One-Pot Synthesis of PtNi Alloy Nanoparticle-Supported Multiwalled Carbon Nanotubes in an Ionic Liquid Using a Staircase Heating Process

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ABSTRACT: High-performance PtNi alloy nanoparticle-supported multiwalled carbon nanotube composite (PtNi/MWCNT) electrocatalysts can be prepared via a one-pot preparation for oxygen reduction reaction. This route of preparation utilizes the pyrolytic decomposition of metal precursors, such as Pt(acac)_2 with Ni precursors, nickel bis(trifluoromethanesulfonylamide) (Ni[Tf_2N]_2) or nickel acetylacetonate (Ni(acac)_2), in an ionic liquid (IL), N_4N_4N_3-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide ([N_1,1,1,3][Tf_2N]). Currently, there is insufficient information concerning the effect of difference in preparation conditions on the formation mechanism and catalytic activity of PtNi/MWCNT. In this article, a staircase heating process was used to investigate the PtNi alloy nanoparticle formation mechanism and catalytic activity of the resulting PtNi/MWCNT. We found that the alloy formation process, composition, and crystal structure, which directly affect the electrocatalytic activity, strongly depended on the Ni precursor species and heating process. The catalytic performance of certain PtNi/MWCNTs collected during the staircase heating process was better than that of PtNi/MWCNTs produced via the conventional heating process.

INTRODUCTION

In recent years, Pt alloy nanoparticles have been actively investigated as a promising catalytic material in the polymer membrane electrolyte fuel cell (PEMFC) system because such nanoparticles can reduce the Pt consumption and enhance the electrocatalytic performance in the oxygen reduction reaction (ORR). Improvement of the catalytic performance is attained by adjusting the alloy composition, i.e., lattice parameters and electronic structures, of the Pt alloy nanoparticles. However, it is not easy to vary the composition of the alloy while maintaining a desired particle size. To date, such Pt alloy nanoparticles have been prepared via commonly used methods, such as electrochemical deposition and colloidal synthesis, wherein the latter is often preferred as it is a controllable synthesis procedure. In most cases, the synthesis is carried out through the following steps: (i) seed growth, (ii) deposition of the second metal on the seed, and (iii) supporting of the prepared nanoparticles onto the carbon materials. By this multistep growing method, Pt alloy nanoparticles can be designed stepwise. Their alloy compositions are roughly controlled by changing the precursor ratio, reaction condition, annealing process, etching condition, and so on. However, such a process is time-consuming, complicated, and unsuitable for a large-scale industrial process.

In our previous work, we studied a two-step Pt nanoparticle-supported carbon composite preparation method, also called the IL-sputtering method. It is consisted of a Pt sputtering process onto an ionic liquid (IL) and an agitation process of the Pt-sputtered IL with the carbon support at 573 K or less. Based on that, we proposed a simple and mass-producible one-pot pyrolysis method with an ionic liquid (IL one-pot process) for preparing Pt and PtNi alloy nanoparticle-supported multiwalled carbon nanotube composite (Pt/MWCNT and PtNi/MWCNT) electrocatalysts for ORR. The PtNi/MWCNT prepared using the one-pot process in the IL, N_4N_4N_3-trimethyl-N-propylammonium bis(trifluoromethanesulfonylamide) ([N_1,1,1,3][Tf_2N]), with platinum(II) acetylacetonate (Pt(acac)_2), nickel(II) bis(trifluoromethanesulfonylamide) (Ni[Tf_2N]_2), and MWCNT had a mass activity 1.4 times higher than that of a commercially available electrocatalyst. Such was not case when nickel(II) acetylacetonate (Ni(acac)_2) was used, thereby suggesting that the alloying mechanism varies with the precursor species. Herein, we examine the PtNi alloy nanoparticle formation mechanisms in ILs containing Ni[Tf_2N]_2 or Ni(acac)_2 directly leading to control of the alloy composition in the process of the one-pot process and improvement of catalytic activity. The PtNi/MWCNTs collected throughout the heating process were characterized using transmission electron microscopy.
(TEM), bright-field (BF) and high-angle annular dark-field (HAADF) modes of scanning transmission electron microscopy (STEM), energy dispersive X-ray spectrometry (EDS), X-ray diffractometry (XRD), inductively coupled plasma atomic emission spectrometry (ICP-AES), and electrochemical measurements. We determined the effects of the nickel precursor species and the heating conditions on the particle size and crystal structure of the PtNi nanoparticles as well as the catalytic performance of the PtNi/MWCNTs.

