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Effect of Pt nano-particle size on the microstructure of PEM fuel cell catalyst layers: Insights from molecular dynamics simulations

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ABSTRACT

The effect of Pt nano-particles size on the microstructure of catalyst layers in a Polymer Electrolyte Fuel Cell is investigated by means of molecular dynamics simulations. The catalyst layer model includes carbon-supported platinum, perfluorosulfonate ionomer (PFSI), hydronium ions and water molecules. Three different Pt nano-particle sizes, i.e. 1, 2 and 3 nm, are studied, and simulations provide visualization of the distinct micro-morphologies of the CL corresponding to each nano-particle size. The results are analyzed using pair correlation functions, showing that different microstructures are obtained for different Pt nano-particle sizes, and also that inclusion of PFSI in the simulations impacts significantly the final configuration of Pt nano-particles. Water molecules are found to distribute near the side chains of PFSI and surface of Pt nano-particles, but far from the graphite surface. Side chains form clusters and exhibit different dispersion toward the Pt surface. The orientations of the side chains in the vicinity of the Pt surface are analyzed in detail. The dispersion of perfluorosulfonate ionomer is found to strongly influence the merging of Pt nano-particles and, consequently, the CL microstructure formation.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are one of the most promising candidates for providing clean energy conversion for a range of power applications ranging from milliwatt to kilowatt scales. High power density, high efficiency and low temperature operation make PEMFCs particularly well suited for road vehicles and portable electronics. The basic structure of a PEMFC consists of layers of materials/components each having specific functions. The electrolyte consists typically of a perfluorosulfonic acid ionomer membrane, which exhibits excellent ionic conductivity when well humidified. The membrane, the catalyst layers (CLs) and the two electrodes (also referred to as gas diffusion layers or GDLs) are assembled into a sandwich structure to form the so-called Membrane-Electrode Assembly (or MEA). The MEA is placed between two graphite bipolar plates with machined grooves that provide flow channels for distributing the fuel (H₂) and oxidant (O₂ from air). Hydrogen diffuses through the porous electrode and is oxidized at the anode CL, while oxygen is reduced at the cathode CL. The protons produced at the anode migrate through the polymer electrolyte membrane to the cathode, and the electrons released

at the anode flow around an external circuit to generate electric power. The electrons eventually recombine with the protons and oxygen on the cathode side to produce water.

The catalyst layer (CL) is a composite layer of order 10,000 nm thickness in which transport of reactants, products and charged species takes place in conjunction with chemical kinetics. This array of processes combined with a complex microstructure make the CL a very challenging component from the view point of fundamental understanding as well as design. Improving the performance of the CL is a pacing item in PEMFC development [1]. The microstructure formed during fabrication has a significant impact on the CL performance [2–8]. Generally speaking, carbon-supported platinum (Pt/C) and perfluorosulfonate ionomer (PFSI) are mixed together to form the microstructure during CL fabrication. The porous network established by these heterogeneous components is responsible for the transport of different species and for the electrocatalytic activity. Control and tailoring of the structure, composition and transport properties of the porous network is key to optimizing the CL not only in terms of performance, but also cost [8,9].

The carbon particles in the CL serve two functions: to support Pt, which promotes the catalytic reaction, and to conduct electrons. Different types of carbon, such as carbon black, activated carbon and graphite can be used as supporting material. Detailed chemical and physical properties of these carbon materials have been investigated by Auer et al. [2]. When supporting material and Pt are combined, individual Pt/C particles tend to aggregate and form agglomerates of dimension in the order of 100 nm. The pores within

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Fig. 1. Chemical structure of the Nafion oligomers used in the simulation.

the Pt/C agglomerate are referred to as primary pores, while those forming between different Pt/C agglomerates are the secondary pores. Increasing the PFSI content in the CL generally increases the active reaction sites in the secondary pores. However, if PFSI content exceeds optimal values [3,8,9], PFSI may partially block transport of reactant species, hence reducing the overall performance of the CL. Carbon support, surface area of carbon support, and surface area of Pt, all have a significant impact on the CL microstructure [4]. Organic solvents, which are often added into the catalyst ink in order to increase paintability, also affect the formation of CL microstructure. This is mainly due to the organic solvent residues that remain inside the CL even after heat treatment, although a steam process can be used to remove these residues [5]. Litster and McLean [6] and Antolini [7] provided comprehensive reviews of the state-of-the-art fabrication techniques, microstructural characteristic and stability of low temperature fuel cell catalyst layers. The main fabrication methods include thin film, colloidal, vacuum, and spray deposition [6,7]. While each of these techniques presents trade-off in terms of performance, quality control and cost, the thin film method is the most commonly employed technique and achieves good proton conductivity and low Pt loading [6].

