



Surface segregations in platinum-based alloy nanoparticles



Shunsuke Yamakawa^{a,b,*}, Ryoji Asahi^a, Toshiyuki Koyama^b

^a Toyota Central R&D Labs, Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan

^b Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

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ABSTRACT

A phase-field model that describes the radial distributions of the ordered–disordered phase and surface segregation in a single-alloy nanoparticle is introduced to clarify the overall behavior of surface segregation of various Pt-based alloy nanoparticles. One of the obstacles to apply a platinum–transition metal alloy as a cathode electro-catalyst of a polymer electrolyte fuel cell is the need to ensure the retention of the designed surface composition in an alloy nanoparticle against the alloy combinations, a particle size, and heat treatment. From the results of calculations for CrPt, FePt, CoPt, NiPt, CuPt, PdPt, IrPt, and AuPt binary nanoparticles with diameters below 10 nm at 973.15 K, the compositional variation within a single particle was found to depend on the balance between the atomic interaction within particles and the surface free energy. In addition, the obtained specific steady-state composition of the surface varied significantly with alloy combination and particle diameter. Based on the general tendencies of a binary system to exhibit segregation, attempts to control the amount of platinum segregation on the surface using a ternary-alloy system were examined.

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1. Introduction

Recently, intensive efforts have been made to develop polymer electrolyte fuel cells (PEFCs) for applications in vehicles [1]. Nanoscale particles of platinum supported on a carbon carrier are widely used as a catalyst for PEFCs. To achieve further improvement in the oxygen reduction reaction (ORR) in the cathode layers of PEFCs, implementations of platinum–transition metal alloy nanoparticles as cathode electro-catalysts are expected [2]. The alloying technique is also expected to reduce the required amount of platinum loading by replacing some platinum with less expensive metals. Because the catalytic activity of the alloys in the ORR is significantly affected by the surface structure, the surface structure of the platinum alloy nanoparticles has been evaluated as a function of the alloying element and its composition [3]. Theoretical estimations, including first-principles calculations, indicate that the catalytic activity of a Pt–3d-transition-metal binary alloy depends on the oxygen adsorption energy, which is explained by the d-band center [4]. Among numerous candidate alloys, the catalytic activities of some Pt-based alloys are predicted to be superior to that of pure platinum. Recently, evaluations of the electro-catalyst alloy system have been expanded from binary to ternary alloys [5,6].

On the other hand, it has been experimentally observed that the alloy compositions of nanoparticles often differ from the nominal bulk composition, because the variability in surface energy caused by the particle size distribution influences on the thermal equilibrium

microstructure [7]. Therefore, the phase state and atomic composition of an alloy nanoparticle must be discussed in association with the alloying combinations, particle size, and heat treatment temperature. We believe that computational simulation can play a key role in understanding and predicting surface properties.

Atomistic simulations such as first-principles calculation, molecular dynamics, and Monte-Carlo simulation have been regarded as powerful tools to accurately probe the mechanism of microstructural formation from the viewpoint of atomic motion. However, in practical calculations, the system size is limited by an increase in the computational cost. In our previous study [8], as an alternative approach, we proposed a continuum method based on the thermodynamic theory of alloys and the surface free energy which simultaneously calculates the atomic segregation and phase transformations within single platinum-based alloy nanoparticles. According to thermodynamics, the steady state of the atomic distribution and phase parameter corresponds to the minimum free energy. This numerical simulation technique, the so-called phase-field method, has sufficient accuracy to evaluate the effects of the particle size, alloy composition, and heat-treatment temperature on the ordered–disordered and solid–liquid phase transitions, and thus describes the atomic surface segregation in Pt-based binary alloy nanoparticles.

In the present paper, we first examine the surface compositions resulting from the balance between the surface and the chemical interaction among atomic components for various alloy combinations. The radial distribution of the phase state and the atomic compositions of CrPt, FePt, CoPt, NiPt, CuPt, PdPt, IrPt, and AuPt nanoparticles with diameters below 10 nm at 973.15 K were investigated. In addition, the validity of the simulation results were examined through comparisons with

* Corresponding author at: Toyota Central R&D Labs, Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan. Tel.: +81 561 71 7127; fax: +81 561 63 5258.

E-mail address: e1044@mosk.tytlabs.co.jp (S. Yamakawa).

previously reported Monte Carlo simulations. Second, with these results, a general scheme of the binary-alloy system to obtain a thinly coated Pt surface structure in a nanoparticle is derived. Finally, applications of this method to a ternary-alloy system are presented.

2. Computational details

The distribution of the alloy composition and the ordered–disordered phase from the center to the surface in a single spherical particle is evaluated by performing a one-dimensional phase-field calculation along the particle radial coordinates. The details of the numerical calculation scheme for a binary-alloy nanoparticle were presented in our previous paper [8]. In the present paper, this model is extended to a multinary alloy system.

