Abstract. Platinum supported on a carbon carrier is widely used as a catalyst for polymer electrolyte membrane fuel cells. The catalytic activity is significantly affected by the size distribution and morphologies of the platinum particles. The objective of this study is to extend the phase-field approach to describe the formation process of platinum particles onto the substrate. The microstructural evolution of a nanoparticle was represented by the temporal evolution of the field variables related to the platinum concentration, long-range crystallographic ordering and phase transition. First-principles calculations were performed in order to estimate the interaction energies between several different types of platinum clusters and a graphene sheet. The platinum density profile concentrated over the substrate surface led to the formation of three-dimensional islands in accordance with the Volmer-Weber mode of growth. The size distributions of the platinum particles were sensitive to the heterogeneity of the substrate surface and to the competitive nucleation and growth processes.

1. Introduction
Recently, intensive efforts are made to develop polymer electrolyte membrane fuel cells for vehicle applications. Platinum (Pt) supported on a carbon carrier is widely used as a catalyst for fuel cell systems. Generally speaking, since smaller particles possess higher activities, Pt is dispersed on a nanometer scale. However, nanoparticles are fairly unstable and easily change the morphologies when affected by initial loading conditions and operating conditions. The degradation of the catalytic activity arising from the coarsening of the primary particle microstructure is regarded as a serious problem. Therefore, the formation process of Pt particles is of great interest from the view of retaining the activity. Pt nanoparticles that are electrochemically deposited on highly oriented pyrolytic graphite have been observed by using atomic force microscopy [1,2]. Nucleation processes tend to have the following characteristics: (1) The nucleation of three-dimensional islands occurs according to the Volmer-Weber mode of growth. (2) Pt nanoparticles grow both at step edges and on terraces. However, there is a preference for nucleation at the step edges.

The phase-field method [3] has recently attracted more attention as a possible numerical simulation for investigating nano-scale phenomena. In this study, the deposition process of Pt particles on carbon black has been investigated. Initially, we extended the phase-field approach to describe the formation process of Pt particles by correlating it with first-principles calculations. Secondly, we investigated
several aspects of Pt particles deposited on carbon black, in particular, the nucleation property such as the mode of growth and the dimensional dispersities such as the size and shape distributions arising from the heterogeneity of the substrate surface.

2. Formulation

In order to represent the multi-phase microstructure, we introduce three types of field variables related to the Pt concentration $c$, long-range crystallographic ordering $\phi$ and phase transition $\theta$. We modified the previously proposed formulation of the free energy function [4–6] in order to be appropriate for the three above-mentioned field variables. As shown in the following equation, the total chemical free energy $F_{\text{System}}$ was expressed as the integration of the local free energy and the gradient energy term over the entire system.

\[
F_{\text{System}} = \int \left[ h \left( F_{SV} + \frac{\alpha_s}{2} \left| \nabla c \right|^2 \right) + (1-h) \left( F_{LV} + \frac{\alpha_v}{2} \left| \nabla c \right|^2 \right) + g \left( \sum_i \frac{\alpha_g}{2} \left| \nabla \phi_i \right|^2 + \frac{\alpha_w}{2} \left| \nabla \theta \right|^2 \right) + cE_{Pt-C} \right] dV \tag{1}
\]

here, $F_{SV}$ and $F_{LV}$ denote the local free energies under the solid-vapor and liquid-vapor equilibrium conditions, respectively. Basically, the energies were calculated according to a regular solution model of a metal atom-vacancy complex system. The gradient energy coefficient $\alpha$ is regarded as the term related to the surface energy and vacancy formation energy. The functions $h$ and $g$ that are related to the variables $\theta$ and $c$, respectively, are used to represent the contribution of each phase. According to thermodynamics, the equilibrium state of a multi-phase system corresponds to the minimum free energy. The microstructural evolution was obtained by solving the Cahn-Hilliard [4] and Allen-Cahn [7] equations. The equations were solved using explicit finite differences.

Figure 1 shows the numerical calculation model. The dimensions of the calculation region are 40 \( \times \) 40 \( \times \) 20 nm\(^3\). The grid spacing was set to 0.2 nm. Supersaturated Pt vapor was supplied over the carbon substrate surface. The numerical simulation was conducted at a temperature of 293.15K. We constructed a carbon black surface model that was as consistent as possible with the experimental values. The crystallite size and the fraction of energetic surface sites were estimated from the X-ray diffraction profile [8] and gas adsorption isotherms [9], respectively. The interaction energy between a Pt cluster and a graphitic plane was obtained from the first-principles calculations. The energies of sites at the grain boundary are approximately two or three times larger than that of sites on the graphitic plane because of the existence of the free bonds of the carbon atoms. This model is set at the

**Figure 1.** Numerical calculation model. Carbon black surface model is set at the bottom. The values on the right-hand side show the varying range of Pt-substrate interaction energies normalized by Pt-graphene energy.

**Figure 2.** Dependence of Pt-graphene interaction energy on the coordination number of platinum. Site-dependence of single-atom adsorption energy is averaged.
bottom of the calculating region, as shown in figure 1.