The formation of the CL microstructure involves complex interactions of various species over a range of scales. The resolution and information provided by current experimental techniques is inadequate to fully describe the characteristics and formation of the CL microstructure. Computer simulations, especially molecular level techniques, have consequently become a powerful tool complementing experiments to probe the fundamentals of CL formation. Classical molecular dynamics (MD) simulations have for instance been used to study the hydronium ions and water transport in the bulk membrane of PEMFCs [10–16]. These studies have provided important insight on the conduction mechanisms of proton through sulfonated acid groups via water clusters [10,11]; on the influence of membrane water content [10] and of morphology of nanophase in Nafion [13,14]; and on the effect of temperature [15,16]. Although atomistic models are widely used to investigate ion transport in bulk membrane, there have been relatively few studies of composite catalyst layer using this approach. These include the recent work of Liu et al. [17] and Selvan et al. [18] who were able to show how structural and transport properties of water and hydronium ions at membrane/vapor interface are related to membrane water content. Lamas and Balbuena [19] examined the role of Nafion content in the CL. Malek et al. [20] performed a coarse-grained MD simulation based on meso-scale calculations

Fig. 2. Initial configuration of the Pt nano-particles for different sizes: (a) Pt38, (b) Pt201 and (c) Pt586.

(i.e. treating several atoms as one larger pseudo atom to perform the simulation) to analyze the microphase segregation during the CL fabrication process.

The dependence of the distribution of Pt particle sizes on the fabrication process is well documented [7,21–23] and the distribution has some effect on PEMFC performance [23]. The instability of Pt nano-particles for low temperature fuel cell has also been

Fig. 3. Arrangement of Pt nano-particles on graphite sheets.

discussed by Shao-Horn et al. [24], who presented evidence for different mechanisms including Ostwald ripening, crystal migration, detachment of particle from carbon support and dissolution of Pt in the ion phase. Franco and Tembely [25] proposed a mechanistic model of the electrochemical process for the aging phenomena that take place in PEMFC cathodes. Further fundamental studies and quantitative analysis are however required to improve understanding of the effect of Pt particle size on the CL microstructure. In this paper, we contribute to this by investigating the structural characteristics of the CL and the dynamics of water and ion transport via molecular dynamic simulations. The analysis is focused on the different microstructure formations that take place in the presence of various Pt nano-particle sizes and incorporates the effect of PFSI.

2. Theory

Five different species are included in the present atomistic CL model. These species are PFSI, water, hydronium ions, Pt nano-particles and carbon sheets. The PFSI used in the simulation is represented by the Nafion oligomer, consisting of six monomers. The equivalent weight of the oligomer is approximately 1100 and the structure is shown in Fig. 1. It has been reported that one of the possible equilibrium shape for Pt nano-particle is truncated cubo-octahedral [26] confirmed by some experimental data [27]. Therefore a truncated cubo-octahedral geometry is employed for the Pt nano-particles of three different sizes. These nano-particles are approximately 1, 2 and 3 nm and consist of 38, 201 and 586 Pt atoms, respectively (corresponding to Pt38/small, Pt201/medium and Pt586/large particles), cf. Fig. 2. The carbon support is modeled by two parallel graphite sheets which are arranged in an ABAB configuration. A 500 ps NVT simulation is performed for the graphite sheets alone in vacuum to allow some deformation on the graphite surface. The graphite sheets were then fixed at the rest of the simulations (the CL simulations). The initial configuration is obtained from the following procedure. Three Pt nano-particles are initially

Fig. 4. Final configuration of the simulated system (water molecules are represented by transparent Connolly surface) for (a) small, (b) medium and (c) large Pt nano-particle case.

