Original Article

Tracking the Mn Diffusion in the Carbon-Supported Nanoparticles Through the Collaborative Analysis of Atom Probe and Evaporation Simulation

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Abstract

Carbon-supported nanoparticles have been used widely as efficient catalysts due to their enhanced surface-to-volume ratio. To investigate their structure–property relationships, acquiring 3D elemental distribution is required. Here, carbon-supported Pt, PtMn alloy, and ordered Pt3Mn nanoparticles are synthesized and analyzed with atom probe tomography as model systems. A significant difference of Mn distribution after the heat-treatment was found. Finally, the field evaporation behavior of the carbon support was discussed and each acquired reconstruction was compared with computational results from an evaporation simulation. This paper provides a guideline for studies using atom probe tomography on the heterogeneous carbon-supported nanoparticle system that leads to insights toward a wide variety of applications.

Key words: atom probe tomography, carbon-supported nanoparticles, field evaporation simulation, intermetallic compounds, local magnification effect

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Introduction

Atom probe tomography (APT) is a powerful analytical method for mapping the three-dimensional (3D) atomic distribution and determining the local chemical composition of materials with sub-nanometer spatial resolution and ppm-level elemental sensitivity (Kelly & Miller, 2007; Gault et al., 2012; Miller, 2012; Felfer et al., 2018). Due to its unique capability, this technique has been adopted to reveal grain boundary segregation (Kim et al., 2020; Lee et al., 2019; Jung et al., 2019). Due to its unique capability, this technique has been adopted to reveal grain boundary segregation (Kim et al., 2020; Lee et al., 2019; Jung et al., 2019). Due to its unique capability, this technique has been adopted to reveal grain boundary segregation (Kim et al., 2020; Lee et al., 2019; Jung et al., 2019). Since investigation of chemical composition and information of 3D elemental distribution is very important in the understanding of property–structure correlation in nanoparticles, there have been many analysis attempts with APT (Barroo et al., 2019; Lee et al., 2019a). Tedsree et al. analyzed Ag–Pd core–shell metal nanoparticles to reveal the relationship between formic acid decomposition and Pd shell thickness (Tedsree et al., 2011). Li et al. performed APT measurements on the carbon-supported Pt, Pt/Co alloy, and Ir–Pt core–shell nanoparticles by depositing the nanoparticles to pre-sharpened tips using electrophoresis (Li et al., 2014). Feller et al. used PVD-Cr sputtering on the Au–Ag core–shell nanoparticles dispersed on the Si substrate to embed the nanoparticles (Feller et al., 2014). More recently, Qiu et al. have analyzed Au nanoparticles contained in aqueous solution using a graphene encapsulation technique to observe the liquid–NP interface (Qiu et al., 2020). Among these emerging sampling techniques, Kim et al. developed the co-electrodeposition of a metal to embed various nanomaterials including freestanding hollow TiO2 nanowires (Lim et al., 2020), MoS2 nanosheets (Kim et al., 2020), Li4Ti5O12 (Kim et al., 2022), Pd nanoparticles (Kim et al., 2018; Jang et al., 2021), and Pd@Au core@shell nanoparticles (Kim et al., 2020a).

While successful APT measurements of the nanoparticles have been performed using the aforementioned methods, the discussions of the analyzed data are mainly focused on nanoparticles, and the effect of the carbon support has often been neglected. For the fuel cell catalysts, Pt-based nanoparticles showing catalytic activity are loaded on the carbon support for purpose of improving nanoparticles’ dispersion and maximizing electrochemical surface area. Carbon black is comprised of amorphous carbon particles with sizes of 15–50 nm (Uchida et al., 1995). Because of their high electrical conductivity (4 S/cm) and large surface area (58–1,500 m2/g), they are used as carbon supports (Antolini, 2009).

