the carbon slab can be created accurately without getting lost in the volume of information.[30, 31] The carbon slab is modeled by eight layers of the zigzag graphene structure, and each layer has a regular hexagonal net of carbon atoms with the C-C bond length of 1.42 Å. The interlayer spacing is equal to 3.35 Å and the layers are interacted by van der Waals force.[23] In the following step, the CG Builder from the VMD (Visual Molecular Dynamics) software[32] is employed to provide a shape-based coarse graining (SBCG) tool for transforming structures from all-atom representations to CG beads.[33, 34] Based on a neural network learning algorithm,[35] the shape-based method is used to determine the placement of the CG beads, which also have masses correlated to the clusters of the represented atoms. Neighboring beads are connected by harmonic springs, while separate molecules interact through non-bonded forces (Lennard-Jones and Coulomb potentials).[33] Interactions are parameterized on the basis of all-atom simulations and available experimental data. Therefore, there are 36 carbon atoms in

one bead of the slab (r=0.43 nm), as shown by the shaded rings. By this method, the typical carbon slab with the size of $5 \times 5 \times 2.5$ nm^3 is represented by 224 nonpolar beads (type of N0). Similar to carbon slabs, the Pt nano-cluster is firstly constructed by the ASE software and then coarse-grained by the VMD software. Thus, the $10 \times 10 \times 6$ fcc-Pt (111) cluster is represented by 30 nonpolar beads (type of Na) in Fig. 3b. Therefore, each bead consists of 20 Pt atoms with the radius of 0.43 nm, as shown by the shaded rings.

Based on the study on polyolefins, the chains of degree of polymerization 48 are sufficiently long to capture the polymeric structure of PTFE in the melt state.[36] Therefore, one of the PTFE chains is represented by 6 apolar beads (C3), each of which contains four-monomer unit ($-(CF_2CF_2)_4-$) as the backbone of Nafion chains. As for the solvents, four water molecules are represented as one single polar CG site (type of P4) with the radius of 0.43 nm. For the electroneutrality condition, three water molecules plus a hydronium ion are also added into the system and represented by one charged bead (type of Qd) of radius 0.43 nm. Similarly, other solvent molecules, ethylene glycol (EG), isopropanol (IPA) and hexanol (HX), are also coarse grained as listed in Table 1.

2.3 Experimental procedure for preparation of the catalyst-coated membranes (CCMs)

As mentioned above, the reconstruction of CLs follows the fabrication process of the catalyst-coated membranes (CCMs) technique. In this part, the CCMs technique is discussed on the five steps:

Step 1. The Pt/C electrocatalysts (40 wt. %, BASF) are firstly weighed, and then

mixed with the distilled water and isopropyl alcohol.

Step 2. After ultrasonic treatment for 30 min, the 3M™ Dyneon™ PTFE dispersion (diluted to 10 wt. %, average particle size of 210 nm) is dripped into the catalyst ink to reach the content of 5 wt. %, stirring to reach a well-distributed condition. [37]

Step 3. The catalyst ink is sprayed onto a smooth aluminum foil, which is sintered at 240 °C for 30 min and 340 °C for 30 min under a nitrogen atmosphere. After the heating and drying process, water and other impurities are removed from the system.

Step 4. Nafion® perfluorinated resin solution (5 wt. % in lower aliphatic alcohols, containing 15-20% water) is sprayed onto the CLs. During this process, Nafion® penetrates the catalyst layer to form the proton transfer network.

In this study, in order to exploit the effect of the solvent on the evolving CL microstructure, three different solvents are examined, respectively, which represent a wide range of dielectric permittivity, viz., ethylene glycol (EG; $\varepsilon=37.7$), isopropyl alcohol (IPA; $\varepsilon=18.3$), and hexane (HX; $\varepsilon=1.9$), as listed in table 1.

Step 5. The electrode is dried in an oven at 90 °C for 2 hours to evaporate the residual solvent, and then the CL is hot-pressed onto a Nafion® 212 (N212 from DuPont Corporation) membrane on both sides. The ratio of dry Nafion® to carbon is 0.8 by weight and the loading of Nafion ionomer in the electrode is kept 32~38 wt. %, in the range of a typical value used in CLs.[24] The Pt loading of the prepared CCM is 0.40 mg cm^{-2} on each side.

