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Phase-field model for deposition process of platinum nanoparticles on carbon substrate

S. Yamakawa[1], K. Okazaki-Maeda[2], M. Kohyama[2] and S. Hyodo[1]

[1]Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan
[2]Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda 563-8577, Japan

Platinum (Pt) supported on a carbon carrier is widely used as a catalyst for polymer electrolyte membrane fuel cells. The efficiency of the catalyst is significantly affected by the size distribution and morphologies of the Pt particles. The degradation of the catalytic activity arising from the coarsening of the Pt many particle system is regarded as a serious problem. Therefore, the formation process of Pt particles is of great interest. In this study, the deposition process of Pt particles on carbon black has been investigated. The phase-field method has recently attracted increasing attention as a possible approach to understand nano-scale phenomena. 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.

Figure 1 shows the numerical calculation model. We constructed a carbon black surface model that was as consistent as possible with the results from first principles calculations and experimental characterizations [1]. The crystallite size and the fraction of energetic surface sites were estimated from the X-ray diffraction profile [2] and gas adsorption isotherms [3], respectively. The interaction energy between a Pt cluster and a graphitic plane was obtained from the first-principles calculations based on the density-functional theory within a generalized gradient approximation and the ultra-soft pseudopotential method [4]. For these calculations, the STATE program was employed using a plane-wave basis set. 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. These interaction energies are added to the free energy function using for a phase-field model by multiplying it with the Pt concentration. The bulk chemical free energy was based on the regular solution approximation to the metal-vacancy complexes. The microstructural evolution of a nanoparticle was described by the temporal evolution of the field variables related to the concentration of vacancy, long-range crystallographic ordering, and phase transition [1]. The simulation was conducted at a temperature of 293.15K. Supersaturated Pt vapor was supplied over the carbon black surface model as an initial state.

Figure 2 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. When the coordination number of the adsorbed Pt atom increases, the interaction energy between a Pt cluster and a graphitic plane decreases. As a result, there is no significant large interaction such as a large charge transfer between Pt and the graphene sheet. Thus, the Pt 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 (TEM) images. These results implied that the phase-field method provided a reasonable microstructural evolution of the Pt nanoparticles.

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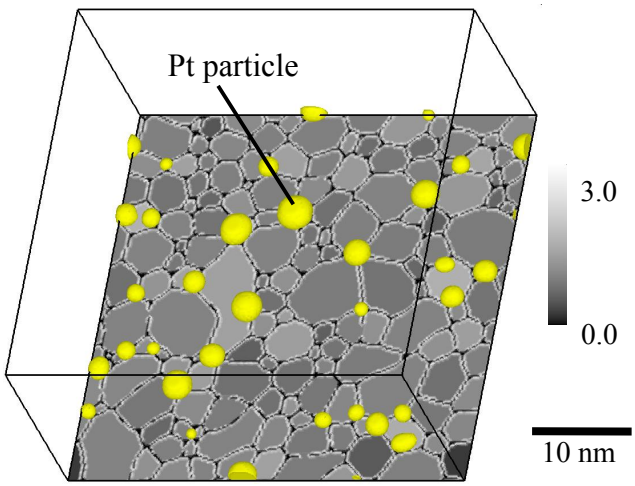

Figure 1. Numerical calculation model and quasi-stationary microstructure of Pt particles. Carbon black surface model is set at the bottom. The values on the right-hand side show the varying range of Pt-substrate interaction energies normalized by Pt-graphitic plane energy. The Pt loading condition is 1.9 mg/m^2.

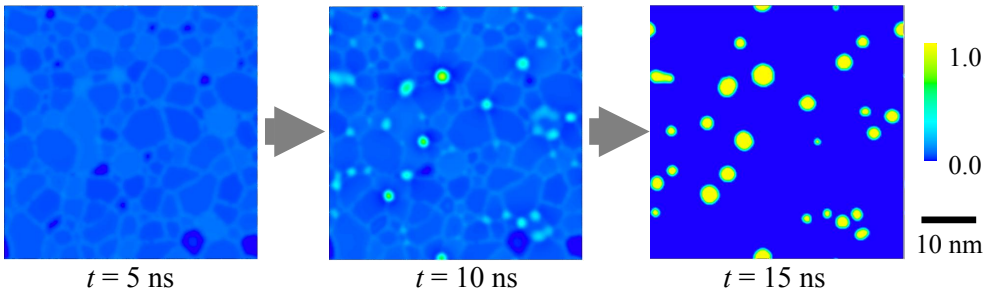

Figure 2. Pt particle growth process on a carbon black surface model. The Pt loading condition is 1.9 mg/m^2. In each figure, light dots denote the cross-sectional images of the Pt particles. The values on the right-hand side show the varying range of normalized Pt concentration.