The community has recently started to expand the analysis capabilities to carbon-based materials, such as carbon fiber (Johansen et al., 2021; Johansen & Liu, 2021), carbon nanotubes (Raghuvanshi et al., 2020), diamond (Schirhagl et al., 2015), graphene (Exertier et al., 2021), and self-assembled decanethiol molecules (Gault et al., 2010; Stoffers et al., 2012; Solodenko et al., 2021).
not limited to metals or intermetallic compounds. However, since elemental carbon has the highest intrinsic evaporation field compared with any metallic element, the accurate data interpretation of carbon materials, i.e., the carbon black support, is challenging; the evaporation field value of covalent-bonded carbon is calculated to be 103 V/nm, whereas most metals show theoretical evaporation fields in the range of 15–60 V/nm (Gault et al., 2012; Larson et al., 2013). Due to the high evaporation field, the analysis of covalent-bonded carbon in pulsed laser mode requires a high laser pulse energy, ranging up to 500 pJ (Schirhagl et al., 2015). More importantly, the presence of a carbon support adjacent to a metallic nanoparticle will generate inhomogeneous evaporation behavior at the specimen’s surface and eventually result in a distorted 3D atom map of the actual specimen, which is known as the local magnification effect (LME). The LME is critical to the data reconstruction algorithm since it influences atomic density fluctuation, interface shape distortion, and apparent intermixing of phases in acquired data that may provide mis-interpretation. The area of the LME affected region can reach up to a few nanometers (Madaan et al., 2015) depending on both composition and structure, thus, it is crucial to study the artifacts caused by the carbon support on the nanoparticles and validate the reliability of the carbon-nanoparticle APT data.

Hence, for demonstration, we have chosen a series of PtMn and Pt$_2$Mn nanoparticles that are known as effective oxygen reduction electro-catalysts (Peng et al., 2020; Lim et al., 2022) as our model systems for investigation of the carbon-nanoparticle field evaporation. Here, we compared the acquired APT data of each nanoparticle sample with numerical simulation using TAPSim software developed by Oberdorfer et al. (2013) systematically. With a better understanding of the evaporation artifacts induced by carbon support, the Mn and Pt elemental distributions are subsequently correctly interpreted. Detailed discussions about catalytic activity and stability dependence on the structure of the nanoparticles are provided in previous report (Lim et al., 2022).

**Experimental Section**

**Materials**

Manganese (III) acetylacetonate [Mn(acac)$_3$, technical grade], 2-hexadecanediol (HDD, 90%), and diphenyl ether (99%) were purchased from Aldrich. Cobalt sulfate heptahydrate (CoSO$_4$$\cdot$7H$_2$O, 98%), cobalt chloride hexahydrate (CoCl$_2$$\cdot$6H$_2$O, 97%), and boric acid (H$_3$BO$_3$, 99.5%) were purchased from Daejung Chemicals & Metals. All other reagents were purchased from Samchun Chemical. All chemicals were used as received without further purification.

**Preparation of Carbon-Supported Nanoparticles**

To synthesize PtMn/C catalysts, 12 mg of manganese (III) acetyl-acetonate [Mn(acac)$_3$], 250 mg of 2-hexadecanediol (HDD), and 50 mL of diphenyl ether were mixed in a 200 mL three-neck flask and sonicated for 5 min. Next, 50 mg of commercial Pt/C (TKK, 20 wt% Pt) dispersed in 5 mL of hexane was injected into the prepared solution. The mixture was heated to 259°C for 30 min while stirring at 100 rpm. After the reaction, PtMn/C catalysts were synthesized and extracted from the resultant mixture solution by adding acetone and washed three times with a 40 mL of mixture of acetone and hexane (3:1). After the washing procedure, the PtMn/C catalysts were dried in a vacuum for 12 h. Atomically ordered Pt$_3$Mn/C catalysts were obtained by applying heat treatment on the synthesized PtMn/C catalysts, at 700°C under the reductive atmosphere (4% H$_2$ and 96% Ar) for 4 h.

**Preparation of Atom Probe Specimens**

In order to embed the carbon-supported nanoparticles in a metal film, we performed co-deposition of the nano-catalysts with the Co film. Co was selected as a matrix material since Co has a single isotope in nature. A Co electrodeposition bath was prepared by dissolving 48 g of CoSO$_4$$\cdot$7H$_2$O, 12 g of CoCl$_2$$\cdot$6H$_2$O, and 9 g of H$_3$BO$_3$ in 250 mL of distilled (DI) water. Dried nano-catalysts were weighed and dispersed in the Co bath solution in 0.1 g/L ratio. After the mixture was sonicated for 30 min at room temperature, 1 mL of colloidal solution was immediately transferred to a vertical cell with Cu foil (0.2 cm$^2$ surface area) as a cathode and the Pt wire as an anode. Pulsed electrodeposition with a 10% duty cycle and 0.1 Hz pulse frequency was performed to enhance the number density of the embedded nanoparticles and to reduce the formation of H$_2$ bubbles (Jun et al., 2021). Each specimen was electrodeposited for 8,000 s.