Table 1

Composition of the system for different cases.

	Pt38/small	Pt201/medium	Pt586/large
Nafion oligomer (wt%)	18.83	16.84	15.04
Platinum (wt%)	21.14	50.02	65.1
Carbon (wt%)	46.75	20.91	9.3
H ₂ O (wt%)	12.94	11.92	10.26
H ₃ O ⁺ (wt%)	0.33	0.29	0.26
Pt coverage (mole/m ²)	0.339 × 10 ⁻⁵	1.794 × 10 ⁻⁵	5.23 × 10 ⁻⁵

put onto the graphite sheets and the distance between each particle is set within the cut-off radius. The schematic diagram of the arrangement is shown in Fig. 3. Nafion oligomers are introduced into the carbon-supported Pt model and hydronium ions are then added according to the number of side chains involved in the simulation, for the sake of electroneutrality. Water molecules are then randomly distributed into the system according to the water content (H₂O/SO₃⁻). In order to fix the weight percentage of Nafion

Fig. 5. Final configuration of Pt nano-particles for (a) Pt38-with PFSI, (b) Pt38-without PFSI, (c) Pt201-with PFSI, (d) Pt201-without PFSI, (e) Pt586-with PFSI and (f) Pt586-without PFSI.

during simulation, the number of Nafion oligomers is adjusted to meet the fixed value (~ 17 wt% in the present study). The composition of the system and corresponding Pt coverage at different Pt size cases is shown in Table 1.

All interaction forces in the simulation are calculated according to the force field, therefore, the choice of an appropriate force field is critical. The DREIDING force field [28] has been applied to study the dynamic and transport properties of the bulk membranes, yielding satisfactory results in several previous work [11,13–16,19]. We employ this force field in order to describe most of the inter- and intra-molecule interactions. The interactions between the Pt atoms are described by the Sutton-Chen model [29], which is suitable for describing metal–metal interactions in metallic systems. Simple Point Charge (SPC) model [30] is adopted for the water molecules.

Lennard-Jones potential is applied for non-bonding interaction between Pt and other species. Corresponding parameters are calculated by the Lorentz-Berthelot mixing rules [35]. MD simulations are carried out using DLPOLY [31] (version 2.19). The Verlet leap frog scheme [32] is used to integrate all the Newtonian motion equations with a time step of 0.5 fs. The temperature of the system is maintained at 300 K by the Nose-Hoover thermostat [33] with a relaxation time of 1.0 ps. We apply Periodic boundary conditions to the whole system. The bond length is constrained by the Shake algorithm [34]. The electrostatic interactions are treated by the Ewald summation method [35]. The cut-off radius is set to be 12 Å. The dimension of the simulation system is 7 nm $\times$ 8 nm $\times$ 9 nm. A 500 ps NVE simulation is first applied to the simulation system to attain an appropriate equilibrium configuration. The Nafion oligomers grad-

Fig. 6. RDF of the (a) Pt-Pt and (b) Pt-sulfur atoms.

ually deposit onto the surface of the carbon-supported Pt during this period. The NVE simulation is followed by another 1500 ps canonical (NVT) simulation. The data generated during this stage are then used for further analysis.

Each case is run on a computer cluster with (2.0 GHz AMD CPU; 16 cores for each case). The computational time varies with the system size, but typically is around 2–3 days for one case. Preliminary simulations with different time steps ranging from 2.0 to 0.5 fs were first performed. It was found that the optimal time step is around 0.5 fs in terms of computational efficiency and accuracy. The simulations analyzed here were all performed using a time step of 0.5 fs. The convergence of the system to equilibrium is ensured by monitoring the value of total potential energy and system temperature. Various initial configurations were tested to assess the influence of the initial configuration, and similar results were obtained in all cases.

