Review on the Properties of Nano-/Microstructures in the Catalyst Layer of PEMFC

Xiao Yu
Jinliang Yuan¹
e-mail: jinliang.yuan@energy.lth.se

Bengt Sundén

Department of Energy Sciences, Faculty of Engineering, Lund University, 22100 Lund, Sweden

The catalyst layer (CL) of a proton exchange membrane fuel cell involves various particles and pores that span a wide range of length scales, from several nanometers to a few microns. The success of the CL design depends decisively on understanding the detailed structure in microscale or even in nanoscale. In this paper, the properties of nano-/microstructures are outlined, and the physical and chemical processes are analyzed on the Pt surfaces. A software package of automatic simulation environment is developed and applied to investigate the electronic structure of the Pt–H system. Then, the H₂ dissociative adsorption process is obtained using the nudged elastic band approach. The modeling of the nanocomposites in the CLs is a multiscale problem. The nanoscale models are used for investigating the structural evolution and the interactions between Pt/C particles and polymer components; while the microscale simulations, which aim to bridge molecular methods and continuum methods, are extended to describe the morphology of heterogeneous materials and rationalize their effective properties beyond length- and time-scale limitations of the atomistic simulations. However, there are still some major challenges and limitations in these modeling and simulations. The multiscale modeling should be developed to demonstrate the usefulness for engineering design with the longstanding goal of predicting particle-structure-property. [DOI: 10.1115/1.4003170]

Keywords: nanostructure, microstructure, property, multiscale, model, PEMFC

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising electrochemical devices for a direct conversion of the chemical energy of hydrogen into electrical work. It is supposed that they could replace the internal combustion engines (ICEs) in light duty vehicles and offer benefits in transportation, stationary, and portable power applications. Due to their high efficiency, fast and easy start-up, and environment friendliness, PEMFCs are distinguished as a primary solution to vehicle development.

The basic component of PEMFCs is a membrane-electrode assembly. A proton exchange membrane (Nafion type, for example) is in contact with the anode and cathode catalyst layers (CLs) and further with two gas diffusion layers (GDLs). The typical CLs are fabricated as random heterogeneous composites to meet the multifunctional requirements of transport phenomena and electrochemical activity. They are composed of Pt nanoparticles, carbonaceous substrates, and Nafion ionomers to form a proton conduction network. A schematic representation of the CLs is shown in Fig. 1 [1]. Its structure involves various particles and pores that span a wide range of length scales, including Pt nanoparticles on carbonaceous substrates and primary pores with sizes of 3–10 nm at the microscale. The agglomerates and the secondary pores between agglomerates have sizes in the range of 10–50 nm [2] at the mesoscale, and the catalyst layer as a complex composite medium has sizes of about 10 μm at the macroscopic scale.

The species and processes that occur in the CLs include electrochemical reactions, diffusion of hydrogen or hydrocarbon-based fuels (anode) and oxygen (cathode), migration and diffusion of protons, migration of electrons, water transport by diffusion, permeation, electro-osmotic drag, and vaporization-condensation of water. Electrical current is generated/consumed at Pt nanoparticles, which are randomly dispersed on a high-surface carbon matrix. During fabrication, the colloidal solution of carbon/Pt and an ionomer self-organizes into a phase-separated composite with interpenetrating percolation phases for the transport of electrons, protons, and gases.

A main goal of studying CLs is to get a rapid and accurate prediction of the properties and features, which is very difficult to achieve with traditional modeling and simulation methods at a single length and time scale with the current computer power. The catalyst layer models can be classified into two groups according to the level that these models are able to deal with: (i) the macroscopic models that have been developed to describe the fuel cell working behavior, with a common assumption of infinitesimally thin CLs, and (ii) the microscopic or nanoscale models that consider the transport phenomena at the pore or even particle level. Therefore, it is expected to use the multiscale simulation strategies to bridge the models and simulation techniques across a broad range of length and time scales. Then, the macroscopic or mesoscale behaviors of CLs can be addressed from a detailed description of the nano-/microstructures, and the calculated parameters, properties, and numerical information can be efficiently transferred across scales. It is so required because the observable properties of the CLs depend on the inhomogeneous structures at different length scales, such as chemical details and transport phenomena at the nanoscale, aggregation, and self-organizing process at the microscale up to continuum phenomena at the macroscale. As a result, the complete description of the nano-/microstructures in the CLs typically requires a wide range of length scales from the chemical bond, at around 1 Å in length, up to chain aggregates extending for many hundreds of angstroms and beyond.

In order to achieve the longstanding goal of predicting particle-structure-property in material design and optimization, this paper will outline the properties of nano-/microstructures and analyze the physical and chemical processes in the catalyst layer and then provide the basic theories and simulation approaches to solve the multiscale problems involved.

2 The Properties of Nano-/Microstructures

2.1 Challenges for the Structural Design. For the catalyst layer, the most important objective is to produce the highest current density with a minimum amount of the catalyst, which will greatly reduce the cost (DOE targets of $30/kW by 2015) [3]. This means a huge electrochemical active surface area, small kinetic barriers to bulk transport, and interfacial transfer of protons, electrons, and reactant gases.

The importance of the catalyst structure has been previously described by Vojislav et al. [4]. An enhanced activity was revealed for specific crystal surfaces over that for Pt deposited on carbon (Pt/C). United Technology Co. (UTC) Power and Brookhaven National Laboratory (BNL) are developing core-shell structured Pt...
catalysts to reduce Pt content while increasing activity [3]. Two major improvements in the catalyst layer design have appeared by incorporation of Pt or Pt group metals (PGMs) with sizes on the range of 2–5 nm and by the impregnation of mixing large surface carbon support with ionomer. The former way provides a great enhanced electrochemical active surface area, while the latter ensures uniform access of protons to active Pt atom surface throughout the complete layer. As first demonstrated by Los Alamos National Laboratory (LANL) [5,6], these methods enabled a dramatic reduction of catalyst loading. Recent efforts in improving the fabrication of CLs have explored ways to replace polytetrafluoroethylene (PTFE) by ionomer to form a major component as a binder and a hydrophobizing agent [7]. In addition, Pt alloys are also being investigated for improved durability, as well as increased activity. By these methods, the catalyst loadings have been reduced from about 4–10 mg Pt cm⁻² (in 1980s) to about 0.2 mg cm⁻² today [3].

Naturally, the success of the CLs design depends decisively on understanding the detailed structure in the microscale or even in the nanoscale with the assistance of supercomputers and the advanced experimental methods.

### 2.2 Experimental Methods for the Structural Properties

Physical properties of PEMFC CLs include measurement of the surface area, the electrochemical active surface area, the phase and composition of active components, the particle size and size distribution of active components, the morphology and crystal planes, and other features. Some of the related test methods are highlighted as follows.