In order to facilitate the site-specific lift-out and increase the chance of capturing the nanoparticles within the topmost region of the resulting atom probe specimen, a new approach using cross-sectional sampling was developed (see Scheme 1). In a previous sample preparation method (upper part in Scheme 1), an electrodeposited composite film of nano-catalysts and matrix on a substrate was directly moved to a dual-beam focused ion beam (FIB, Helios NanoLab 450 F1) chamber. By contrast, in this study’s modified method (lower part in Fig. 1), the composite film was vertically mounted in a conductive resin, and polished to reveal the cross-section of electrodeposited matrix. A wedge of composite material is extracted using the standard lift-out procedure, and fabricated into an APT specimen by annular milling, as described in the previous report (Thompson et al., 2007). We describe the detailed observation of APT specimens in Supplementary Figure S1.

**Characterization**

The crystal structures of the synthesized PtMn/C, Pt$_2$Mn/C, and commercial Pt/C (TKK, 20 wt% Pt) catalysts were determined by X-ray powder diffraction (XRD; RIGAKU SmartLab operated at 45 kV and 200 mA using Cu-Kα radiation). Bright-field transmission electron microscopy (BF-TEM) images were obtained using an FEI Tecnai TF30 ST operated at 300 kV. Aberration-corrected high-angle annular-dark field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) were performed at 300 kV in an FEI Titan cubed G2 60-300. APT analyses were carried out using a local electrode atom probe (CAMECA Instruments LEAP 4000X HR™) at a base temperature of 50 K. The laser pulse energy and frequency were 50 pJ and 125 kHz, respectively. Data reconstruction and analyses were performed with the IVAS 3.8.2 software provided by CAMECA instruments.

**Simulations of Field Evaporation**

To investigate the evaporation field-induced artifacts during the atom probe measurement, a computational simulation, using the TAPSim software, developed by Oberdorfer et al. (2013),...
was performed. Virtual APT specimens consisting of Co, with a radius of 6 nm, a shank angle of 20 degrees, a total length of 15 nm, and a lattice parameter of 0.36 nm were constructed using a custom Python 3.8 script. Each carbon-supported nanoparticle (Pt/C, PtMn/C, and Pt3Mn/C) was included in the virtual APT specimens, respectively, based on the detected number of atoms from APT results. PtMn nanoparticle was set to have Pt core with a radius of 1.320 nm and Mn shell with a thickness of 0.145 nm, yielding a 3:1 ratio of Pt and Mn. The Pt3Mn nanoparticle was set to have a homogeneous-ordered L12 structure. Additionally, a carbon sphere with radius of 15 nm adjacent to the metallic nanoparticle was included in the specimen as a representation of the carbon support. The center of the carbon sphere had the same height as the metallic nanoparticle.

Evaporation fields of each metallic element in the nanoparticles were set at 37, 30, and 45 V/nm for Co, Mn, and Pt, respectively, referring to the theoretically calculated evaporation field values (Gault et al., 2012; Larson et al., 2013). In addition to the predicted value of 103 V/nm, the evaporation field of a carbon support was varied from 50 to 75 and to 103 V/nm for systematic study. The evaporation simulation was performed at fixed temperature of 0 K, and the effect of laser pulse was not accounted for in the simulation. The resulting detector hit map data from TAPSim evaporation simulation was reconstructed using a standard shank angle reconstruction protocol (Larson et al., 2013), and re-visualized using IVAS 3.8.2 software.

