



Efficient amorphous platinum catalyst cluster growth on porous carbon: A combined molecular dynamics and experimental study



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ABSTRACT

Amorphous platinum clusters supported on porous carbon have been envisaged for high-performance fuel cell electrodes. For this application, it is crucial to control the morphology of the Pt layer and the Pt–substrate interaction to maximize activity and stability. We thus investigate the morphology evolution during Pt cluster growth on a porous carbon substrate employing atomic scale molecular dynamics simulations. The simulations are based on the Pt–C interaction potential using parameters derived from density functional theory and are found to yield a Pt cluster morphology similar to that observed in low loaded fuel cell electrodes prepared by plasma sputtering. Moreover, the simulations show amorphous Pt cluster growth in agreement with X-ray diffraction and transmission electron microscopy experiments on high performance low Pt content ($10 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$) loaded fuel cell electrodes and provide a fundamental insight in the cluster growth mechanism.

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1. Introduction

Physical and electronic properties of metal clusters deposited on various substrates have recently received a great deal of attention. Noble metal clusters, particularly Ru, Rh, Pd, Pt and Au [1], are very often used in catalytic reactions [2,3]. In heterogeneous catalysis, reactions occur at the catalyst surface, so that a high surface-to-volume ratio leading to a large fraction of accessible atoms is required for increasing the activity of the catalyst [4–6], and for decreasing its cost. There is thus a real interest to obtain the highest catalytic surface area from a low metal weight. Currently, a very important application of noble metals is their use for activating electrochemical reactions occurring in proton exchange membrane fuel cells (PEMFCs) [7–9], such as the sluggish oxygen reduction reaction [10,11]. In this latter case, Pt-based clusters are supported by nanostructured carbon substrates, among them disordered porous carbon structures [12,13] and ordered carbon structures, such as nanotubes (CNTs)/carbon nanofibers (CNFs) [14,15].

Lee et al. reported on the Pt cluster size distribution as a function of Pt loading for electrodeposited Pt nanocrystal on highly orientated pyrolytic graphite (HOPG) surfaces and demonstrated that the average cluster size increased as the Pt loading increased [16], resulting in the decrease of the active surface area. Several methods were proposed for lowering the Pt loading: by alloying Pt with foreign metal atoms [17,18], by forming Pt-based core–shell structures [19,20], by localizing the catalytic particle close to the proton conductive solid electrolyte [21], by modifying Pt cluster surface with a proton conductive polymer [22,23], etc. One of the major degradation factors of the electrical performances of PEMFC electrodes however is the agglomeration process of metal clusters under fuel cell working conditions [24,25], due to their mobility on the carbon supports [26]. It is then necessary to keep the Pt clusters well attached to and dispersed on the nanostructured carbon support to avoid their agglomeration over time, which would lead to the loss of surface area and mass activity [27]. However, Clark and Kesmodel [28] studied very small Pt clusters in the order of a few nm and demonstrated that their migration over the nanoporous surface leads to coalescence which in turn leads to the formation of a more stable and larger cluster. Accordingly, Lee et al. [16] reported that the diameter distribution of mobile Pt clusters have a maximum around 14 nm. The morphology, microstructure and interaction with the support of the metal clusters are therefore

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properties recognized as driving the activity and stability of the catalyst. Many efforts are then directed at optimizing the catalytic performance, which in turn requires a thorough understanding of both the relationship between the nanocatalyst deposition process and the nanocatalyst activity, as well as the Pt–substrate interactions [29,30]. The ability to predict – and ultimately – design stable and highly active Pt clusters supported on a porous carbon substrate is thus of paramount importance. Classical reactive molecular dynamics (MD) simulations was used to investigate the dynamical and structural evolution of platinum cluster growth on a nanostructured porous carbon substrate at the atomic scale by a plasma sputtering method. Such metal deposition method has proven to be very efficient for the preparation of highly active low Pt loaded PEMFC electrodes [31–33].

We will demonstrate how these atomic scale simulations provide insight in the influence of the deposition conditions on the cluster growth and the resulting Pt morphology. Finally, we develop a plasma method for preparing Pt cluster deposited on carbon and provide a comparison between our simulation results and experimental results on the structural and morphological evolution of the Pt-clusters during the growth, which are leading to high performance fuel cell electrodes.

2. Experimental

The deposition chamber is equipped with two rectangular targets: one of pure carbon and one of Pt_{0.01}C_{0.99}. Deposition conditions are as follows: power 530 W, target voltage 700 V, and target current 0.78 A. The growth rate is 4 nm min⁻¹. The target-to-substrate distance is 6.5 cm. Targets are 45° tilted with respect to the substrate. Conventional uncatalyzed E-Tek carbon porous layers (CPL) on a carbon woven web are used as substrates. Electrodes are loaded at 0.010 mg cm⁻²_{Pt}. The Pt loading and localization profile inside the CPL was determined by performing Rutherford backscattering spectroscopy: 90% of Pt atoms were localized in the first 200 nm depth of the material.

TEM images were obtained using a JEOL JEM 2010 (equipped with a LaB₆ filament and with a resolution of 0.35 nm). The size distribution was estimated from the determination of the diameter from 100 particles using ImageJ free software [34].