#### 2.2.1 MSCP

A method of standard contact porosimetry (MSCP) was developed in the 1980s [8] and was discussed in detail in Ref. [9]. This method can be used to investigate the porous structure of fuel cell components; for example, the influence of ionomer on the porous structure of ten different carbon substrates (CSs) was investigated [10].

The MSCP is based on the laws of capillary equilibrium. If two (or more) porous bodies partially filled with a wetting liquid are in capillary equilibrium, the values of the liquid’s capillary pressure in these bodies are equal. According to the Laplace equation, the amount of a wetting liquid in the test sample (Vₜ) is measured. Simultaneously, the amount of the same wetting liquid is measured in a standard specimen of known porous structure (Vₛ). The liquids in both porous samples are kept in contact. After some time, a thermodynamic equilibrium is established. The measurements are performed for different overall amounts of the liquid Vₛ₋ₜ=Vₛ₊ₜ. During measurements, this overall amount is changed by gradual evaporation of the liquid. This method can establish the distribution of pore volume versus pore size of the test sample by comparing with the known specimen.

MSCP has several substantial advantages over mercury porosimetry and other methods because of high accuracy (the error is less than 1%) and broader measurement range of pore radii from 1 to 3 × 10⁻⁵ nm. Further, the method makes it possible to obtain a great deal of diverse information about the porous structure, as well as about sorption and hydrophilic–hydrophobic properties, of all porous and disperse materials.

#### 2.2.2 TEM

Electron microscopes use a beam of highly energetic electrons to examine objects on a very fine scale. The transmission electron microscope (TEM) was the first type of electron microscope developed by Knoll and Ruska [11] in Germany in 1932, 35 years after Thompson’s discovery of the electron.

The TEM passes an accelerated electron beam through a thin sample (50–300 Å). Some of the electrons are scattered by the atoms in the sample. A phase distortion is created, resulting in a phase contrast that is used to create an image. The TEM builds an image by means of differential contrast. Those electrons that pass through the sample go on to form the image, while those that are stopped or deflected by dense atoms in the specimen are subtracted from the image. In this way, a black and white image is formed.

A much lower wavelength of electrons makes it possible to achieve a resolution a thousand times better than that of a light microscope. It enables the operator to see the “inside” of the sample rather than the surface. The main use of the TEM is to examine the structure, composition, or properties of a specimen in submicroscopic detail in the order of a few angstroms. For the CLs of PEMFC, it is possible to study the microscopic morphology down to near atomic levels by the high resolution (HR)-TEM [12].

#### 2.2.3 XPS

X-ray photoelectron spectroscopy (XPS) has been widely used for the surface characterization of materials, especially catalysts. It is the greatest applicability among all the methods of electron spectroscopy for chemical analysis (ESCA), which is the most important and useful method for surface analysis. XPS can be used to study electrons in both valence band and core to identify the atoms at surfaces by comparing the observed lines with either calculated core level binding energies or experimentally derived spectra from standards. It is possible to examine the chemical elements present at successive depths within a sample by running an electron spectrum after each short treatment with ions. In addition to qualitative analysis, XPS can be applied for a quantitative analysis because the number of emitted electrons is a function of the number of atoms on the surface.

It is clear that XPS analysis can give sufficient information about the qualitative and quantitative elemental surface composition of a catalyst, the oxidation state of an atom, the chemical environment, as well as the precise sites of atoms in relation to crystal structures [13].

For the fuel cell catalysts, the oxidation states of Pt and the crystallites’ contents can be determined by XPS [14]. A survey XPS scan on the nanocomposites can provide a qualitative analysis of the elemental composition on the CL surface [15]. It also provides a better insight into the surface properties of the carbon-supported Pt-alloy electrocatalysts in relation to platinum metal [16]. The electrocatalysts were characterized by XPS to determine the valence states of the elements, the compositions, and the atomic ratios of the metal components.

#### 2.2.4 EDS

Energy-dispersive x-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of x-ray fluorescence spectroscopy, which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that
each element has a unique atomic structure allowing x-rays that are characteristic of an element’s atomic structure to be identified uniquely from one another [17].

There are four primary components of the EDS setup: the beam source, the x-ray detector, the pulse processor, and the analyzer. A number of freestanding EDS systems exist. However, EDS systems are most commonly found on scanning electron microscopes (SEM-EDS) and electron microprobes. A broad area of small particles on the SEM or TEM images can be selected for EDS analyses to obtain composition information for the selected region. Element mapping with EDS can be used to obtain the distribution of elements on the surface. The source of the x-rays is manifested as a grouping of extremely bright dots against a dark background, indicating where that element is absent.

For the fuel cells, EDS analysis has been used to investigate the composition of the alloy particles in the catalysts [18]. In addition, it can provide the distribution of active components on the surface and through the cross-section of the membrane [19].

2.3 The Structure of Pt-Based Nanocatalyst. The typical CLs are fabricated as random heterogeneous composites to meet the multifunctional requirements of transport phenomena and electrochemical activity. They are composed of Pt or Pt-alloy nanoparticles, carbonaceous substrates, and Nafion ionomers to form a proton conduction network. Considering various nanoparticles, carbonaceous substrates, and Nafion ionomers to minimize their surface availability.

2.3.1 Catalyst Supported on Carbonaceous Materials. Currently, carbon black supports, Vulcan X (VC-X) and Ketjen Black (KB), are widely used in platinum catalysts. TEM images provide the information of Pt particle size and distribution, as shown in Fig. 2 [20]. All prepared catalysts showed a good distribution and clear Pt lattice structures. It is found that the particle sizes are in the range of 2–4 nm with different distributed networks.

However, recent publications suggest that novel carbon supports, such as ordered mesoporous carbon [21], carbon nanofibers (CNFs) [22], and carbon nanotubes (CNTs) [23], may improve the efficiency of electrocatalysts, reduce Pt loading, and increase the surface area of the catalysts, as shown in Fig. 3.