RESULTS AND DISCUSSION

As shown in Figure S1, thermogravimetric (TG) measurements of the metal precursors and the IL [N\textsubscript{1,1,1,3}][Tf\textsubscript{2}N] indicated that the thermal decomposition of the nickel precursors gradually initiated prior to that of the Pt precursor. Moreover, the [N\textsubscript{1,1,1,3}][Tf\textsubscript{2}N] IL was a viable reaction medium for the IL-based one-pot process when the heating temperature was less than ca. 650 K. Based on these results, a staircase heating process with three temperature plateaus at 373, 473, and 573 K was employed to examine the nanoparticle formation mechanism during the one-pot process and was applied to TG measurements of the metal precursors (Figure 1). Slight weight losses for Ni[Tf\textsubscript{2}N]\textsubscript{2}, and Ni(acac)\textsubscript{2} were observed at the 373 K plateau. At the onset of the 473 K plateau, the weight losses became clearer and were nearly unchanged until the end of this plateau. As for Ni(acac)\textsubscript{2} and Pt(acac)\textsubscript{2}, minimal corresponding weight loss resulting from metal deposition was observed after the onset of the plateau at 573 K. However, Ni[Tf\textsubscript{2}N]\textsubscript{2} showed a constant weight loss throughout the heating plateau at 573 K.

Further investigation was carried out using the staircase heating of the IL mixtures containing Pt(acac)\textsubscript{2}, Ni precursors, and MWCNTs. Figure 2 shows TEM images of the specimens prepared in [N\textsubscript{1,1,1,3}][Tf\textsubscript{2}N] with 5 mmol L\textsuperscript{-1} Pt(acac)\textsubscript{2}, 5 mmol L\textsuperscript{-1} Ni[Tf\textsubscript{2}N]\textsubscript{2}, and 1.25 g L\textsuperscript{-1} MWCNT. Samples were taken from the IL mixture at sampling points A, B, C, D, E, F, G, H, J, K, and L as labeled in Figure 1.

During the prolonged heating at 573 K, i.e., at sampling points A and B, Ni content of the nanoparticles was considerably low (up to 4 atom %) until the onset of the heating plateau at 573 K, wherein Ni content gradually and linearly increased for the next 3 h and finally remained at temperature of 373 K, i.e., at sampling points C, D, E, F, G, H, J, K, and L as shown on the top axis.

![Figure 1. Heating profile (black solid line) employed for the staircase heating process and TG measurement results of Pt(acac)\textsubscript{2} (gray solid line), Ni[Tf\textsubscript{2}N]\textsubscript{2} (red dashed line), and Ni(acac)\textsubscript{2} (blue dash-dotted line) obtained using the staircase heating process. Samples were taken from the IL mixtures containing the metal precursors and MWCNTs at points A–L as shown on the top axis.](image)

![Figure 2. Typical TEM images of PtNi/MWCNTs prepared in [N\textsubscript{1,1,1,3}][Tf\textsubscript{2}N] with 5 mmol L\textsuperscript{-1} Pt(acac)\textsubscript{2}, 5 mmol L\textsuperscript{-1} Ni[Tf\textsubscript{2}N]\textsubscript{2}, and 1.25 g L\textsuperscript{-1} MWCNT.](image)
approximately 30 atom %. The variation of the Ni content of the specimens produced in the IL mixtures containing Ni(acac)₂ was the opposite. That is, at the onset of the plateau at 573 K (sampling point F), the Ni content was approximately 90 atom % but rapidly decreased to ca. 30 atom % within 60 min. Interestingly, all the specimens obtained at sampling points I−L had similar Ni contents, ca. 34 ± 4 atom %.