2.4 Simulation parameters

For every fabrication process, the centers of the beads are randomly placed on

cubic lattice points in the initial stage. Firstly, the initial structure is optimized for 250 ps at T_0=320 K, using 25 fs time steps in the course of a step integration procedure. This short energy minimization displaces the overlapped beads at the beginning. Equilibrium of this resulting structure is achieved by an annealing procedure. The temperature is controlled by the Berendsen algorithm,[38, 39] which simulates a weak coupling to an external heat bath with the given temperature T_0. The weak coupling algorithm is applied separately for each component (Nafion, carbon slabs, Pt clusters and water beads) with a time constant of 1.0 ps and a reference temperature T_0. The system is further expanded over a period of 3.0 ps by gradually increasing the temperature from 300 to 325 K. After that, the MD simulation is employed for another 3.0 ps in a canonical (NTV) ensemble,[25] followed by a cooling procedure to 300 K. During the simulation, the results and data are saved every 1000 steps (40 ps) and used for later analysis. All these simulations are performed with the GROMACS simulation package version 4.5.3.[21]

3 Results and Discussion

3.1 CCMs based step formation

As shown in Fig. 4, the numerical reconstruction of a CL is performed through the CG method by the GROMACS package, mimicking the experimental fabrication process.[3] In Step I, the Pt/C catalyst (40 wt. %, BASF) nanoparticles, represented by 30 carbon slabs and 16 Pt clusters, are mixed with the water and isopropyl alcohol beads in the $50\times25\times25$ nm^3 box. After MD running for 10 ns, the final formation configuration is obtained for the equilibrium state, as shown in Fig. 4I. For better

clarity, the solvents are not shown and the phenomenon of self-aggregation is easily observed. It is also clear to see that the lateral part of the Pt clusters adsorbs on the carbon surface. In Step II, add 176 PTFE chains (for the content of 5 wt. %, as suggested in Ref. [37]) to the catalyst ink and keep MD running for another 10 ns to reach the equilibrium state in Fig. 4II, shown without the solvent beads. In Step III, the catalyst ink is sintered to remove all the solvent from the target box. After MD running for 50 ns, the framework structure is formed, in which the PTFE breads embed themselves in the carbon aggregates to cause a more hydrophobic property (see Fig. 4III). In Step IV, 100 Nafion chains are introduced to the box, together with three different solvents, respectively, to exploit the solvent effects on the evolvement of the microstructure. For the three cases in table 3, there are 200 000 CG beads of EG, IPA or HX in the box to represent a wide range of dielectric permittivity. Taking the case 2 as an example, after MD running for 10 ns, the snapshot (see Fig. 4IV) is obtained to show the self-assembled configuration, meanwhile, the solvents are invisible for better clarity. It is easy to find that the ionomer backbones assemble into a separate interconnected phase in the void spaces of the Pt/C aggregates. During the final Step V, excess water and other solvents are evaporated and all the components of a CL can be expressed in the final equilibrium state (see Fig. 4V, after MD running for 50 ns). Corresponding to 13 waters per side chain,[25] the number of water beads is 4500 (including 2000 beads with hydronium ions for keeping electroneutrality condition). From the final snapshot in Fig. 4V, it can be found that the Pt/C nano particles with the embedding PTFE chains form the aggregates, while the hydrated

ionomers do not penetrate into the Pt/C aggregates but form a separate phase that is attached to the surface of the aggregates. The CL thus segregates into hydrophobic and hydrophilic regions. Viewed from the inside of the agglomerate, the hydrophobic region consists of PTFE chains, carbon slabs and the backbones of the Nafion. However, most of the residual solvent beads dwell on the small pores and gas, and surround the side chains of the Nafion ionomers to form the hydrophilic region. It is easy to understand that the hydrophilic beads form a three-dimensional network of irregular water-filled channels, which evolve the primary pore structure in the agglomerate of CLs.