2.3.2 Pt-Based Electrocatalysts. Among metals, Pt exhibits the highest catalytic activity for low-temperature fuel cells. However, Pt is expensive and rare, so its loading must be minimized without weakening the cell performance. Thus, there has been great focus on synthesizing Pt nanoparticles on carbon to maximize their surface availability [24]. A surfactant-stabilized colloidal method was used to control the sizes of the Pt particles, as shown in Fig. 4 [25]. The TEM image in Fig. 4(a) presents the particle size and dispersion of the Pt/C catalyst prepared with surfactants Brij 35 (B)+Tween 20 (T) at ten times of the critical micelle concentration (or 10× CMC). These Pt nanoparticles are in the range of 1–4 nm with the average size of 2.4 nm. At a mixed binary surfactant concentration of 10×CMC, Pt nanoparticles are surrounded by the surfactants to form spherical micelles, which inhibit aggregation (Fig. 4(b)). When the concentration is increased to 50×CMC, severe aggregation of Pt nanoparticles occurs, as witnessed in Fig. 4(c). When the surfactant concentration is too high, the spherical micelles are converted to cylindrical micelles, and hence tubular-shaped Pt nanoparticles are formed (Fig. 4(d)).
In order to promote both the activity and the oxidation of the chemisorbed CO, the Pt-based alloy catalysts, which involve the use of a secondary metal (e.g., Ru, Sn, Mo, and Cr), have been the focus of extensive research in the past decade [26]. Figure 5(a) shows a HR-TEM image of the 3Pt1Sn/C catalyst. It was found that the PtSn nanoparticles, with an average particle size of 2.3 nm (Fig. 5(b)), were uniformly well-dispersed on the carbon support. By using XPS, the surface chemical state and bonding of the PtSn catalysts were also analyzed [27].

Although the alloy catalysts show improved oxygen reduction reaction (ORR) activity compared with Pt/C catalysts, their stabilities are still poor. Recently, the Pt/C catalyst adding metal oxides has been extensively investigated for enhancing the ORR activities [28]. In Fig. 6(a), CeO$_2$ nanoparticles can be found near Pt nanoparticles, as the crystal phases of Pt and CeO$_2$ are identified by lattice analysis. The lattice spacing of Pt and CeO$_2$ is about 0.22 nm and 0.31 nm corresponding to Pt(111) and CeO$_2$(111), respectively. The EDS spectrum (Fig. 6(b)) of the 20Pt–10CeO$_2$/C catalyst proves the coexistence of Pt and Ce on the carbon support [29].

Additionally, catalyst agglomeration could be avoided with the addition of polybenzimidazole (PBI). Fujigaya et al. [30] discovered that pyridine-containing compounds such as PBI (PyPBI) could exfoliate and enwrap multiwalled carbon nanotubes (MWCNTs). Pt ions have been efficiently adsorbed onto PyPBI wrapped MWCNTs via coordination, and subsequent reduction of Pt ions formed uniform Pt nanoparticles on the surface of MWCNT/PyPBI. Figure 7 shows HR-TEM results of the nanocatalyst.

3 Transport Phenomena and Chemical Reactions

3.1 Surface Adsorption. The embedding methods are employed to investigate interactions between the surface and adsorbrates [31], which work best if a strong chemisorption bound is formed so that other interactions are secondary. The adsorption energy is calculated by

$$E = E_{\text{adsorbate}} + E_{\text{substrate}} - E_{\text{adsorbed system}}$$  \hspace{1cm} (1)

For the adsorption on metals, there is a model [32] to predict the adsorption bound strength based on the electronic properties of the metals,

$$E_{d_{\text{hyb}}} = -2(1-f) \frac{V^2}{|E_d - E_a|} + 2(1+f)\alpha V^2$$  \hspace{1cm} (2)

where $E_{d_{\text{hyb}}}$ is the energy gained from hybridization of the adsorbate orbital with the metal d-band, $E_a$ is the adsorbate orbital energy, and $\alpha$ is a constant, which is independent of the metal but depends weakly on the identity of the adsorbate. From this model, three surface properties contribute to the ability of the surface to make and break adsorbate bonds: the energy center ($E_a$) of the d-bands, the degree of filling ($f$) of the d-bands (number of d electrons), and the coupling matrix element ($V$) between the adsorbate states and the metal d-states.

The interaction between the adsorbate states and the metal d-states is an important part of the interaction energy because of the narrowness of the d-band. When the structure of the surface changes, the d-band center will alter due to the change in the

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Fig. 5  (a) The HR-TEM image and (b) the particle size distribution of the 3Pt1Sn/C catalyst [27]. Reprinted from Ref. [27] with permission from Elsevier.

Fig. 6  HR-TEM image of (a) 20Pt–10CeO$_2$/C catalysts and (b) EDX pattern for the 20Pt–10CeO$_2$/C catalyst [29]. Reprinted from Ref. [29] with permission from Elsevier.
3.1.1 Adsorption of H$_2$ on Pt. In the adsorption, hydrogen is attached to the surface of a material either as hydrogen molecules or as hydrogen atoms. In absorption, hydrogen is dissociated into H atoms, which are incorporated into the solid lattice framework. Platinum is also of particular importance due to the central role it plays in hydrogenation reactions; hence, the interactions of hydrogen with Pt surfaces have been investigated in a large number of studies [34]. Potential energy (PE) for H$_2$ dissociative adsorption on the Pt(111) surface is as functions of (1) the H$_2$ interatomic distance $r$, (2) the distance $Z$ from H$_2$ center of mass (CM) to the surface, (3) the H$_2$ polar and azimuthal orientations with respect to the surface normal and parallel, (4) the surface relative position of the H$_2$ CM, and (5) the surface coverage of H on Pt(111), as shown in Fig. 8. It was found that the reaction paths were without or with very low barriers leading to dissociation of H$_2$ on the Pt(111) surface [35], and vacant sites increased the surface reactivity of Pt(111) by lowering the activation barriers for the dissociative adsorption of H$_2$ on the substrate [36]. By performing quantum dynamics calculations on ab initio potential energy surfaces (PESs), Arboleda et al. [37] also investigated the effects of the initial kinetic and vibrational energies and the orientation of the incident hydrogen molecule (H$_2$) on the dissociative adsorption dynamics of H$_2$ on a Pt(111) surface.

3.1.2 Diffusion of H Atom on Pt. A software package of Automatic Simulation Environmental (ASE) is developed and applied to investigate the electronic structure of the Pt–H system. A 2×2 unit cell (corresponding to 0.25 ML coverage of adsorbates) is provided, which has a three-layer slab of the Pt(111) facet of a face-centered cubic (fcc) crystal of platinum atoms with the experimental lattice parameter of 2.77 Å.

In order to speed up the calculations, all the adsorbates and the top layer of Pt(111) slab were relaxed to the equilibrium structure. The convergence criterion was that the force on all atoms should be less than a certain value. Initial estimates of transition states for reactions were obtained using the nudged elastic band (NEB) approach, which could calculate the minimum energy path (MEP) for any given chemical processes when both the initial and final states were known. The NEB activation barrier was refined by linear interpolation of a set of images between the known initial and final states, and each “image” corresponded to a specific bound length and energy. Thus, once the energy of the string of images got the minimum value, the true MEP was revealed.