Throughout the heating processes at 373 and 473 K, most of the limited number of Ni metal nanoparticles produced was likely consumed by the electrochemical substitution reaction between Ni(0) and Pt(II). We deduced that this reaction step hampered the formation of Ni metal nanoparticles at the said temperatures, and thus, nucleation was more difficult in the IL mixture containing Ni(acac)₂. Because nucleation was difficult and the particle growth proceeded on the minimal nuclei, the resulting nanoparticles were larger, as summarized in Table S1.

Further information on the crystal structure of the nanoparticles deposited on MWCNTs was collected using XRD measurements. As shown in Figure 5a, all the Pt diffraction patterns of the specimens prepared in the mixture containing Ni[Tf₂N]₂ appear to be similar, except for that of the sample obtained at point L. However, the Pt diffraction pattern of the sample taken at point L showed a slight shift to a higher angle, suggesting that PtNi alloy nanoparticles with a face-centered cubic (fcc) solid solution phase were formed under the experimental conditions. Although the Ni content at point L was similar to that of the specimens taken at sampling points J and K, the XRD patterns of samples taken at points J and K did not show similar behavior to that of L. This may indicate Pt/Ni or Pt/patch-like Ni core−shell structure formation. For the IL mixture containing Ni(acac)₂, all the XRD patterns of the specimens notably shifted to a higher angle, except for that of the Ni-rich specimen at sampling point F, due to the formation of PtNi alloy nanoparticles with an fcc solid solution phase (Figure 5b). The results of the XRD measurements indicate that a PtNi alloy solid solution nanoparticle with an fcc crystal structure was eventually produced on the MWCNTs during the staircase heating process regardless of the Ni precursor used. However, the alloy formation mechanism itself depended on the Ni precursor species used. As indicated in Figure S8, selected area electron diffraction (SAED) patterns of Pt metal nanoparticles were also recorded at sample points C−L after the final heating processes.

### Table 1. Summary of the Properties of PtNi/MWCNTs Prepared in [N₁₁₁₁][Tf₂N] with 5 mmol L⁻¹ Pt(acac)₂, 5 mmol L⁻¹ Ni[Tf₂N]₂, and 1.25 g L⁻¹ MWCNT

| sampling point | condition   | mean particle size (nm) | Pt loading amount (wt %) | Ni content in nanoparticles (atom %) | ECSA (m² g⁻¹ Pt) | current density at 0.90 V (mA cm⁻²) |
|---------------|-------------|-------------------------|--------------------------|-------------------------------------|----------------|------------------------------------|
| C             | 473 K       | 1.0 (0.3)               | 1.0                      | 0                                   | 0.397         | 0.397                              |
| D             | 473 K, 1 h  | 1.9 (0.6)               | 12.5                     | 4                                   | 80.0          | 0.895                              |
| E             | 573 K       | 2.4 (0.5)               | 26.4                     | 6                                   | 46.1          | 1.102                              |
| I             | 573 K, 1 h  | 2.7 (0.4)               | 28.7                     | 18                                  | 50.8          | 2.123                              |
| J             | 573 K, 2 h  | 2.8 (0.4)               | 27.0                     | 26                                  | 66.2          | 1.431                              |
| K             | 573 K, 3 h  | 2.4 (0.5)               | 26.6                     | 34                                  | 46.8          | 1.102                              |
| L             | 573 K, 4 h  | 2.6 (0.5)               | 23.3                     | 30                                  | 50.8          | 2.123                              |

*The values in parentheses are standard deviations.*
For category (i), such as the combination of Pt(acac)$_2$ and Ni[Tf$_2$N]$_2$, Pt nanoparticles were generated at sampling point L also corroborate the aforementioned conclusion.

