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Nanoparticle adhesion in proton exchange membrane fuel cell electrodes

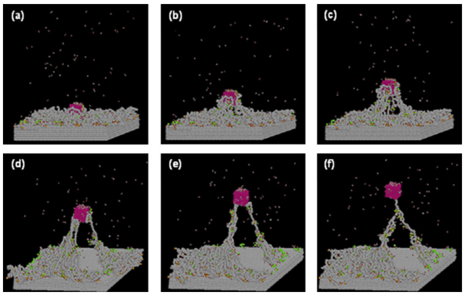
Qianping He[a], David C. Joy[b,c], David J. Keffer[b,*]

[a] Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA
[b] Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA
[c] Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

HIGHLIGHTS

- MD simulations investigate the binding energy and force of Pt nanoparticles on graphite.
- Adhesion of Pt nanoparticles to graphite is a function of particle shape.
- Adhesion of Pt nanoparticles to graphite is a function of particle size.
- Adhesion of Pt nanoparticles to graphite is enhanced by a Nafion film.
- The hydration of Nafion has a complicated effect on Pt nanoparticle adhesion.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon supported platinum (Pt/C) catalyst remains among the most preferable catalyst materials for Proton Exchange Membrane (PEM) fuel cells. However, platinum (Pt) particles suffer from poor durability and encounter electrochemical surface area (ESA) loss under operation with the accompany of Pt nanoparticle coarsening. Several proposed mechanisms have involved the Pt detachment from its carbonate support as an initial step for the deactivation of Pt nanoparticles. In this study, we investigated the detachment mechanism from the nano-adhesion point of view. Classic molecular dynamics simulations are performed on systems contain Pt nanoparticles of different sizes and shapes. A thin Nafion film (1 nm) at different hydration levels is also included in the system to study the environmental effect on nanoparticle adhesion. We found that the adhesion force strengthens as the Pt size goes up. Pt nanoparticles of tetrahedral shape exhibit relatively stronger connection with the carbon substrate due to its unique 'anchor-like' structure. Adhesion is enhanced with the introduction of a Nafion. The humidity level in the Nafion film has a rather complicated effect on the strength of nanoparticle adhesion. The binding energies and maximum adhesive forces are reported for all systems studied.

1. Introduction

Proton Exchange Membrane (PEM) fuel cells are the most popular type of fuel cells, due to their high energy conversion efficiency and power density, fast startup and low/zero emission level [1]. Yet, their further commercialization is limited at the current stage by technological bottlenecks. For example, the durability of fuel cells, especially the catalyst stability, remains one of the primary limitations for PEM fuel cells [2–6]. According to a recent review, the lifetime of transportation PEM fuel cells still need to be doubled to meet the DOE's target (5000 h) compared with lifetime value achieved in 2009 (2500 h) [7]. A molecular-level understanding of the mechanisms of the catalyst deactivation is needed to seek the next generation of fuel cell materials with improved performance and prolonged operating life.

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[*] Corresponding author. Tel.: +1 865 974 5322; fax: +1 865 974 7076.
E-mail address: dkeffer@utk.edu (D.J. Keffer).

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Carbon supported platinum catalyst (Pt/C) has remained among the most preferable catalyst materials for PEM fuel cells. It has very high kinetics for the hydrogen oxidation reaction (HOR) and one of the best electrode performances at low temperature and in the acidic environment inside PEM fuel cells [8]. However, previous studies have found that platinum (Pt) particles suffer from poor durability and will rapidly lose electrochemical surface area (ESA) under operation [9–14]. The process is usually accompanied with the behavior of Pt nanoparticle growth. Ferreira et al. proposed three fundamentally different mechanisms of Pt deactivation: (i) platinum dissolution and redeposition (the Ostwald ripening process), (ii) coalescence of platinum nanoparticles via platinum nanocrystallite migration on the carbon support and (iii) platinum particle agglomeration triggered by detachment of Pt particles from the carbon support (caused by carbon corrosion) [9]. Recently, Mayrhofer's group proposed a new corrosion mechanism for Pt catalyst, demonstrating that whole Pt particles can detach from the support and dissolve into the electrolyte without redeposition [15]. Huang's group also reported the observation of detachment of small Pt clusters from the carbon support in their MD simulations [16]. Besides, TEM images of catalyst materials before and after testing indicate that many platinum particles are not sufficiently anchored to the carbon support and move into the ionomers portion of the catalyst layer before such testing as potential cycling [17]. Furthermore, Groves et al. has attributed the Pt catalyst detachment and agglomeration to the weak interaction between the Pt and carbon support [18]. And this mechanism is also mentioned in several review papers regarding the durability enhancement of carbon supported platinum catalyst [19,20]. Experimental evidence also substantiates the link between binding energy and catalyst durability. For example, doping fullerenes with nitrogen increases the binding energy and also shows an increase in dispersion of platinum, a resistance to agglomeration of nanoparticles, and a less significant deterioration of activity when compared with pure carbon cases [21–26]. It is possible that a combination of mechanisms contribute to the observed Pt agglomeration and ESA loss. This fact has motivated many studies into agglomeration mechanism of Pt catalyst in PEM fuel cells [2,8,9,11,15,27–29]. For example, Bi et al. proposed a physical based Pt/C catalyst model with a simplified bi-modal particle size distribution and they were able to clearly demonstrate the catalyst coarsening with Pt nanoparticle growth [2]. Diloyan et al. investigated the effect of mechanical vibration on Pt particle agglomeration [8]. More et al. believe that a combination of Pt particle coalescence and Pt solution/re-precipitation within the solid ionomer is the mechanism predominantly responsible for Pt degradation [30]. Groves et al. investigate the binding energy between one Pt atom and five different graphene surfaces (one pure and four singly doped with beryllium, boron, nitrogen, and oxygen) to explore the most stable Pt-surface bond, and they believe that by finding the highest binding energy surface, the durability of a platinum catalyst can be greatly improved [18].