When the H atom was set in the fcc position as the initial states and the place where the atom moved to another fcc site by diffusion as the final states, the NEB approach could be used to calculate the MEP and got the images under the equilibrium states. For the cases above, the energy changes look like two humps with the maximum value of 0.089 eV (that is, 8.587 kJ mol$^{-1}$), which represents the diffusion barrier for the H atom in the Pt(111) surface. It is smaller than that predicted by Blaylock et al. [38], in which they got 13.4 kJ mol$^{-1}$ for the H atom on the fcc site. As observed in Fig. 9, the H atom also reached a steady state when it passed through a cubic closest-packing (hcp) site, where the energy became nearly zero. Thus, fcc and hcp were both the preferable sites for the H atom diffusion.
3.1.3 Adsorption of O$_2$ on Pt. For the interaction of oxygen with the Pt(111) surface, three molecular O$_2$ adsorption states have been identified. When the surface temperature is below 30 K, a weakly bound physically adsorbed species exists. At about 150 K and higher temperature, the experiments at the platinum-ultrahigh frequency (UHV) interface have shown that there are two different kinds of molecularly chemisorbed states, which have been characterized as peroxo-like (O$_2^{-}$) and superoxo-like (O$_2^{-}$), respectively [39,40].

To theoretically describe the adsorption process of O$_2$ on Pt(111), we performed ab initio calculations of the atomic and electronic structures of the adsorbate-substrate system using the Vienna ab initio simulation program (VASP) [41]. The superoxo-like (O$_2^{-}$) paramagnetic precursor was formed at the bridge site (s-b-t) with the molecule parallel to the surface. The O–O bond length was 1.39 Å, and the O–O stretching frequency was 850 cm$^{-1}$. The calculated adsorption energy was 0.72 eV. The peroxo-like (O$_2^{-}$) nonmagnetic precursor was formed in the threefold hollow, with the atom slightly canted in a top-hollow-bridge geometry. The O–O bond length was 1.43 Å for t-f-b (1.42 Å for t-h-b). The O–O stretching frequency was 690 cm$^{-1}$ (710 cm$^{-1}$ for t-h-b), and the adsorption energy was 0.68 eV (0.58 eV for t-h-b) [42].

3.2 Activation Energy. The activation energy for the elementary electron transfer step is a key to understand the electrocatalyzed reaction mechanism. For a multi-electron reaction transfer, it is a challenge to identify the rate determining step. Several theoretical models to account for the electron transfer process have been developed since the initial work by Gurney [43]. Bockris and Abdu [44] reported the first theoretical prediction of activation energy for the first step of the ORR, based on Gurney’s model. Anderson and Albu [45,46] introduced the local reaction center electron transfer theory. Thus, the activation energy, the transition state energy minus the reactant energy, can be predicted by this approach.

The theoretically predicted activation energies were compared in a later paper with experimental data for platinum alloys [47]. Overall agreement between the theoretical prediction and the measured current density was observed: (i) The first electron transfer step, forming OOH$_{ads}$, was the rate-limiting step, and (ii) the active catalyst sites for the various catalyst systems were similar. The presence of alloying atoms adjacent to the active site did not dramatically affect the activation energy.

To account for the electronic field, the O$_2$+H$^+$ (H$_2$O)$_3$ + e$^-$/Pt(111) system was modeled in Ref. [48]. The study observed that at first the proton transfer intermediate was formed rapidly, similar to results reported by Jinmouchi [49]. The formation of the end-on chemisorption precursor H–O–O–Pt had an energy barrier of about 0.4 eV. They suggested that the mechanism for the first electron transfer involved (1) proton transfer, (2) electron transfer, and (3) dissociation and hydroxyl adsorption [48]. Hyman and Medlin [50] reported an activation barrier for O$_2$ protonation and OOH dissociation. Using the H$_2$O$_2$ $^*$ model, the O$_2$ protonation had a more stable precursor and a lower activation barrier (0.07 eV) than O$_2$ dissociation (0.22 eV).

Activation energy studies suggest that with Pt as the catalyst, proton transfer precedes O$_2$ dissociation and is involved in the rate determining step of the oxygen reduction reaction. Without catalysts, the third electron transfer step has the largest activation energy, followed by the first electron transfer step. An efficient ORR catalyst should activate the first and third electron transfer steps.

3.3 Reaction Thermodynamics. The thermodynamics of the reactions was established as a function of voltage by calculating the stability of the reaction intermediate, and the overpotential of the reaction could be linked directly to the proton and electron transfer [51] The procedure to calculate the free energy of the intermediates of the electrochemical reactions is outlined and discussed below with different reaction mechanisms.

3.3.1 Hydrogen Reduction Reaction. The oxidation of hydrogen occurs readily on Pt-based catalysts [52]. The kinetics of this reaction is very fast on Pt catalysts, and in a fuel cell the oxidation of hydrogen at higher current densities is usually controlled by mass-transfer limitations. The oxidation of hydrogen also involves the adsorption of the gas on the catalyst surface followed by a dissociation of the molecule and the electrochemical reaction to hydrogen ion as follows:

$$2\text{Pt}(s) + \text{H}_2 \rightarrow \text{Pt} - \text{H}_{ads} + \text{Pt} - \text{H}_{ads}$$

$$\text{Pt} - \text{H}_{ads} \rightarrow \text{H}^+ + e^- + \text{Pt}(s)$$

where Pt(s) is a free surface site and Pt–H$_{ads}$ is an adsorbed H-atom on the Pt active site.

By the ASE software, the H$_2$ dissociative adsorption process was simulated in this paper using the NEB approach. In the initial state, the molecule was adsorbed on the same Pt(111) surface, as discussed in Sec. 3.1.2. At the beginning, both of the H atoms moved to the bridge site (shown as the arrow in Fig. 10) as the molecular status; after that, they were separated with large energy changes, and the dissociation process happened; at last, one H atom went back to the fcc site, and another went to another fcc site to keep the whole system energy in a higher state. In such cases, the system needed extra energy provided from the environment, and the reaction barrier was 4.371 eV.

Although this reaction is fast on the Pt catalysts in PEMFCs, some problems may arise as to when impure hydrogen is used. Thus, some studies on various alloys have been carried out to improve the catalyst activity with contaminated hydrogen [53,54].

3.3.2 Oxygen Reduction Reaction. For some reasons, the kinetics of the cathode reaction is much slower than the anode reaction. The ORR process is

$$\frac{1}{2}\text{O}_2 + 2(\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O}$$

The simple dissociative mechanism was first introduced in [51]

$$\frac{1}{2}\text{O}_2 + \ast \rightarrow \text{O}^-$$

$$\text{O}^- + \text{H}^+ + e^- \rightarrow \text{HO}^*$$

$$\text{HO}^* + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} + \ast$$

where $\ast$ denotes a site on the catalyst surface. In the following section, the associative mechanism, where O$_2$ does not dissociate.
before it is hydrogenated, was described in detail. Several studies [55] have suggested that oxygen reduction on Pt surfaces takes place via peroxy intermediates, for example, in a reaction given by the elementary steps:

$$\begin{align*}
O_2 + * &\rightarrow O_2^* \quad (9) \\
O_2^* + (H^+ + e^-) &\rightarrow HO_2^* \quad (10) \\
HO_2^* + (H^+ + e^-) &\rightarrow H_2O + O^+ \quad (11) \\
O^+ + (H^+ + e^-) &\rightarrow HO^+ \quad (12) \\
HO^+ + (H^+ + e^-) &\rightarrow H_2O + O^+ \quad (13)
\end{align*}$$

The last two steps are the same as the ones of the dissociative mechanism above. The new steps in Eqs. (9)–(11) involve adsorption of molecular O2 and direct proton/electron transfer to it and to OOH.