Differences in the nanoparticle formation temperatures of Pt and Ni, $T_{Pt}$ and $T_{Ni}$ respectively, estimated from Figure 4, seemed to cause the different PtNi alloy formation mechanisms, which can be divided into two categories: (i) when $T_{Pt}$ is lower than $T_{Ni}$ and (ii) when $T_{Pt}$ is higher than $T_{Ni}$. For category (i), such as the combination of Pt(acac)$_2$ and Ni[Tf$_2$N]$_2$, Pt nanoparticles were first generated at lower temperatures and served as the seeds for Ni deposition at higher heating temperatures. Eventually, PtNi alloy solid solution nanoparticles with an fcc crystal structure were produced. Such an assertion is supported by the absence of clear peak shifts in the XRD patterns of Pt in some specimens, even when the Ni contents in the PtNi/MWCNTs exceeded ca. 30 atom %. For category (ii), such as the combination of Pt(acac)$_2$ and Ni(acac)$_2$, as shown in Figure 4, Ni-rich PtNi alloy nanoparticle production occurred at the onset of heating at 573 K due to the lower nanoparticle formation temperature of Ni. However, the PtNi alloy nanoparticles shifted from Ni-rich to Pt-rich upon further heating due to the slower Pt deposition step. In summary, we can depict the schematic illustration of the plausible PtNi alloy formation mechanisms, as shown in Figure 6.

The PtNi alloy nanoparticle formation mechanism, which was clarified using the staircase heating process, indicates that the alloy composition and the crystal structure vary during such processes. It can be deduced that the electrocatalytic activities of the PtNi/MWCNTs for ORR also change with the particle size, alloy composition, and crystal structure of the PtNi alloy nanoparticles supported on the MWCNTs. Figure 7 shows cyclic voltammograms recorded using the GC electrodes with select PtNi/MWCNT samples in a N$_2$-saturated 0.1 M HClO$_4$ aqueous solution. Several commonly observed redox waves due to hydrogen and oxygen electrochemical reactions were observed at potentials ranging from 0.10 to 0.35 V and from 0.60 to 1.00 V, respectively. The electrochemical surface area (ECSA) data of the PtNi alloy nanoparticles are summarized in Figure 8, along with their corresponding electron diffraction (SAED) patterns of the specimens collected at sampling point L also corroborate the aforementioned conclusion.

Mean particle size. For the PtNi/MWCNTs obtained using Ni[Tf$_2$N]$_2$, the highest ECSA value (80.0 m$^2$ gPt$^{-1}$) was observed in the specimen taken at sampling point L. In the case of the specimens prepared from Ni(acac)$_2$, the highest ECSA value was 76.9 m$^2$ gPt$^{-1}$ (sampling point H). In both cases, the ECSA values varied according to a volcano-shaped curve and seemed to be independent of the mean particle size. Such a phenomenon may have been caused by a synergistic effect of better PtNi alloy nanoparticle dispersibility on the MWCNTs (Figure 2d), an appropriate Ni content in the PtNi/MWCNTs, and a favorable crystal structure for the PtNi nanoparticle.

The catalytic ability of the samples for ORR was evaluated using the polarization curve of select PtNi/MWCNTs. Figure 9 shows the RDE-LSVs taken under revolution speeds of 1600 rpm using the GC rotating disk electrodes with different PtNi/MWCNTs and a commercial Pt/C catalyst in an O$_2$-saturated 0.1 M HClO$_4$ aqueous solution. We observed that the current densities of the specimens produced using Ni[Tf$_2$N]$_2$ at 0.90 V increased with longer heating times (Figure 9a). A similar trend was also observed among the specimens prepared using Ni(acac)$_2$ (Figure 9b). In both cases, the maximum current density was obtained with the PtNi/MWCNTs that had similar features, such as mean particle size, Pt loading amount, and Ni content in the nanoparticles. Particularly, the Ni content seemed to be an important factor. When the Ni content was approximately 30 atom %, a favorable catalytic performance was attained. The binary phase diagram of Pt and Ni shows that the Pt$_3$Ni alloy, which has a considerably high catalytic performance, was formed when the Ni content was approximately 30 atom % and the temperature was 573 K. Additionally, most limiting current densities for ORR shown in Figure 9 did not reach the commonly observed value, which is approximately $-6$ mA cm$^{-2}$. Such a decrease in the limiting current was not observed at the GC rotating disk electrodes with a commercial Pt/C catalyst and recognized in our previous study on the IL one-pot preparation process with heating at 573 K. However, the aforementioned study did not include the heating steps at lower temperatures, 373 and 473 K. Such an unexpected result is peculiar for the staircase heating process. We guess that longer heating time over 4 h and/or lower heating temperature below 473 K give some sort of negative impact to the PtNi/MWCNTs. In addition to this, thermal decomposition products derived from Ni precursors under such heating conditions may cause the undesirable ORR performance. Although we investigated the unexpected catalytic behavior, unfortunately, the reason(s) could not be revealed. Despite the insufficient electrode performance, some PtNi/MWCNTs prepared in this research had a better ECSA. Capacity.
and current density for ORR at 0.90 V, compared with those of samples previously obtained via a similar IL-based one-pot process but not the same heating process. By using the staircase heating process, we were able to understand the appropriate conditions for designing PtNi/MWCNTs with a higher ORR catalytic activity using an IL one-pot process.