Results and Discussion

Characterization of Carbon-Supported Nanoparticles

XRD measurements were performed to analyze the crystal structures of catalysts (see Supplementary Fig. S2). The background peak at 2θ of 20–30 degree representing amorphous carbon
(Ungar et al., 2002) is observed in all samples. In both Pt/C and PtMn/C samples, the relatively board peaks are originated from the disordered FCC Pt. No Mn-related peak is found. After the reductive heat-treatment of PtMn/C, the ordered FCC peaks were observed, indicating Mn ions were first reduced during the reaction in the solution and heat-treatment induced the chemical ordering of PtMn. The average diameters of Pt/C, PtMn/C, and Pt3Mn/C were measured to be 2.6 ± 0.4, 3.3 ± 0.5, and 4.2 ± 0.8 nm, respectively (see Supplementary Figs. S3a–S3c), implying a mild agglomeration occurred during the heat-treatment at 700°C, which is in accordance with the calculation result using the Scherrer equation (see the Supplementary Material). In addition, high-resolution STEM-EDX results from the Pt3Mn/C showed a fully ordered Li2 structure (see Supplementary Fig. S3d; Jung et al., 2017).

**APT Results of Carbon-Supported Pt Nanoparticles**

Figure 1a shows the 3D atom map of the Pt/C embedded in the Co matrix. There are low-density volumes with a small amount of Co atoms at the top-right and bottom-left side of the specimen (see Fig. 1a). In addition, Pt and C atoms were detected with high density at the border between low density and normal region. A two-dimensional (2D) contour plot, a graphical technique for representing the atom-density surface of overall collected atoms by plotting along the measurement direction, taken using plate-shaped ROI with dimension of $60 \times 60 \times 0.1$ nm$^3$ illustrates a clear low-density region in the reconstructed specimen (see Figs. 1b, 1c). Low-density regions in Figures 1b and 1c are facing different directions, indicating that the direction of density fluctuation is not linked with incident laser direction, but rather likely to be caused by preferential evaporation and the resulting local magnification effect. Figures 1d and 1e show the one-dimensional (1D) concentration and the number of detected atoms taken with a cylindrical ROI with dimension of $3 \times 3 \times 30$ nm$^3$, placed across the Pt particles located on the interface between nanoparticle and matrix. Standard error values were calculated as the following equation: 

$$\sigma = \sqrt{\frac{1}{N_c}}$$

where $\sigma$ is the standard error, $c_i$ is the concentration of each element, and $N_c$ is the number of atoms of each element (Miller & Forbes, 2014). Every error bar represented in this study was calculated by using the above equation. Measured diameters of Pt particles were 2–3 nm based on a full-width half-maximum of the Pt concentration in 1D concentration profile (Fig. 1e). It is noteworthy to mention that the shape and size of the observed particles contain artificial effects (which will be discussed in the section below). More importantly, Pt atoms were detected at the border of low-density and normal-density regions. Since Pt nanoparticles were located between carbon support and electrodeposited Co layer, these severe density fluctuations imply the strong LME occurred due to their large evaporation field difference.

**Simulated Results of Carbon-Supported Pt Nanoparticles**

In APT analysis data of carbon-supported metallic nanoparticles, two major artifacts, namely formation of low-density area and overlapping of constituent elements, were observed. Both artifacts are reported to occur in atom probe analysis of specimens containing phases with large evaporation-field differences (Kim et al., 2020a; Jun et al., 2021). To elucidate what causes the severe distortion, TAPSim analyses were conducted on each nanoparticle/carbon case. Figure 2 shows evaporation simulation result of the virtual APT specimen containing the Pt nanoparticle (red) on the carbon support (purple), performed using various evaporation field of carbon. In the initial state before evaporation (Fig. 2a), the atomic density is uniform across the whole specimen. The 2D contour plot (Fig. 2e) taken from the XY plane across the nanoparticle (dotted square in Fig. 2a) thus shows uniform distribution inside the nanoparticle. 1D concentration profile across the nanoparticle from carbon support toward Co matrix is given in Figure 2f. The number of detected atoms per fixed bin width of 0.2 nm (marked as blue squares) is uniform, indicating that the number density of atoms is uniform across the atom map regardless of whether C (marked as black squares) or Pt (marked as red squares) is enriched at the position.