An alternative to form water in Eq. (11) is to form hydrogen peroxide. Therefore, the associative mechanism can also be termed as a peroxy mechanism. Figure 11 illustrates the possible reaction pathways, and the possibilities of the ORR pathways are summarized as follows [56]:

1. a “direct” four-electron reduction to H2O (in acid media) or to OH− (in alkaline media)
2. a two-electron pathway involving reduction to hydrogen peroxide
3. a “series” pathway with two- and four-electron reduction
4. a “parallel” pathway that is a combination of 1–3
5. an “interactive” pathway in which the diffusion of species from a series path into a direct path is possible

A four-electron oxygen reduction yields water, while a two-electron reduction produces hydroxide, which not only reduces the efficiency but also poisons the catalysis and cell because of its high oxidizability. The standard potentials for direct four-electron, two-electron, and one-electron reactions involved in the ORR are shown as follows:

$$\begin{align*}
O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O, \quad 1.23 \text{ V} \quad (14) \\
O_2 + 2H^+ + 2e^- &\rightarrow H_2O_2, \quad 0.68 \text{ V} \quad (15) \\
H_2O_2 + 2H^+ + 2e^- &\rightarrow 2H_2O, \quad 1.77 \text{ V} \quad (16) \\
O_2 + H^+ + e^- &\rightarrow HO_2^+ \quad -0.13 \text{ V} \quad (17)
\end{align*}$$

There are three types of ORR catalysts used nowadays: transition metals and alloys, non-noble metals and metal oxides, and transition-metal macrocyclic complexes. For transition-metal catalysts, two-electron reduction is reported for less active metals, such as Au and Hg. For the most active catalyst, Pt, four-electron reduction is generally believed to occur. For the ORR on Pt, two Tafel regions have been observed in both acid and alkaline solutions. At low current densities, a Tafel slope of $-60 \text{ mV/dec}$ was noted, and at the high current densities, the slope was $-120 \text{ mV/dec}$ [57]. The difference in Tafel slopes is attributed to a partial coverage of the Pt surfaces by intermediates, especially by PtO. It is reported that at a potential $>0.8 \text{ V}$ (NHE, normal hydrogen electrode), the Pt surface coverage by PtO could be about 30% [58]. Thus, the adsorbed intermediates and their coverage on Pt affect the ORR kinetics dramatically.

4 Modeling and Simulation Method

The major objective of CL modeling is to establish the relations between the structures and the properties of the transport processes and the reactions. In the following, the modeling is separated into two levels: the nanolevel and the microlevel. The reason is that the individual Pt nanoparticles and primary pores are in the order of 1 nm, while the sizes of the secondary pores, Pt/C agglomerates, and polymer components are in the order of 100 nm. Hence, the modeling of the CL structure is a multiscale problem: The microscale model, extended to study the microscopic structure of agglomerates and phase separation of the polymer nanocomposites, is able to simulate the phenomena on the microscale and time scales, while the nanoscale model with the resolution of 1 nm is used for investigating the structural evolution and the interactions between Pt/C particles and polymer components.

4.1 Nanoscale Theories and Simulations

4.1.1 MD. The molecular dynamics (MD) simulation was employed to predict the time evolution of a system involving interacting particles and to provide insights into structural correlations and transport properties of CLs, particularly in three-phase boundaries (TPBs) of carbon/Pt, ionomer, and gas phase. Furthermore, it provides the information about atomic positions, velocities, and forces. In classical MD simulations, the system is treated as a set of N interacting particles [59]. The atoms are presented by spherical nuclei that attract and repel each other. After assigning point charges to each particle, the forces acting on the particles are derived from a combination of bonding, nonbonding, and electrostatic potentials. The motions of the atoms are calculated using the laws of classical mechanics. The result of a MD simulation is a trajectory in terms of positions and velocities of all N particles in the system. The thermodynamic properties, spatial and temporal correlation functions, and transport properties can be exactly calculated when simulating with an appropriate time step and a sufficient time length.

Nowadays, computationally feasible time trajectories in atomistic MD simulations extend from a few nanoseconds (ns) up to hundreds of nanoseconds. The time trajectory of an MD system is obtained from solving a system of second order differential equations:

$$m_i \frac{d^2 r_i}{dt^2} = \sum_j F_{ij} + \sum_k F_{ik}, \quad i = 1, \ldots, N$$

here $i$ denotes the considered particle; $m_i$ and $r_i$ are the mass and the position vector of this particle, respectively. The forces $F_{ij}$ represent two-body interactions between atom $i$ and $j$. Forces $F_{ik}$ were the action of external fields. The force field includes van der Waals interactions and electrostatic interactions, and it is the key to get an accurate solution. Thus, by solving a set of the classical Newtonian equations, the motions for all particles in the system can be established. The forces acting on the nuclei are derived from the gradients of the potential energy function,

$$F_i = - \nabla_r V$$

Such a force field may be obtained by the quantum theory (e.g., ab initio [60]), the empirical method (e.g., Lennard–Jones (LJ), Mores, and Born–Mayer) or the quantum-empirical method (e.g., embedded atom model, glue model, and bond-order potential). It can be split up into two contributions: nonbonded interactions between all nuclei and bonded interactions between nuclei that are part of the same molecule. The nonbonded interactions consist of electrostatic interactions, van der Waals interactions, and polarization effects. Polarization effects are the result of varying electron densities and cannot be described explicitly using force field methods, which invariably ignore electron dynamics. It is com-
mon practice to include them implicitly in the van der Waals interactions. This leaves two terms for the nonbonded interactions. The first term corresponds to Coulomb interactions

\[ V = \sum_{ij} \frac{q_i q_j}{4 \pi \epsilon_0 r_{ij}} \]

between two charged spheres at a distance \( r_{ij} \) from each other. In this equation, \( q_i \) represents the charge of particle \( i \) and \( \epsilon_0 \) is the dielectric permittivity of vacuum. The particles can be assigned partial charges or integer values in the case of ions.