3. Results and discussion

3.1. Microstructure formation

Fig. 4 illustrates the final configurations of the CL, where water molecules are represented by the transparent 3-dimensional Connolly surface [36]. The Connolly surface is formed by rolling a spherical probe which has a given radius over the van der Waals (vdW) surface of the model. The radius of the probe is set to be 1.52 Å which is the vdW radius of the oxygen molecules. A major asset of our simulations is that one can visualize CL microstructure

Fig. 7. Distribution of the side chains in the CL: (a) Pt38, (b) Pt201 and (c) Pt586 (the backbone part is hidden and side chains are represented by the S-C-C-O-C-O segments for clearer visualization).

evolution. Fig. 4 depicts that the microstructure formed at different sizes of Pt nano-particles are very different. The first finding is that neither Nafion oligomers nor water molecules entirely cover the surface of the Pt surface. There are still regions that directly expose to the void space. In the case of small Pt nano-particles, only few sulfonated acid groups are present in the vicinity to the surface of Pt nano-particle, whereas most of the side chains are positioned away from the Pt nano-particle. The small surface area of these Pt nano-particles is likely the main reason for this observation. The hydrophobic backbones of the Nafion oligomers occupy most of the available surface area, so that the side chains are pushed away from the Pt nano-particles. By increasing the size of Pt nano-particles, more sulfonated acid sites are dispersed close to the surface of Pt nano-particles. Most of the sulfonated acid sites are embedded in the water clusters. Based on this observation, three possible conduction mechanisms are speculated for reactants (e.g.

Fig. 8. Different side chain orientations (with backbone part hidden) observed during the simulation: (a) “standing” on the Pt surface and (b) “lying” on the Pt surface.

Fig. 9. RDF of the (a) sulfur–hydronium and (b) sulfur–water atoms.

Fig. 10. RDF of the (a) water–water and (b) hydronium–hydronium atoms.

H₂ or O₂) at this CL regime. (I) Dissolve into water: since there are water molecules on the Pt surface, dissolving reactants into water phase is a possible process. (II) Pt surface diffusion: reactants may be absorbed on to the Pt surface and surface diffusion is another possible conduction process. (III) Mixing process of the above two process. Although the effect of reactants was not included implicitly in our simulations, these possible conduction mechanisms can be speculated from direct observation of our simulation results.

3.2. Effect of PFSI on CL microstructure

In addition to observing the entire CL microstructure, we also study the influence of PFSI on the CL microstructure formation. First, observation of the motion of the Pt nano-particles show that these nano-particles do not move significantly during the simulation, but only exhibit slight deformation as a result of vibration of the Pt atoms. The position of each Pt nano-particle, however, remains on average at the initial configuration; cf. Fig. 5(a), (c) and (e). Although no major agglomeration of Pt nano-particles is observed in our simulations, previous simulations by Chen and Chan [37] showed that Pt nano-particles on graphite surface tend to aggregate at different Pt agglomerate sizes (20, 50, 100 and 200 atoms per Pt nano-particle). This can be explained by the presence of PFSI in our model, which was not included in the previous work in [37]. In order to clarify the influence of PFSI, we performed several independent simulations. First, all species but Pt and graphite sheets were removed from the simulation box, and simulations

Fig. 11. RDF of the (a) hydronium–water and (b) sulfur–sulfur atoms.

Fig. 12. RDF of the (a) Pt–water and (b) Pt–hydronium atoms.

were then performed under the same conditions as the original cases. Fig. 5(b), (d) and (f) shows the final positions for each Pt nano-particle size for the cases without PFSI. It is evident that the final configurations of Pt nano-particles are quite different in the presence or absence of PFSI. In the absence of PFSI, Pt nano-particles with different sizes tend to merge. These results indicate that the interactions between Nafion and Pt atoms stabilize the Pt nano-particles and prevent Pt agglomeration. The latter shows that dispersion of PFSI inside the CL is an important factor that influences the microstructure stability of the CL.

3.3. Structural analysis of the model

The site–site radial distribution functions (RDFs) are employed to study the structure evolution of different species during the simulations. The RDF is defined by:

$$\text{RDF} = \frac{\langle N(r, \Delta r) \rangle}{(1/2)N\rho V(r, \Delta r)} \quad (1)$$

where N is the total number of atoms in the system, ρ is the number density, $N(r, \Delta r)$ is the number of atoms within the spherical shell of radius $r + \Delta r$, and $V(r, \Delta r)$ is the volume of the shell; brackets $\langle \rangle$ indicates time averaging. Fig. 6(a) shows the RDFs of Pt–Pt atoms for simulations using the different nano-particle sizes. All Pt nano-particles show slight distortion while still maintaining their face centered cubic (FCC) structure. The side chains of PFSI are responsi-