3.2 Pt particle size distribution

In order to mimic the feature of the CLs, the TEM sample is prepared by mixing the Pt/C electrocatalysts (40 wt. %, BASF) in the Isopropanol-Nafion[®] solution, in which the Nafion[®] content is 17.2 wt. %. A small volume, approximately 5 μL of the sample, is deposited onto the copper grids in order to ensure that a thin sample is created. The sample is analyzed in the JEOL JEM-2000EX (Japan) microscope at an accelerating voltage of 120 kV. A part of the TEM image with the size of 100 nm×50 nm (see Fig. 5a) is analyzed by the ImageJ software,[40] which is a public domain Java image processing and analysis program. For a comparison purpose, the Pt nano-particles in the reconstructed equilibrium state are displayed in a 2D-image in the same size of 100 nm×50 nm (repeated by 2×2 simulation box), as shown in Fig. 5b. In Fig. 5c, the particle size and dispersion of the Pt nanoparticles in Fig. 5a are evaluated, and the particles are found in the range of 2-16 nm. Due to a high degree of

overlap of Pt particles, the ImageJ software cannot make distinctions of some bigger

agglomerates; thus it may predict a higher mean size of the Pt particles. Also analyzed

by the ImageJ, the number of Pt particles in each bin[41] in Fig. 5b is counted and

compared in Fig. 5c. It is found that most of the Pt nano-particles have the Feret's

diameters (which represent the longest dimension of the particle, independent of its

angular rotation at the time that the image is captured) in the range of 2 to 6 nm. The

same finding is also indicated in the experimental measurement, as shown in Fig. 5c

in terms of the relative abundance (%).

3.3 Primary pore structure analysis

In Fig. 6a, the frame structure of the agglomerate under the equilibrium state

(t=100 ns) for the case 3 is presented by the VMD software. It is easy to find some

primary pores of 3-10 nm appearing in the agglomerate. The pores are intricate and

connected to form the channels, which can act as large networks within the

agglomerates. They are more likely to be filled with liquid water for water and

hydronium ions transport, and thus have more influences on the properties of CLs. In

this work, an analysis technique based on the Voss Volume Voxelator (3V) web server

is employed to get the overall shape of the channels.[42] It uses the rolling probe

method,[43] which essentially works by rolling a virtual probe or ball of a given radius

around the surface of a macromolecule or the agglomerate to calculate the volumes.

When a probe of zero size is used, the van der Waals radius is obtained. For the CG

system, the effective bead diameter (σ_{ij}) is 0.43 nm; therefore, the original appearance

can be obtained by rolling the probe with the radius p=0.43 nm, as shown in Fig. 6b.

However, as the probe radius increases, the surface features are filled in and the calculated volume will increase (see Fig. 6c, p=5 nm). In addition, the increased probe ball can not go into some of the primary pores anymore and the calculated volume will increase obviously, which will be further discussed in the next part. Furthermore, the geometric solid obtained by rolling the probe with the radius p=2.8 nm is sliced along with the x, y and z axis separately. Thus, the solid part is coloured in sky-blue and the primary pores can be observed, as shown in Fig. 6d. At the same place, the three-dimensional slices of the agglomerate at p= 3.0 nm are displayed in yellow. It is clearly found that one pore space, captured at p=2.8 nm, now becomes the solid part, because the probe ball with the radius p= 3.0 nm is too large to go inside. It means that the size of this primary pore is in the order (the maximum radius) of 2.8 nm.

3.4 Pore size distribution

The primary pore size distributions of the cases 1 and 2 are experimentally determined by Mercury injection porosimetry (MIP),[6] on the instrument of PoreMasterGT 60. The MIP enables the measurements of both the pressure required to force mercury into the pores of CLs and the intruded Hg volume at each pressure. The employed equipment operates from 13 kPa to a pressure of 410 MPa, equivalent to the pores with the diameters, d, ranging from 100 μm to 0.0036 μm. On the other hand, the 3V method provides a tool to theoretically calculate the agglomerate volume depending on the probe radius. In analogy to the principle of MIP, the introduced volumes and the corresponding pore diameters can be collected, to identify the primary pore size distribution among the agglomerate, as shown by the coloured cures

in Fig. 7.

It is worthwhile to point out that, the volume differential distributions (normalized dV/dD) are employed to estimate and evaluate the pore size distribution (PSD) of the CLs. In Fig. 7, the normalized dV/dD values are presented for the two MIP tests and three computational simulations, only in the range of the pore diameters from about 3 to 20 nm. It is clear that the pores are mainly distributed between 3 to 10 nm in both experiments and simulations, and the results of MIP tests of cases 1 and 2 are nearly the same. In contrast, the simulation results from the three solvents reveal the distinct pore size distributions. For example, with the weakening of the polarity in case 3, the PSD becomes more uneven, i.e., more complex pore structures are obtained in the agglomerate. In addition, the agglomerate volume (V_0) is also evaluated at the probe radius of 4 nm, which is appropriate for the primary pore analysis. The predicted V_0 are also shown in table 3; obviously, the CCM prepared with nonpolar solvents (such as HX) acquires bigger size agglomerate involving well-developed primary pores, which may produce better cell performance.