As the evaporation-field value of carbon increases from 50 to 103 V/nm, a larger distortion in shape and density of the reconstructed atom maps (Figs. 2b–2d) is observed. While the phase with the lower evaporation field (Co matrix, Pt nanoparticle) laterally contracts, the phase with the higher evaporation field (C support) expands, resulting in increased atomic density at Co/Pt region and severely decreased atomic density at carbon support region. A 2D contour plot taken across the XY plane across the nanoparticle from each atom map (Figs. 2f–2h) supports this observation, showing higher atomic density at Co/Pt region, and lower atomic density at carbon support region. In the 1D concentration profile across Pt clusters in each atom map (Figs. 2j–2L), a clear separation of the low-density region and normal-density region is observed. The atomic density rises more sharply as the evaporation field of carbon support increases. Additionally, the peak of Pt concentration is located at the border of the low-density and normal-density region, which is in good qualitative agreement with the APT analysis result (Fig. 1). The result indicates that the large evaporation field difference between metal and carbon atom could cause the severe density fluctuation within the atom map during APT analysis of carbon-supported metallic nanoparticles.

**APT Results of Carbon-Supported PtMn and Pt3Mn Nanoparticles**

In order to reveal the difference in the distribution of Mn atoms and the concentration of the as-synthesized PtMn/C and Pt3Mn/C catalysts, APT measurements were performed. Mass spectra of both atom maps are given in Supplementary Figure S4. Both mass spectra have showed mass peaks originating from Co, Mn, C, O, and Na. Elements included in electroplating solution other than Co, i.e., B and Cl, were also observed in both mass spectra. Figures 3a and 3b show 3D atom maps of the PtMn/C and the Pt3Mn/C cylindrically cut with a diameter of 25 nm and a thickness of 25 nm, including iso-concentration surfaces of 2.5 at% C (black surfaces) and 4 at% Pt (red surfaces). The high evaporation-field difference among multi-elements (Pt, Mn, Co, and C) as well as uneven evaporation of carbon complexes results in overlapping of the elements between nanoparticles and matrix. Pt-rich volumes represent the PtMn or Pt3Mn nanoparticles. In order to calculate the chemical compositions of nanoparticles, we cut the cubic region of interest with volume of $10 \times 10 \times 10$ nm$^3$ and counted the number of atoms for Pt and Mn. The resulting compositions of nanoparticles were 73.8 ± 1.2 at% of Pt and 26.2 ± 1.2 at% of Mn for PtMn nanoparticle and 79.8 ± 0.8 at% of Pt and 20.2 ± 0.8 at% of Mn for Pt3Mn nanoparticles,
Fig. 2. Simulated 3D atom maps of APT specimen containing Pt/C nanoparticle (a) before evaporation, after evaporation simulation of Pt/C with evaporation field of carbon set at (b) 50, (c) 75, and (d) 103 V/nm, (e–h) 2D contour plots, and (i–l) 1D concentration profiles from each atom map (direction: yellow arrow in atom maps).
respectively, which are close to the composition of Pt\(_3\)Mn intermetallic compound.

Figures 3c and 3d show detected Pt and Mn atoms in the nanoparticles. The majority of Mn atoms were measured at the center of the nanoparticles in Pt\(_3\)Mn/C revealing a homogeneously distributed concentration profile (Fig. 3f), whereas in PtMn/C nanoparticles, the Mn atoms were observed near the outer surfaces of the particle (Fig. 3e) indicating a core–shell structure. In addition, Mn atoms were mainly detected in the form of Mn\(_2\)O ions in PtMn nanoparticles compared with the Pt\(_3\)Mn nanoparticles (see Supplementary Figs. S5 and S6). These Mn\(_2\)O ions were located at near the surface of both particles. 3D ion maps and 1d concentration profiles for additional PtMn (Supplementary Fig. S5) and Pt\(_3\)Mn nanoparticles (Supplementary Fig. S6) are shown in the Supplementary material.

Simulated Results of Carbon-Supported PtMn Nanoparticles

Since the computational simulation has shown that position and concentration artifacts could occur in the region near to the carbon support, the reliability of the relative position of Mn and Pt atoms could be also questioned. In order to find out whether the distribution of Mn atoms within nanoparticles could be analyzed under the effect of the carbon support, evaporation simulation with APT specimens containing PtMn and Pt\(_3\)Mn nanoparticles with carbon supports were performed. Figures 4a–4d show the 3D atom maps of specimen containing PtMn nanoparticle before evaporation (Fig. 4a), and reconstructed after evaporation simulation with various evaporation fields of carbon (Figs. 4b–4d). Pt and Mn atoms are shown in red and green spheres in each atom maps. 1D concentration profiles taken in the direction of yellow arrow are presented in Figures 4e–4h.