ble for the proton conductivity in the CL, and Pt particles represent the active site, thus structural characteristics between these two species are important, as shown in Fig. 6 (b). Dispersion of side chains of PFSI is quite different in the case of small Pt nano-particle compared to the other cases. In addition to dispersing around the Pt surface, many side chain aggregations take place away from the Pt nano-particles in the small particle size case. This RDF result can be further elucidated by visual inspection, showing that the surface of small Pt nano-particle is mostly occupied by the PFSI backbones (in addition to few side chains). Since the region close to the Pt nano-particle is occupied, most of the side chains are dispersed away from the Pt nano-particle. In the other two cases (medium and large Pt nano-particle size), side chains are more likely to form a layer dispersed over the Pt surface. Fig. 7 shows distributions of the side chains (the backbone part is hidden for clearer visualization) in the CL for different cases. Each side chain is represented by segment which only composes of S–C–O–C–O atoms. This figure shows the distribution of side chains as well as the orientation of the side chains. In general, side chains which disperse near the Pt surface all show orientations as indicated in Fig. 8. The head (sulfur atom) of the side chain always point to the surface of the Pt nano-particle. These side chains are either “standing” (Fig. 8(a)), i.e. side chain segments are either perpendicular or inclined with respect to the Pt surface, or “lying” (Fig. 8(b)), i.e. parallel to the Pt surface. In fact, most of the side chain segments are in the “standing” orientation, and only a few side chain segments are in the “lying” orientation. The hydrophilic characteristic of side chains draw water molecules,

Fig. 13. RDF of the (a) C-S, (b) C-water and (c) carbon-hydronium atoms.

and hydronium ions distribute close to them, cf. Fig. 9. Fig. 10(a) shows that water molecules interact with each other and form clusters during the simulated period. The RDF curves shown in Fig. 10(b) exhibit a significant first peak only for the Pt38 case. These RDF distributions are similar to those for side chains shown in Fig. 11(b). Fig. 11(a) shows that hydroniums not only have strong interaction with side chains but also with water molecules. Side chains in the

Fig. 14. MSD curves of the (a) hydronium ions and (b) water molecules.

medium and larger Pt nano-particle size cases show similar cluster behavior; while those for the small Pt size case do not, cf. Fig. 11(b). This is because most side chain clusters formed in the medium and large Pt size cases tend to spread over the Pt surface, while in the small Pt size case most of the side chains tend to form clusters away from the Pt surface. These different side chain dispersion characteristics directly affect the water and hydronium ion distributions toward Pt surfaces. In general, water and hydronium ions all disperse around the Pt surface, as shown by the first peaks in Fig. 12. Examination of the RDF curves of Pt38 in Fig. 12, shows that many water molecules and hydronium ions can be found away from the Pt surface. One should notice that, for RDF curve of Pt38 in Fig. 12(b), the amount of hydronium ion increases with distance from the Pt surface. Thus, most conduction of hydronium ions takes place at locations not close to the Pt surface. The reaction cannot be completed if the hydronium ions are not conducted to the vicinity of Pt surface. Fig. 13 shows that water molecules, side chains and hydronium ions all distribute away from the carbon sheet. Side chains disperse away from the carbon surface, and the dispersion of water and hydronium ions strongly correlates with the side chain distribution (as discussed earlier and shown in Fig. 9), as illustrated by the simulation trends shown in Fig. 13(a)–(c).

3.4. Dynamics of the water molecules and hydronium ions

The dynamics of water and hydronium ions inside the CL can be characterized by the mean square displacements (MSD) which are

Fig. 15. Log plot of MSD curves of the (a) hydronium ions and (b) water molecules.