4 Conclusions

In this work, a CG-MD method has been performed as a microscopic structure reconstruction technique to reflect the step formation of a CL. Based on the MARTINI force field, the groups of atoms, such as Nafion ionomer, PTFE, carbon slab, Pt cluster and solvents, are defined as CG beads at the predefined length scales. The bonded and nonbonded interactions between these CG beads are then implemented by the GROMACS package.

Following the fabrication processes during the CCM preparation, the reconstruction of the CL microscopic structure follows fives steps, which are also mimicked in this work. The main features of each step are captured in the modeling. The self-aggregation of Pt/C nano-particles is easily observed in the step I. After removing all the solvents to mimic sintering process in the step III, the PTFE chains (added in the step II) embed themselves in the carbon aggregates to generate more hydrophobic property. In the step IV, Nafion ionomers are added and three different solvents (EG, IPA and HX) are examined, respectively, to exploit the effect of the solvents on the evolution of the CL microstructure. After the heating and drying processes in the step V, the CL microstructure segregates into the hydrophobic and hydrophilic regions. One of the important findings is that the hydrophilic beads form a three-dimensional network of irregular water-filled channels, which evolve the primary pore structure in the agglomerate. In addition, the Pt nano-particle size distribution is evaluated and compared with the TEM image with a reasonable agreement. It is also found that the Pt nano-particles with the Feret's diameters of 2 to 6 nm are more common in the natural evolution of CLs.

The rolling probe method provided on the 3V web server is employed to get the overall shape of the agglomerate. For a certain probe radius, the surface features are filled in and the corresponding volume can be calculated. By comparing with the shapes obtained by rolling the different sizes of probes (e.g., with the radius of 2.8 and 3.0 nm), the structure and the properties of the primary pores can be calculated and analyzed. In analogy to the principle of MIP, the method is also developed to

estimate the primary pore size distribution (PSD) of the three cases, and the PSD is more uneven for the solvent with weak polarity. Well agreed with the experimental results, the reconstructed CLs prepared with nonpolar solvents (such as HX) acquire a bigger size of the agglomerate involving well-developed primary pores.

Acknowledgment

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Table 1 Defined CG beads

CG beads	Color	Represented atoms	Symbol	Specified Type
1	Yellow	-O-CF$_2$CF(CF$_3$)-... -O-CF$_2$CF$_2$-SO$_3$H	SO	Qa
2	Blue	-(CF$_2$CF$_2$)$_3$-CF$_2$-	B0	C3
3	Blue	-(CF$_2$CF$_2$)$_4$-	B1	C3
4	Gray	36×C	C	N0
5	Golden	20×Pt	Pt	Na
6	Green	4×H$_2$O	W	P4
7	Magenta	3×H$_2$O+H$_3$O$^+$	Wh	Qd
8	White	-(CF$_2$CF$_2$)$_4$-	PTFE	C3
9	Cyan	HOCH$_2$CH$_2$OH	EG	P4
10	Pink	CH$_3$CH(OH)CH$_3$	IPA	P1
11	Violet	CH$_3$(CH$_2$)$_5$-OH	HX	C1

Table 2 Lennard-Jones interaction parameters used in the CG-MD simulations, (C6 = $4\varepsilon_{ij}\sigma_{ij}^{6}$ and C12 = $4\varepsilon_{ij}\sigma_{ij}^{12}$) [19]

	W C6, C12	Wh C6, C12	B C6, C12	S C6, C12	C C6, C12	PTFE C6, C12	Pt C6, C12	EG C6, C12	IPA C6, C12	HX C6, C12
W	0.216, 0.0023	0.241, 0.0026	0.116, 0.0013	0.241, 0.0026	0.151, 0.0016	0.116, 0.0013	0.173, 0.0019	0.216, 0.0023	0.194, 0.0021	0.086, 0.0009
Wh		0.216, 0.0023	0.099, 0.0011	0.241, 0.0026	0.151, 0.0016	0.099, 0.0011	0.216, 0.0023	0.216, 0.0023	0.216, 0.0023	0.454, 0.0258
B			0.151, 0.0016	0.099. 0.0011	0.151, 0.0016	0.151, 0.0016	0.116, 0.0013	0.116, 0.0013	0.151, 0.0016	0.151, 0.0016
S				0.216, 0.0023	0.151, 0.0016	0.099. 0.0011	0.172, 0.0019	0.216, 0.0023	0.194, 0.0021	0.454, 0.0258
C					0.151, 0.0016	0.151, 0.0016	0.151, 0.0016	0.151, 0.0016	0.172, 0.0019	0.116, 0.0013
PTFE						0.151, 0.0016	0.116, 0.0013	0.116, 0.0013	0.151, 0.0016	0.151, 0.0016
Pt							0.173, 0.0019	0.173, 0.0019	0.194, 0.0021	0.116, 0.0013
EG								0.216, 0.0023	0.194, 0.0021	0.086, 0.0009
IPA									0.194, 0.0021	0.116, 0.0013
HX										0.151, 0.0016