Many of the mechanisms discussed above originate in detachment of the Pt nanoparticle from the substrate surface, which could possibly arise from a weak binding energy between the catalyst and the carbon support. When the interaction between Pt and its substrate is not strong enough, nanoparticle detachment could easily happen under certain conditions. For example, the mechanical vibration during the automobile transportation when fuel cells are used as an alternative energy source in vehicular applications could cause shearing stresses between the bipolar plate (BP), gas diffusion layer (GDL) and membrane electrode assembly (MEA), which may lead to the deformation of MEA including the catalyst layer. The deformation of materials surrounding the Pt nanoparticles on the carbon substrate may cause the Pt nanoparticle to detach from the carbon substrate, especially in cases when Pt nanoparticles are not sufficiently anchored to the carbon support. Besides, the formation of perforations, cracks, tears or pinholes on fuel cell membrane and catalyst layer as a result of degradation could also cause external force such as detachment force on Pt nanoparticles. Therefore, investigating the nanoparticle adhesion between Pt and its carbon support could help us characterize the strength of the nanoparticle interaction with the substrate, and thus allow us to estimate how easily Pt could be detached from the carbonate support, providing both a better fundamental understanding of the mechanisms in ESA loss as well as addressing practical issues such as whether the common vibrations in automobile transportation are sufficient to induce Pt detachment.

In this work, a set of molecular dynamics (MD) simulations calculating the nanoparticle adhesion between Pt and its carbon support is conducted to study the effect of nano-adhesion on the platinum nanoparticle detachment mechanism. Specifically, the effect on adhesion of nanoparticle size, nanoparticle shape, presence of polymer electrolyte binding film, and extent of hydration are investigated. The details of the simulations, results and conclusion are presented in the following sections.

2. Simulation methodology

In the work described here, classical molecular dynamics (MD) simulations in the canonical (NVT) ensemble are performed using an in-house code written in Fortran 90 and parallelized using MPI to determine the adhesion energy and force of platinum nanoparticles on a carbon surface, intended to represent the part of the catalyst layer of a PEM fuel cell. The Pt nanoparticles are equilibrated on either a clean carbon surface or on a surface upon which a hydrated Nafion film is present. Once equilibrated the nanoparticles are pulled from the surface at a constant velocity via an externally applied force. From these simulations, the binding energy and force are measured. The molecular-level mechanisms responsible for variations in adhesion are also revealed.

Catalytic activity of Pt nanoparticles is strongly dependent on the particle size, shape and morphology. And with the advance of modern synthetic technology, Pt nanoparticles can be synthesized with various shapes (cubes, tetrahedrons, octahedrons, decahedrons, icosahedrons) bounded by different number of facets and with different defects [21,31,32]. All of these shapes were found successfully synthesized in a Nafion recast film with high yields [33–35]. In this work, four nanoparticle shapes—cubic, tetrahedral, truncated octahedral and octahedral nanoparticles—were simulated. For each shape, three nominal sizes—2 nm, 4 nm and 6 nm—were simulated. The number of atoms in the nanoparticle ranged from 56 (2 nm tetrahedron) to 14,896 (6 nm cube). As to the choice of nanoparticle size, we followed Ferreira et al. [9], who performed a size distribution analysis of 200 Pt nanoparticles in the pristine Pt/C sample and powders scraped from the cycled membrane electrode assembly (MEA) cathode surface. They found a mean particle diameter of 2.8 nm for pristine Pt/C and 5.9 nm for the cycled sample.

The nanoparticles were obtained from the bulk Pt crystal with an fcc structure, with corresponding lattice parameters ($a = b = c = 0.392420$ nm and $\alpha = \beta = \gamma = 90^\circ$) and space group of Fm-3m [36]. The various shaped nanoparticles were obtained by making cuts in the bulk crystal along the appropriate planes. The cutting planes were different depending on the shape and were always parallel to the face that had to be exposed in each case. For example for the cubic shape, three cuts were made with planes parallel to the {1 0 0}, {0 1 0} and {0 0 1} faces. Thus a cubic particle enclosed by six 1 0 0 faces was built. The Pt models used in this work are defect free. While it is known that there are slight changes