calculated based on the following equation:

$$\text{MSD} = \frac{1}{N} \sum_{n=1}^N \langle |r_n(t_0 + t) - r_n(t_0)|^2 \rangle \quad (2)$$

where N is the number of atoms, $r_n(t)$ is the position vector of atom n at time t , and t_0 is the initial time step. Fig. 14 shows the MSD curves of hydronium ions and water molecules. In most cases, the slopes in log-log plots deviate from unity. The movement of the hydronium ions in the hydrated Nafion ionomers cannot therefore be characterized as pure Brownian motion. The slopes in the log-log plots (cf. Fig. 15) vary according to the time and size of Pt particles. In the time period from 0.3 to 1.0 ns, the slopes increase with decreasing Pt particle sizes for both water and hydronium ions, i.e. the motion of the hydronium ions and water molecules becomes more random with decreasing Pt size. Diffusion coefficients of water molecules can be calculated within this short period (0.3–1.0 ns), and are 4.51×10^{-5} , 3.47×10^{-5} and $0.31 \times 10^{-5} \text{ cm}^2/\text{s}$ for Pt38, Pt201 and Pt586, respectively. The slopes in the time period 1–1.5 ns are also sensitive to the Pt size, but still deviates from unity. To further investigate the features of hydronium ion transport, the trajectories of randomly chosen hydronium ions should be taken into account. The hydronium ions belonging to large water clusters travel a relatively long distance. On the other hand, hydronium ions in small water clusters remain at their original positions. Therefore, transport of hydronium ions takes place mainly within water clusters on the surface of the Nafion ionomers and Pt particles. The motion

of the confined hydronium ions in the small water clusters is most likely anomalous. The motion of the hydronium ions in the large water clusters might be relatively close to Brownian motion, and it is expected that for longer simulation times, most of the hydronium ions will transfer between water clusters. Our primary analysis did not show any clear Brownian motion for hydronium ions over the simulation time that was achievable (1.5 ns). This simulation period is insufficient to represent the canonical ensemble of hydronium ions for our system. It involves a rather small number of ions, and hence statistics over longer simulation periods might show different diffusion behaviour. Although we do equilibrate our system before performing statistic, the system may not strictly equilibrated properly. Longer equilibration time (0.5 ns in the present study) and different equilibration methods (different annealing procedure or ensemble) is expected to yield improved diffusion data.

4. Conclusions

The effect of Pt nano-particle size on the microstructure formation of PEMFC catalyst layers has been studied using an atomistic model. MD simulations were performed for catalyst layers consisting of carbon, platinum, PFSI and water, and results presented and analyzed for three Pt nano-particle sizes. Visualization of the CL microstructures show that the Pt nano-particles are not fully covered by the PFSI/side chains, and the parts not covered by PFSI, are covered by water molecules or exposed to void space. Three possible mechanisms of ion transport are inferred from the simulation results: (I) dissolution into water (II) surface diffusion (III) dissolution into water and surface diffusion. Comparison of simulations with and without PFSI shows that the dispersion of PFSI has a significant effect on the merging of Pt nano-particles. The correlations of different species are investigated to gain insight into the structural characteristics and local configuration of the CL. Most of the PFSI side chains are found to distribute in to the vicinity of the Pt nano-particle surface and cluster with water molecules and hydronium ions. This hydrophilic aggregation formed by the side chains, water molecules and hydronium ions provide the conducting network for protons. In the case of small Pt nano-particle, most of the proton conduction happens in the region away from the Pt surface. The observed orientation of side chains which disperse close to the Pt surface can be classified into two types: “standing” and “lying”.

The atomistic scale simulations presented in this work provide some fundamental insights about the CL formation process. However, the model has some limitations. Cases of different Pt nano-particle sizes are studied, but considering uniform particle size for each case. Situations where different Pt nano-particle sizes are present are not considered in this paper. Such non-uniform particle size distributions may result in the occurrence of Ostwald ripening (migration of atoms from small nano-particles to larger nano-particles). The effect of an electric field is neglected in this paper. An electric field may enhance the aggregation of the Pt nano-particles. Inclusion of these two effects will be considered in future model developments.

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References

- [1] US DOE, Fuel Cell Handbook, 7th ed., U.S. Department of Energy, Morgantown, WV, 2004, Chap. 3.
- [2] E. Auer, A. Freund, J. Pietsch, T. Tacke, Appl. Catal. A: Gen. 173 (1998) 259.
- [3] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, J. Electrochem. Soc. 142 (1995) 4143.