First-principle calculations were performed for the model consisting of a Pt cluster and a graphene sheet in order to represent the initial nuclei of Pt deposited onto the carbon substrate [10]. For these calculations, the STATE program was employed using a plane-wave basis set. The calculations were based on the density-functional theory within a generalized gradient approximation and the ultra-soft pseudopotential method. When the coordination number of the adsorbed Pt atom increases, the interaction energy decreases, as shown in figure 2. As a result, there is no significant large interaction such as a large charge transfer between Pt and the graphene sheet. This interaction energy $E_{Pt-G}$ is added to the free energy functions by multiplying it with the Pt concentration. When the coordination number of Pt is unsaturated, this energy decreases the free energy barrier. Therefore, the Pt atoms are expected to be concentrated on the substrate surface.

3. Calculation results

Figure 3 shows the dependence of the particle sizes and nearest neighbour inter-particle distances on the Pt-loading conditions. We examined two loading conditions: The first is that the Pt atom concentration is maintained at the initial state, leading to an instantaneous nucleation. The other condition is that the Pt atoms are gradually supplied by fixing the concentration in a field far from the substrate surface, leading to a progressive nucleation. There are remarkable differences between the above two conditions. In the case of instantaneous nucleation, the particle size is nearly constant under the examined amount of loading. This is because an increase in the amount of Pt loading leads to an increase in the number of Pt particles. As a result, the inter-particle distance decreases. In the end, the distance approaches the mean diameter of the graphitic crystallite. This tendency suggests that the Pt particle dispersity is sensitive to the carbon surface heterogeneity. In the case of gradual supply of Pt atoms, the particle diameter and its standard deviation increase as the amount of Pt loading increases. This is because an increase in the amount of Pt loading leads to a heterogeneous particle growth.

![Figure 3](image-url)

**Figure 3.** Dependence of microstructural characteristics on the loading conditions: (a) Pt particle size and (b) nearest neighbour inter-particle distance. Filled squares and filled circles denote the results of instantaneous and progressive nucleations, respectively. Standard deviations are shown as error bars. The dotted line in (b) denotes the mean particle diameter of the graphitic crystallite.

Figure 4 shows the temporal evolution of the Pt density profile over the substrate surface. Islands of initial nuclei appear separately due to fluctuations in the Pt concentration induced by the heterogeneity of the substrate. Thus, the adsorbate forms three-dimensional islands instead of a complete layer; this implies that the Volmer-Weber mode of growth is dominant. The overall size of the Pt particles is found to be less than 10 nm. The particle shape is nearly spherical or hemispherical. At a glance, our results are consistent with the experimental results such as high-resolution...
transmission electron microscope images [11]. If the nucleation occurs progressively, coarsening and size dispersity become apparent. Since the growth durations of individual particles are non-uniform and nucleation competes with the growth process, in the case of instantaneous nucleation, the nucleation and growth process occur separately. Therefore, all the particles have approximately the same growth duration, and monodisperse particles are obtained. Thus, it is confirmed that size distributions of the Pt particles are sensitive to the carbon surface heterogeneity and to the competitive nucleation and growth processes.

4. Conclusions
We have examined the phase-field model utilizing the first-principles calculations as a nano-scale numerical simulation technique. This method was applied to the deposition process of Pt particles on a carbon black. The Pt density profile concentrated on the carbon black led to the formation of three-dimensional islands in accordance with the Volmer-Weber mode of growth. The size distributions of the Pt particles were sensitive to the heterogeneity of the substrate surface and to the competitive nucleation and growth processes. These results implied that the phase-field method provided a reasonable microstructural evolution of the Pt nanoparticles.

Acknowledgment
This study was supported by a grant from Core Research for Evolutional Science and Technology (CREST) by the Japan Science and Technology Agency (JST), Japan.

References
[1] Zoval J V, Lee J, Gor S and Penner R M 1998 J. Phys. Chem. B 102 1166
[2] Lu G and Zangari G 2006 Electrochim. Acta 51 2531
[3] Chen L Q 2002 Ann. Rev. Mater. Res. 32 113
[4] Cahn J W and Hilliard J E 1958 J. Chem. Phys. 28 258
[5] Chen L Q and Yang W 1994 Phys. Rev. B 50 15752
[6] Asp K and Ågren J 2006 Acta Mater. 54 1241
[7] Allen S M and Cahn J W 1979 Acta Metall. 27 1085
[8] Ungár T, Gubicza J, Ribárik G, Pantea C and Zerda T W 2002 Carbon 40 929
[9] Schröder A, Klüppel M, Schuster R H and Heidberg J 2002 Carbon 40 207
[10] Okazaki K, Yamakawa S, Morikawa Y, Akita T, Tanaka S, Hyodo S and Kohyama M 2007 in submitting to J. Phys.: Conference Series
[11] Akita T, Taniguchi A, Maekawa J, Sirorna Z, Tanaka K, Kohyama M and Yasuda K 2006 J. Power Sources 159 461