The XRD measurements were performed on a Bruker D 5005 Bragg–Brentano diffractometer operated with a copper tube powered at 40 kV and 40 mA (Cu K_{α1} = 1.5406 Å) with 0.06° step and a fixed acquisition time of 10 s/step. The catalytic powder scraped from a catalyzed CPL was deposited on a Kanthal foil and measurements were carried out in the 2θ range from 20° to 60°. The acquisition of the whole pattern was performed for 183 s at room temperature. The instrumental resolution function of the diffractometer was evaluated from the pattern (10–155.5°) of the NIST SRM 660 (LaB₆) line profile standard. XPS measurements were performed by using an Escalab MKII (VG scientific) set-up using the magnesium monochromatic beam (1253.6 eV) at room temperature at pressures below 8 × 10⁻⁹ Torr in the analysis chamber. Core level spectra were recorded at a 50 meV resolution. Binding energies were lined up with respect to the C1s peak at 284.6 eV.

The Membrane electrode assembly for fuel cell tests consisted in two 0.010 mg_{Pt} cm⁻² Pt/CPL electrodes with 5 cm² surface area mechanically pressed on a Nafion 212 membrane at 2 N m torque in the cell hardware (Electrochem). No preliminary hot pressing process of electrodes against the Nafion 212 membrane (used as received from Electrochem, Inc.) was performed. No Nafion solution was added in the electrode catalytic layers before use. Under our testing conditions, the pressure is manually regulated with the output valves and hydrogen and oxygen are humidified by bubbling in water at 80 °C and 40 °C, respectively. Measurements in a 5 cm² PEMFC using pure H₂ and O₂ gases are performed using

a ECL150/MTS 150/HSA unit (Electrochem, Inc.). The polarization curves are recorded by applying increasing current values to the cell and reading the voltage stabilization (at least 30 s stabilization time for each current value).

3. Molecular dynamics modeling

The MD simulations are intended to mimic the Pt-cluster growth process from Pt-atom deposition on a carbon nanoporous substrate. A realistic model for this substrate is constructed by applying a constrained reverse Monte-Carlo procedure designed to reproduce a set of high resolution transmission electron microscopy pictures [35]. The dimensions of the model substrate are 6 × 6 × 6 nm³, containing 17,040 atoms, corresponding to a density of 1.57 g cm⁻³ and a porosity of 48%. Periodic boundaries are applied in the lateral directions, thus exposing the top of the structure as a free surface.

2500 platinum atoms are released toward the substrate every Δt = 2 ps. The initial position of the Pt atom is 8 Å above the substrate and with randomly chosen {x,y} coordinates. Pt atoms interact with other Pt atoms and with the nanostructured carbon substrate atoms within a cut-off distance of 8 Å. The initial velocities of the incoming Pt atoms are sampled from a Maxwell-Boltzmann distribution with three most probable mean kinetic energies ⟨E_{deposit}⟩ of 1 eV, 0.1 eV and 0.026 eV and with randomly chosen incident angles. The mean kinetic energy ⟨E_{deposit}⟩ of the incoming atoms is calculated according to a modified Thompson formula for atoms travelling through a plasma [36,37] over a defined target-to-substrate distance. In the case of a mean kinetic energy ⟨E_{deposit}⟩ = 1 eV, the simulation corresponds to sputtering experiments at low argon pressure where a small amount of buffer gas only randomizes the sputtered atom velocities with little energy loss. The second case studied, ⟨E_{deposit}⟩ = 0.1 eV, either corresponds to resistive or e-beam evaporation, which produces a vapor at the vaporization temperature of ca. 0.1 eV. Plasma sputtering deposition at a gas pressure around 2 Pa also produces a vapor with mean kinetic energy around 0.1 eV. In the last case, where ⟨E_{deposit}⟩ = 0.026 eV, the simulation mimics a metal vapor at the temperature of 300 K which occurs when sputtered Pt atoms travel across an argon plasma at a pressure of around 5 Pa.

The temperature of the substrate in all simulations is assumed to be 300 K. The substrate temperature is controlled by applying a Berendsen heat bath, employing a relaxation time of 1.17 ps. The carbon–carbon interactions in the substrate are modeled by a Tersoff potential [38]. The platinum–platinum interactions are modeled through an EAM potential [39–43]. The platinum–carbon interactions are modeled using a 12–6 Lennard–Jones (LJ) potential. We used parameters that were derived by Morrow and Striolo [44], based on DFT calculations by Acharya et al. [45] for the binding energy of Pt on various graphite sites. The DFT data was then used to generate a potential energy surface, to which the Lennard–Jones interaction potential was fitted. According to this parameterization, the characteristic Pt–C interaction length is σ_{PtC} = 1.60 Å and energy, ε_{PtC} = 0.1365 eV, which are significantly different from previous sets [46–49]. Indeed, we have chosen to use this new parameterization, as the previously used sets gave rise to very weak substrate bonding and the formation of Pt clusters which are invariably crystalline, contrary to our experiments (see below).

4. Results and discussion

The condensation coefficient of Pt onto the porous substrate is 0.83 ± 0.02 and does depend on the incoming kinetic energy.

Snapshots obtained from these simulations are shown in Fig. 1, for the three impact energy distributions considered here.

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