The second type of nonbonded interactions corresponds to the dispersion or the van der Waals forces. These are the interactions between the atoms that arise from (quantum) fluctuations of the electronic charge densities. Both of these interactions are represented in a second term for nonbonded interactions, for which the use of the LJ potential has become a standard procedure in MD simulations,

\[ V = 4 \epsilon \left[ \left( \frac{a}{r} \right)^{12} - \left( \frac{a}{r} \right)^{6} \right] \]

In the equation above \( \epsilon \) represents the depth of the potential at the minimum \((r_{min}=2^{1/6}a)\) and \( a \) is the point at which \( V=0 \). There are some other bonded integrations that also need to be calculated: bond stretching (two-body), bond angle (three-body), and dihedral angle (four-body) interactions. The first two can be described by a harmonic potential, which can also be used to describe the motion of a vibrating spring or a pendulum with the same mechanism. However, because of the rotational symmetry, the dihedral interaction can be described by a periodic function instead of harmonic potential. All these bonded interactions play an important role when simulating the hydrated Nafion ionomer [61–65].

In MD simulations, the molecular adsorption concept is used to interpret the Pt–C interactions during the fabrication processes. The Pt complexes are mostly attached to the hydrophilic sites on the carbon particles, viz., carbonyl or hydroxyl groups [66]. The adsorption is based on both the physical and chemical adsorptions. Many efforts have been done on the MD simulations of Pt nanoparticles adsorbed on carbon with or without ionomers [67–71]. The Pt–Pt interactions are modeled with the many-body Sutton–Chen (SC) potential [72], whereas a LJ potential is used to describe the Pt–Pt interactions. The SC potential for Pt–Pt and Pt–C interactions provides a reasonable description of the properties for small Pt clusters. Diffusion of platinum nanoparticles on graphite has also been investigated, with diffusion coefficients in the order of \( 10^{-5} \text{ cm}^2 \text{s}^{-1} \) [73].

As for the properties of hydrated Nafion membrane, the concept of cluster formation for ionomers [74] was suggested for configurational dipole-dipole interactions of water and ions. One widely accepted empirical model for hydrated Nafion is the cluster-network model proposed by Hsu and Gierke [75] on the basis of small-angle x-ray scattering (SAXS) experiments. In this model, spherical hydrophilic clusters (about 4 nm diameter) of water are surrounded by sulfonate groups connected through cylindrical channels with \( \sim 1 \) nm diameter. A two site model and a single-point-charge (SPC) model are used for oxygen and water, respectively [76]. The dynamic behavior of water and \( \text{O}_2 \) transport at the three-phase interface gas/catalyst/hydrated membrane are investigated. The view in Fig. 12 shows the nanoparticle surface in detail. Further, the amount of water on the Pt(111) surface is appreciable, and the water forms a network connected by hydrogen bonds.

MD simulations can be performed in many different ensembles, such as grand canonical (\( \mu \)VT), microcanonical (NVE), canonical (NVT), and isothermal-isobaric (NPT) [76]. Applying MD into polymer composites allows us to evaluate the effects of fillers on polymer structure and dynamics in the vicinity of the polymer-filler interface and to probe the effects of polymer-filler interactions on the materials properties.

### 4.1.2 DFT

Based on the MD simulation, density functional theory (DFT) has become a choice for large systems, especially for solid-state surfaces. It came from the Hohenberg–Kohn theorem [77]. According to this, the electron density determines the ground-state wave function and all other electronic properties of the system. The correct density is the case that has the minimum energy. Because the electron density is a function of the position, the DFT approach could significantly reduce the computational demand. First, a fictitious reference system of noninteracting particles was introduced to obtain the electron density. Its state can be calculated by solving a set of one-electron Schrödinger equations [78],

\[ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(r) + v_{\text{H}}(r) + v_{\text{xc}}(r) \right\} \Psi_i(r) = \epsilon_i \Psi_i(r) \]

where the external potential is

\[ v_{\text{ext}}(r) = -\sum_a \frac{Z_a}{|r - R_a|} \]

and the Hartree potential reads

\[ v_{\text{H}}(r) = \int \frac{\rho(r')}{|r - r'|} d^3r' \]

while \( v_{\text{xc}}(r) \) is the exchange-correlation potential.

In principle, if the true exchange-correlation term is known, the exact electron density could be obtained. However, in reality, the exchange-correlation term is unknown, and there is no systematic way of deriving it. There are several types of approximate functions, such as local density approximation (LDA) [79] and generalized gradient approximation (GGA) [80]. In general, as the exchange-correlation function contains both exchange and Coulomb correlation terms, the DFT provides better quality than the single determinant Hartree–Fock (HF) method, which does not have a Coulomb correlation term.

Recent efforts employing DFT calculations focused mainly on morphologies and electrocatalytic properties of small metal nanoclusters [81,82]. With the help of the density functional theory and classical molecular dynamics simulations, the details of ionic and molecular transport can also be elucidated. Balbuena et al. [71] illustrated the formation of ionic clusters in the vicinity of the catalyst sites and revealed how the connectivity of these clusters might determine the transport mechanism of protons and molecular species.

### 4.2 Microscale Theories and Simulations

The modeling and simulation at the microscale aim to bridge molecular meth-
ods and continuum methods and avoid their shortcomings. Microscale simulations can describe the morphology of heterogeneous materials and rationalize their effective properties beyond length- and time-scale limitations of atomistic simulations. Specifically, in nanoparticle-polymer systems, the study of structural evolution (i.e., self-organized phenomenon) involves the description of bulk flow (i.e., hydrodynamic behavior) and the interactions between nanoparticles and polymer components. With the help of the microscale models, it can elucidate whether or not ionomer is able to penetrate into primary pores inside Pt/C agglomerates. Note that the hydrodynamic behavior is relatively straightforward to be predicted by the continuum theories but is very difficult and expensive to be treated by the atomistic methods. In contrast, the interactions between the components can be examined at an atomistic level but are usually not straightforward to incorporate at the continuum level. Therefore, various simulation methods have been evaluated and extended to study the microscopic structure, element distribution, and phase separation of these polymer nanocomposites, including Monte Carlo (MC) methods, dissipative particle dynamics (DPD), and the lattice Boltzmann method (LBM). In these methods, a polymer system is usually treated with a field description or microscopic particles that incorporate molecular details implicitly. Therefore, they are able to simulate the phenomena on the length and time scales currently inaccessible by the classical MD methods.