The conservative temporal evolution of the atomic concentration can be calculated by solving the following equation:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left[\sum_{j=1}^{n-1} M_{ij} \nabla \left(\frac{\delta G_{\text{sys}}}{\delta c_j} \right) \right], \quad i \leq n-1, \quad (1)$$

where c_i is the local atomic concentration of component i as a function of the radial coordinate, r , and the time variable, t , and its value is normalized with respect to the maximum concentration so that it is a dimensionless value between 0 and 1. In the present paper, the binary-alloy (TM–Pt) system is represented by a three-component setup ($n = 3$): Pt (component 1), the transition-metal element alloyed with platinum TM1 (component 2), and the vacancy Va (component 3). In a ternary-alloy (TM1–TM2–Pt) system, component 3 corresponds to the secondary transition-metal element TM2 and component 4 corresponds to the vacancy. The coefficient M_{ij} is the mobility of component i owing to the gradient of the functional derivative of G_{sys} with respect to the concentration of component j ; it is expressed as

$$M_{ii} = c_i(1-c_i)D/RT; \quad M_{ij} = M_{ji} = -c_i c_j D/RT. \quad (2)$$

Here, D is the self-diffusion coefficient; R and T are the gas constant and absolute temperature, respectively. The temporal evolution of the concentration of each component can be calculated under the following condition:

$$\sum_{i=1}^n c_i = 1. \quad (3)$$

The equilibrium radial distributions of the ordered phase–disordered A1 fcc phase within a nanoparticle can be calculated by solving the following non-conservative equation:

$$\frac{\partial s_i}{\partial t} = -L_s \frac{\delta G_{\text{sys}}}{\delta s_i}, \quad (4)$$

where $\mathbf{S} = (s_1, s_2, s_3)$ is defined as the three-component long-range order (LRO) parameter [9]. The parameter (s_1, s_2, s_3) is represented by the values of (1, 0, 0) for complete L1₀ and L1₁ ordering, and (0.5, 0.5, 0.5) for L1₂ ordering. The coefficient, L_s , is the mobility of the ordered–disordered phase interfaces.

The total free energy of the simulated system, G_{sys} , is defined as the volume integral of the local chemical free energy and gradient energy over the entire volume, V , as follows:

$$G_{\text{sys}} = \frac{1}{V} \int \left[G_{\text{chem}} + \frac{1}{2} \sum_{i=1}^n \kappa_i (\nabla c_i)^2 + h(c) \frac{\kappa_s}{2} |\nabla s|^2 \right] dV, \quad (5)$$

$$c = \sum_{i=1}^{n-1} c_i, \quad (6)$$

$$h(c) = c^3 (6c^2 - 15c + 10). \quad (7)$$

Here, G_{chem} denotes the changes in the bulk chemical free energies and is evaluated together with the approximation of the regular solution model as follows:

$$G_{\text{chem}} = \sum_{i=1}^{n-1} c_i G_i + \sum_{i=1}^{n-1} \sum_{j=2, j \neq i}^n L_{ij} c_i c_j + \Delta G^{(\text{ord})} + RT \sum_{i=1}^n c_i \ln c_i, \quad (8)$$

where G_i is the Gibbs formation energy of pure element i in the solid phase from the SGTE (Scientific Group Thermodata Europe) data [10]; L_{ij} ($i, j < n$) and $\Delta G^{(\text{ord})}$ are provided as polynomial equations with respect to the atomic concentrations based on the thermodynamic assessments of the Cr–Pt [11], Fe–Pt [12], Co–Pt [13], Ni–Pt [14], Cu–Pt [15], Pd–Pt [16], Ir–Pt [17], Au–Pt [18], Fe–Cr [19], and Cr–Ir [20] binary systems using the CALPHAD (CALCulation of PHASE Diagrams) method. If the thermodynamic field is not spatially uniform, the bulk free energy, G_{chem} , must be supplemented by an additional energy term with respect to the gradients of the field variables to account for the interfacial interactions. The term κ_i ($i < n$) represents the gradient energy coefficient with respect to the solid–solid interface between two co-existing phases of mixtures with a miscibility gap:

$$\kappa_i = \left(\sum_{j \neq i}^{n-1} c_j \kappa_{ij} \right) / \sum_{j \neq i}^{n-1} c_j, \quad i \leq n-1. \quad (9)$$

The variable, κ_{ij} , represents a significant value in binary systems such as Ir–Pt and Au–Pt with a miscibility gap. Using the interfacial energy heights estimated from the CALPHAD data and assuming an interface width of 1×10^{-9} m, the values of κ_{ij} for the Ir–Pt and Au–Pt binary systems were determined to be 1.66×10^{-15} and 1.67×10^{-15} J·m²·mol⁻¹, respectively.

The coefficient, L_{in} , represents the interaction energy between alloy element i and a vacancy. The coefficient, κ_n , represents the gradient energy coefficient with respect to the solid–vapor interface. Both are obtained using the following equations:

$$L_{in} = \Delta H_{f,i} - T \Delta S_f, \quad (10)$$

$$\kappa_n = \frac{1}{c} \sum_{j=1}^{n-1} c_j (\kappa_{nj} - \kappa_j), \quad (11)$$

where $\Delta H_{f,i}$ and ΔS_f are the enthalpy and entropy of mono-vacancy formation, respectively. The ΔS_f value adopted an approximate formulation of $1.32R$, which was originally used for platinum [21]. The values of $\Delta H_{f,i}$ and κ_{nj} were calculated simultaneously based on the (111) surface energy [22–24] of the pure metal element and assuming an interface width of 3×10^{-10} m. The evaluated values are listed in Table 1.

Table 1
Estimated parameters for alloy elements at 973.15 K.

Atomic element	Mono-vacancy formation energy, $\Delta H_{f,i}/96,485 \text{ J} \cdot \text{mol}^{-1}$	Gradient energy coefficient, $\kappa_{nj}/10^{-15} \text{ J} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
Cr	1.85	6.76
Fe ^a	1.65	5.81
Co ^a	1.45	5.03
Ni ^a	1.31	4.38
Cu ^a	1.05	2.89
Pd	1.22	3.86
Ir ^a	2.15	8.15
Pt ^a	1.42	4.92
Au	0.96	2.74

^a Ref. [8].

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