At initial state before evaporation, the core of the nanoparticle is enriched with Pt (red spheres), and Mn atoms (green spheres) are distributed on the surface of the nanoparticle as shown in Figure 4a. As a result, the 1D concentration profile across the nanoparticle (Fig. 4e) shows a single concentration peak of Pt, with two separated peaks of Mn at each end of the Pt concentration peak. After evaporation simulation, distortions resulting from LME are observed in the reconstruction maps (Figs. 4b–4d). Although the discrepancy from the initial state gets larger as the field of C increases, the concentration profile across each nanoparticle system (Figs. 4f–4h) shows the Mn atoms are enriched at the surfaces of the particle.

Simulated Results of Carbon-Supported Pt\(_3\)Mn Nanoparticles

Figure 5a illustrate the initial simulation condition of the ordered L\(_1\)\(_2\) Pt\(_3\)Mn particle on a carbon support embedded in the Co matrix. The same protocol is used as above and the reconstructions of the particles are severely distorted and exhibit a compressed shape (Figs. 5b–5d). Unlike the PtMn nanoparticles results, in which the Mn atoms are only enriched at the surface, Mn are distributed homogeneously with 3:1 Pt/Mn atomic ratio in all Pt\(_3\)Mn nanoparticles (see Figs. 5f–5h). A clear difference between PtMn and Pt\(_3\)Mn results was observed in both atom...
maps and 1D concentration profiles, even after applying extremely high evaporation field of the carbon support. Field evaporation of carbon indeed influence the acquired atom map however, these results suggest that qualifying the 3D elemental distributions of carbon-supported nanoparticles is possible from APT reconstruction map.

**Mn Diffusion in the Nanoparticles During the Process of Synthesis**

The synthesis of atomically ordered Pt₃Mn/C requires a two-step process: reduction of Mn ions in solution and heat-treatment in reductive atmosphere (see Scheme 2). We observed the Mn atoms near the surface of the particles in PtMn/C and homogeneous 3:1 Pt/Mn distribution in Pt₃Mn/C from the APT experiment (see Fig. 3f). In addition, simulated results of carbon-supported PtMn and Pt₃Mn nanoparticles support the different tendency (see Figs. 4 and 5). Thus, we suggest that Mn ions were reduced and only attached to the surface of Pt nanoparticles after chemical reaction in solution. Subsequently, during the reductive heat-treatment, surface-reduced Mn atoms diffused into the core of the particles and resulted in the ordered L1₂ structure as verified by high-resolution STEM (Supplementary Fig. S3d). Chi et al. reported

Fig. 4. Simulated 3D atom maps of PtMn/C (a) before evaporation and after evaporation with evaporation field of carbon set at (b) 50, (c) 75, and (d) 103 V/nm, and (e–h) 1D concentration profiles of Pt, Mn from each atom maps (direction: yellow arrow in atom maps).
the surface segregation of Pt in Pt₃Co nanoparticle starts at 350°C while L1₂ ordering in Pt₃Co nanoparticles appears at 600°C (Chi et al., 2015), implying the first applied heat treatment (259°C) during synthesis of atomically ordered Pt₃Mn/C in the current work, does not provide enough thermal driving force to initiate Mn diffusion toward the particle core.

**Conclusion**

In this study, we reveal the 3D elemental distribution of carbon-supported Pt, PtMn, and Pt₃Mn nanoparticles. Systematic numerical simulations with varied evaporation-field conditions of the carbon are used to study the local magnification effect or LME. It has been shown that despite the artifacts, including atomic density fluctuation at the carbon/metal interface and lateral compression and bending of the nanoparticles within reconstructed atom maps, the atomic movement within the nanoparticle during the heat-treatment could have been tracked with APT. We envision that the presented study can pave the road for the application of APT analysis for various carbon-supported nanomaterials.

**Supplementary material.** To view supplementary material for this article, please visit [https://doi.org/10.1017/S1431927622012211](https://doi.org/10.1017/S1431927622012211).
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