### 4.2.1 Monte Carlo Method
Monte Carlo methods (or Monte Carlo experiments) are a class of computational algorithms that rely on repeated random sampling to calculate the properties of interest. It is extremely simple in principle: Choose a site at random, propose a change in the sample, calculate the change in energy, \(\Delta E\), and accept or reject the change based on \(\Delta E\). When performing such dynamics, it is required that a probability transition function is defined. There are two common choices, the Metropolis function and the symmetric function. The Metropolis function is

\[
P(E) = \begin{cases} 
1, & \Delta E \leq 0 \\
\exp\left(-\frac{\Delta E}{k_B T}\right), & \Delta E > 0
\end{cases}
\]

and the symmetric function reads

\[
P(E) = \frac{1}{2} \left[ 1 - \tanh\left(\frac{E}{2k_B T}\right) \right]
\]

where \(k_B T\) defines a thermal energy of the simulation; it is analogous to the thermal energy of experimental systems but not directly related. The choice of the probability function has no effect on the thermodynamics of the system, although the choice of the functional form of \(P(E)\) does affect the dynamics of boundary motion slightly. The basic algorithm to determine whether a change is accepted or not using the Metropolis scheme is discussed below.

In an NVT ensemble with \(N\) atoms, a new configuration was hypothesized by arbitrarily or systematically moving one atom from position \(i\) to \(j\). Due to such atomic movement, one can calculate the change in the system Hamiltonian, \(\Delta H\),

\[
\Delta H = H(j) - H(i)
\]

where \(H(i)\) and \(H(j)\) are the Hamiltonian associated with the original and new configuration, respectively. This new configuration is then evaluated according to the following rules. If \(\Delta H < 0\), then the atomic movement would bring the system to a state of lower energy. Hence, the movement is immediately accepted and the displaced atom remains in its new position. If \(\Delta H > 0\), the movement is accepted only with a certain probability \(P_{i \rightarrow j}\), as given by

\[
P_{i \rightarrow j} = \exp\left(\frac{-\Delta H}{k_B T}\right)
\]

where \(k_B\) is the Boltzmann constant. According to Metropolis [83], a random number \(\xi\) between 0 and 1 can be generated, and a new configuration will be determined by the following rule:

\[
\begin{align*}
\text{if } \xi &\leq \exp\left(-\frac{\Delta H}{k_B T}\right), \text{ the movement is accepted} \\
\text{if } \xi &> \exp\left(-\frac{\Delta H}{k_B T}\right), \text{ the movement is not accepted}
\end{align*}
\]

If the new configuration is rejected, one then counts the original position as a new one and repeats the process by using other arbitrarily chosen atoms. While for a \(\mu\)VT ensemble, the computational process is quite similar to an NVT ensemble.

Different from MD, which gives nonequilibrium as well as equilibrium properties, MC provides only the information on equilibrium properties (e.g., free energy and phase equilibrium). In polymer CLs, MC methods have been used to generate a random distribution of three kinds of particles, i.e., Pt/C catalyst, Nafion, and poly-tetra-fluoro-ethylene (PTFE) [84]. Based on such a cluster model, the catalyst utilization was calculated through counting the number of Pt/C clusters and Nafion particle clusters.

In chemistry, dynamic Monte Carlo (DMC) is a method for modeling the dynamic behavior of molecules by comparing the rates of individual steps with random numbers. Unlike the Metropolis Monte Carlo method, which has been employed to study systems at equilibrium, the DMC method is used to investigate nonequilibrium systems such as a reaction and diffusion [85]. This method is mainly applied to analyze the adsorbates' behavior on the surfaces [86,87].

Similar to the DMC method, the kinetic Monte Carlo (KMC) method is also a Monte Carlo method that intends to simulate the time evolution of some processes occurring in nature. Typically, these processes occur with a given reaction rate. It is important to understand that these reaction rates are also the inputs to the KMC algorithm because the KMC method itself cannot predict them. The main difference between KMC and DMC seems to be in terminology and application areas: KMC is used mainly in physics, while the “dynamic” method is mostly used in chemistry. KMC tools are well suited for studying on a time scale much longer than the nanosecond range covered by MD simulators and for handling the extreme large number of molecules to accurately simulate pressures [88]. These models utilize physical property data generated by MD, or experimental analysis—typically in the form of activation energies, mobilities, sticking efficiencies, etc. KMC models cannot identify new reaction paths but rather focus attention on the complexities associated with the interaction of many individual processes. It has been widely developed to simulate the cathode side of an yttria stabilized zirconia (YSZ) fuel cell [89,90], or a so-called solid oxide fuel cell (SOFC), for the objective to determine overpotential limitations for the cathode/YSZ performance.

### 4.2.2 DPD
The DPD method was introduced by Hoogerbrugge and Koelman for simulating the complex hydrodynamic behavior of isothermal fluids [91] and was further developed by Espanol [92], who included stochastic differential equations and conservation of energy. It can simulate both Newtonian and non-Newtonian fluids, including polymer melts and blends, on microscopic length and time scales. In DPD simulations, the particles represent a small cluster of atoms or molecules, and the particle-particle interactions are much softer than the particle-particle interactions used in typical molecular dynamics simulations. There-
fore, it is feasible to take much larger particle size and much larger time step, and DPD simulations are much more efficient than MD simulations for the purpose of simulating macroscopic hydrodynamics.

In general, the particles in the DPD method are defined by their mass $M_i$, position $r_i$, and momentum $p_i$. The interaction between two particles can be expressed as the sum of a conservative force $F_{ij}^C$, a dissipative force $F_{ij}^D$, a random force $F_{ij}^R$, and a harmonic spring force $F_{ij}^H$ for the system,

$$f_i = \sum_{j \neq i} \left( F_{ij}^C + F_{ij}^D + F_{ij}^R + F_{ij}^H \right)$$  \hspace{1cm} (30)

The positions and the velocities of the particles are solved in accordance with the above equations by implementing Newton’s equation of motion and a modified version of the velocity. While the interaction potentials in MD are high-order polynomials of the distance $r_{ij}$ between two particles, in DPD the potentials are softened so as to approximate the effective potential at microscopic length scales. The form of the conservative force is chosen in particular to decrease linearly with increasing $r_{ij}$. Beyond a certain cutoff separation $r_c$, the weight functions and thus the forces are all zero. Because the forces are pairwise and the momentum is conserved, the macroscopic behavior directly incorporates Navier–Stokes hydrodynamics. However, energy is not conserved because of the presence of the dissipative and random force terms.

Recently, DPD methods have been employed to model multiphase flows and among fluid particles and reproduce the microscale mechanism of classical hydrodynamics. Therefore, it belongs to the MD in length scales present in the CLs may span three to four orders of magnitude, from about 1 Å (size of an atom) up to hundreds of nanometers (end-to-end distance) [103]. This broad range of length scales includes chemical details at the atomistic level, individual chains, and microscopic features involving aggregates or self-organized chains, up to continuum phenomena at the meso- and macroscale. A proper study of the CLs requires suitable and simplified models, which allow one to focus on essential features [76]. Then, it is expected to use the multiscale simulation strategies to bridge the models, as seamlessly as possible, from one to the other.