Table 3 Cases based on solvents with different dielectric permittivities.

Cases	Solvents	Symbol	Dielectric permittivity	Et (25℃, polarity)	Agglomerate size* / nm^3
1	Ethylene Glycol	EG	37.7	56.3	5430.591
2	Isopropyl Alcohol	IPA	18.3	48.6	5465.384
3	Hexane	HX	1.9	30.9	5844.051

* Calculated by the rolling method from the 3V web[36] with the probe radius of 4.0 nm

Figure 1. Schematic illustration of the anode catalyst layers in PEMFCs.

Figure 2. Schematic drawing of the complete Nafion copolymer, which is composed of apolar beads (blue) and charged beads (yellow), and also a part of the atomistic level configuration of a Nafion chain. Four-monomer unit ($-(CF_2CF_2)_4-$) is represented by one blue bead as the hydrophobic backbone, while the side chain ($-O-CF_2CF(CF_3)-O-CF_2CF_2-SO_3H$) with the sulfonic acid group is expressed as one yellow bead with hydrophilic property.

Figure 3. (a) Coarse grain representation of the carbon slab, in which there are 36 carbon atoms in each bead. The typical carbon slab with the size of $5\times5\times2.5$ nm^3 is reconstructed by 224 nonpolar beads (type of N0). (b) Atomistic (in the shaded rings) and coarse grain representation of one fcc-Pt(111) cluster. The 10×10×6 Pt cluster is represented by 30 nonpolar beads(type of Na), and each bead contains 20 Pt atoms.

Figure 4. Step formation of a CL based on the CCMs preparation procedure: Step I: randomly disperse Pt/C catalyst in the $50\times25\times25$ nm^3 box and then the self-aggregation happens in the solvent environment (snapshot at t=10 ns, showing without solvent beads). Step II: add the PTFE to the catalyst ink and reach a

well-distributed condition (at t=10 ns, showing without solvent beads). Step III: remove the solvent in the heating and drying process (at t=50 ns). Step IV: add Nafion chains to form the ion transport network (at t=10 ns, showing without solvent beads). Step V: evaporate the residual solvent and exhibit the final snapshot of the equilibrium state at t=50 ns, with the partially enlarged details from the inside. In all these snapshots, Golden: Pt, Yellow and Blue: Side chain and backbone of Nafion ionomer, Grey: Carbon, White: PTFE, Magenta: Hydronium ions and Green: Water, as listed in table 1.

Figure 5. (a) TEM image of the Pt/C catalyst layer prepared with the Isopropanol Nafion® solution, (b) Pt nano-particles in the reconstructed equilibrium state shown in the 2×2 simulation box (c) Pt particle-size distribution in TEM image, and the counts of Pt particles for each bin[39] in the 2D-image of (b).

Figure 6. (a) Snap of the agglomerate at the final equilibrium state after MD running 100 ns for the case 3 with the PBC box size of 50 nm×25 nm×25 nm, (b) the agglomerate surface obtained at the probe radius p=4.3 Å; (c) surface of the agglomerate at p=5 nm; (d) the three-dimensional slices of the agglomerate at the two probe radius, p= 2.8 nm (sky-blue) and p= 3.0 nm (yellow).

Figure 7. Comparison of the primary pore size distribution (PSD) in the CLs obtained by CG-MD step formation (coloured lines) and experiments (grey lines).

(a)

(b)

(I)

(II)

(III)

(IV)

(V)

Pt
Nafion
C
PTFE
Wh
W

(a)

(b)

(c)

(a)

(b)

(c)

(d)

Solid part

Void and pore space

p=3.0 nm

p=2.8 nm