- [4] M. Uchida, Y. Fukuoka, Y. Sugawara, N. Eda, A. Ohta, J. Electrochem. Soc. 143 (1996) 2245.
- [5] M. Chisaka, H. Daiguji, Electrochim. Acta 51 (2006) 4828.
- [6] S. Litster, G. McLean, J. Power Sources 130 (2004) 61.
- [7] E. Antolini, J. Mater. Sci. 38 (2003) 2995.
- [8] M. Secanell, K. Karan, A. Suleman, N. Djilali, Electrochim. Acta 52 (2007) 6318.
- [9] M. Secanell, R. Songprakorp, A. Suleman, N. Djilali, Energy Environ. Sci. 1 (2008) 378.
- [10] J.A. Elliott, S. Hanna, A.M.S. Elliott, G.E. Cooley, Phys. Chem. Chem. Phys. 1 (1999) 4855.
- [11] C.H. Cheng, C.W. Hong, J. Fuel Cell Sci. Tech. 4 (2007) 474.
- [12] S. Urata, J. Irisawa, A. Takada, W. Shinoda, S. Tsuzuki, M.J. Mikami, J. Phys. Chem. B 109 (2005) 4269.
- [13] S.S. Jang, V. Molinero, T. Cagin, W.A. Goddard, J. Phys. Chem. B 108 (2004) 3149.
- [14] A. Vishnyakov, A.V. Neimark, J. Phys. Chem. B 104 (2000) 4471.
- [15] A. Venkatnathan, R. Devanathan, M. Dupuis, J. Phys. Chem. B 111 (2005) 7234.
- [16] C.H. Cheng, P.Y. Chen, C.W. Hong, J. Electrochem. Soc. 155 (2008) B435.
- [17] J. Liu, M.E. Selvan, S. Cui, B.J. Edwards, D.J. Keffer, W.V. Steele, J. Phys. Chem. C 112 (2008) 1985.
- [18] M.E. Selvan, J. Liu, D.J. Keffer, S. Cui, B.J. Edwards, W.V. Steele, J. Phys. Chem. C 112 (2008) 1975.
- [19] E.J. Lamas, P.B. Balbuena, Electrochim. Acta 51 (2006) 5904.
- [20] K. Malek, M. Eikerling, Q. Wang, T. Navessin, Z. Liu, J. Phys. Chem. C 111 (2007) 13627.
- [21] M.S. Wilson, F.H. Garzon, K.E. Sickafus, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 2872.
- [22] M. Inaba, M. Ando, A. Hatanaka, A. Nomoto, K. Matsuzawa, A. Tasaka, T. Kinumoto, Y. Iriyama, Z. Ogumi, Electrochim. Acta 52 (2006) 1632.
- [23] K. Wikander, H. Ekstrom, A.E.C. Palmqvist, G. Lindbergh, Electrochim. Acta 52 (2007) 6848.
- [24] Y. Shao-Horn, W.C. Sheng, S. Chen, P.J. Ferreira, E.F. Holby, D. Morgan, Top. Catal. 46 (2007) 285.
- [25] A.A. Franco, M. Tembely, J. Electrochem. Soc. 154 (2007) B712.
- [26] J.W.M. Frenken, Phys. Rev. Lett. 82 (1999) 3500.
- [27] Z.L. Wang, Adv. Mater. 10 (1998) 13.
- [28] S.L. Mayo, B.D. Olfason, W.A. Goddard, J. Phys. Chem. 94 (1990) 8897.
- [29] A.P. Sutton, J. Chen, Philos. Mag. Lett. 61 (1990) 139.
- [30] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, J. Hermans, Intermol. Forces 331 (1981).
- [31] W. Smith, M. Leslie, T.R. Forester, The DLPOLY_2 User Manual, CCLRC, Daresbury Laboratory, Warrington, UK, 2008.
- [32] L. Verlet, Phys. Rev. 159 (1967) 98.
- [33] W.G. Hoover, Phys. Rev. A31 (1985) 1695.
- [34] J.P. Ryckaert, G. Cicciotti, H.J.C. Berendsen, J. Comput. Phys. 23 (1977) 327.
- [35] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Clarendon, Oxford, 1987.
- [36] M.L. Connolly, Science 221 (1983) 709.
- [37] J. Chen, K.Y. Chan, Mol. Simulat. 31 (2005) 527.