**Fig. 13** A conceptual representation of the implementation of SOFC porous structures into a LBM model. (a) A representation of the pore structure where the white regions are the pore and the black regions represent the dense Ni and YSZ materials. (b) A binary representation of this structure, as read by the LBM, where “1” is a pore and “0” is a dense region. (c) Discrete electrochemical boundary conditions are implemented with a unique binary indicator, “2,” at the interface. False colors are used as a visual guide [99]. Reprinted from Ref. [99] with permission from Elsevier.

Recent lattice Boltzmann models are further simplified by replacing the Boolean algebra with a continuous distribution function and also by linearizing the collision operator by Bhatnagar–Gross–Krook (BGK) approximation [98] based on the idea that the rate at which collisions drive the distribution function toward the local equilibrium value depends linearly on the deviation from local equilibrium.

As an example, LBM provides an effective tool to investigate the transport phenomenon at the pore-scale level. In the TPB of fuel cells, several LB models [99] have been presented in the literature to describe the diffusion process in complex pore structures (as shown in Fig. 13), while in the CLs, an interaction-potential-based two-phase LB model was developed to study the structure-wettability influence on the underlying two-phase dynamics [100]. Further, the possible contributions for the water configuration, such as capillary pressure, gravity, vapor condensation, wettability, and microstructures of the gas diffusion layer (GDL), are discussed using the LBM [101,102].

An important advantage of the LBM is that the microscopic physical interactions of the fluid particles can be conveniently incorporated into the numerical model. Compared with the Navier–Stokes equations, the LB can handle the interactions among fluid particles and reproduce the microscale mechanism of the hydrodynamic behavior. Therefore, it belongs to the MD in nature and bridges the gap between the molecular level and the macroscopic level.

**4.3 Challenges for Multiscale Modeling.** One of the important goals about CL modeling is to rapidly and accurately predict the properties and features, which is very difficult to achieve with traditional modeling and simulation methods at single length and time scales with the current computer power. However, several challenges, both experimental and theoretical, remain as a roadblock to successful research and development, as summarized below.

**4.3.1 The Length Scales.** In particular, the smallest and largest length scales present in the CLs may span three to four orders of magnitude, from about 1 Å (size of an atom) up to hundreds of nanometers (end-to-end distance) [103]. This broad range of length scales includes chemical details at the atomistic level, individual chains, and microscopic features involving aggregates or self-organized chains, up to continuum phenomena at the meso- and macroscale. A proper study of the CLs requires suitable and simplified models, which allow one to focus on essential features [76]. Then, it is expected to use the multiscale simulation strategies to bridge the models, as seamlessly as possible, from one
scale to another. The calculated parameters, properties, and numerical information can be efficiently transferred across the scales.

4.3.2 The Time Scales. The broad range of length scales brings about a correspondingly wide range of time scales, with chemical bond vibrations occurring over tens of femtoseconds and, at the other extreme, collective motions of many chains taking seconds or much longer, while the time step in the continuum equations is governed by the smallest element in the mesh. Therefore, if the mesh is down to the atomic scale, the simulation will evolve very slowly, and many time steps will be used to simulate the dynamics in the areas of little interest. This problem will directly affect the computational cost of the simulation. A means of avoiding this issue by completely separating the two time scales would be necessary. This way, there is no restriction on the mesh to be refined to nanodimensions; therefore the continuum simulation can evolve on a larger time step.

4.3.3 The Integration Algorithms. Time integration algorithms are based on finite difference methods, where the time is discretized on a finite grid. The time step is the distance between successive points on the grid. These algorithms are only approximate and have two errors associated with them [104]. First, truncation errors arise because these algorithms involve Taylor expansions that need to be truncated at a certain order. Second, round-off errors arise from the implementation of the algorithms on operating systems, which use a finite number of digits in their arithmetical operations. Both these errors can lead to a divergence of the solution. As very small time steps need to be used in the atomistic domain, the highly iterative nature of these multiscale simulations can cause error amplification.

4.3.4 The Contact at the Interface. As with any nanosystem, contact remains a critical issue. Small atomic-level changes in the structure of the contact can have a significant impact on the contact resistance, and very little characterization data exist on most experimental contacts. Besides, even though DFT methodologies are becoming faster and more accurate, they are still too limited in realistically representing the contacts. In CNT-polymer composites [105], even if the CNTs are well dispersed, it is also needed to control and study the mechanical, electrical, and thermal coupling between polymer and CNT in much more detail. For some applications, it is necessary to design a truly multiscale method to address the contacts in different length and time scales.

4.3.5 Degrees of Freedom to Design. One of the main goals of multiscale modeling is to drastically reduce the number of degrees of freedom of engineering problems while maintaining accuracy in regions of interest. So far, the developed methods have not achieved the goal of attaining large realistic system sizes. Even with the use of parallel computing techniques, these methods still require a long time to simulate the problems of interest [104]. All single scale modeling methods provide the results that lead to an understanding of the properties under specific conditions. This information is then passed on to designers to learn from and incorporate into future designs. Thus, the multiscale modeling should be developed to demonstrate the usefulness for engineering design. Clearly, the results directing to real engineering problems can be used to assist in CL design.

5 Conclusion

In this review, an overview of the nano-microstructures of the fuel cell catalyst layer based on experimental analysis was presented. The CLs can be considered as a highly dispersed interface between Pt and electrolytes (ionomer or water). Due to the random composition and complex structure, the properties of physical and chemical processes on the Pt surface are outlined. These structural properties include the adsorption energy, the activation energy, and the reaction energy. The study of the adsorption abilities (reactant, intermediate, and product) is widely employed to understand the catalyst activity and the design of CLs. The interactions between the catalysts and the reaction species govern the reactions, and the adsorption energy is relatively easier to calculate than the reaction and activation energies.

The modeling of the nanocomposites in the CLs is a multiscale problem. Theoretical procedures have to provide quantitative predictions about elementary processes at the nanoscale and also offer the morphology of heterogeneous materials (e.g., ionomers, Pt/C agglomerate) and rationalize their effective properties. In this part, many traditional simulation techniques (e.g., MC, MD, and LB) have been employed, and some novel simulation techniques (e.g., DPD) have been developed.

Despite the significant achievements in recent years, there still exist major challenges and limitations in modeling and simulation. Developing such a multiscale method needs new and improved simulation techniques at individual time and length scales. It is also important to integrate the algorithms and explore the contact at a wider range of time and length scales. An ideal coupling method would incorporate all the positive aspects of each method into one sole approach. Therefore, when the computational burden is decreased, it would be possible to reduce the degrees of freedom. Once the efforts are directed to real engineering problems, the structural, dynamic, and mechanical properties, as well as optimizing design can be explored more effectively.

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