**CONCLUSIONS**

The formation mechanism of the PtNi/MWCNTs prepared via an IL one-pot process was examined using the staircase heating process with two different Ni metal precursors, Ni[Tf$_2$N]$_2$ and Ni(acac)$_2$. Although the final products were similar upon completion of the process, regardless of the precursor species, there was a notable composition difference between the initial steps of the PtNi nanoparticle formation, depending on the Ni precursor used. The catalytic performance of the specimens collected throughout the staircase heating process depended on the preparation conditions. In some cases, the catalytic performance was better than those of the PtNi/MWCNTs produced via the conventional heating process. Variations in the catalytic behavior strongly suggest that the heating process is crucial for controlling the characteristics of the PtNi/MWCNTs in an IL one-pot pyrolytic process. The findings reported in this article will be useful for the production of high-performance ORR electrocatalysts that can reduce Pt consumption.

**EXPERIMENTAL METHODS**

*Synthesis of Ni[Tf$_2$N]$_2*.

Ni[Tf$_2$N]$_2$ was synthesized according to reported procedures in the previous literature.35,36
Bis(trifluoromethanesulfonyl)imide (Morita Chemical Industry Co., Ltd., 1.65 g) was dissolved in 36 mL of pure water, and then the solution was treated with N₂ bubbling for 30 min. Ni(OH)₂ (Waco Pure Chemical Industry Co., Ltd., 10.1 g) was added to the aqueous solution, and the solution was agitated at 343 K for 2 h. The solution was then cooled at ambient temperature. Then, the green-colored solution was dried under vacuum at 453 K for 4 h. The final product was a yellow powder.

Preparation of PtNi/MWCNTs. The PtNi/MWCNT fabrication was conducted using a one-pot pyrolytic process under a N₂ atmosphere. The reaction media were composed of Pt(acac)₂ (Mitsuwa Chemicals Co., Ltd.), Ni[Tf₂N]₂ or Ni(acac)₂ (Sigma-Aldrich Co., LLC), 2 mL of [N1,1,1,3][Tf²N] IL (Kanto Chemical Co., Inc.), and 1.25 g L⁻¹ MWCNT (Sigma-Aldrich Co., LLC). The IL mixtures were agitated at room temperature overnight to uniformly disperse the precursors and MWCNTs. The concentration of the Pt and Ni precursors in the IL mixtures was 5 mmol L⁻¹. A staircase heating process was employed for the synthesis of PtNi/MWCNT. The heating conditions are graphically shown in Figure 1, and the samples taken from the IL mixture throughout the procedure are labeled A–L. The resulting PtNi/MWCNTs were washed multiple times with anhydrous acetonitrile and dried under vacuum overnight.

Characterization. TG analysis of the metal precursors was conducted using a Bruker TG-DTA2000SA thermal analysis system under dry flowing N₂ (100 mL min⁻¹) with the temperature increasing from ca. 298 K to the set temperatures at a rate of 10 K min⁻¹. XRD patterns of the as-prepared PtNi/MWCNTs were examined using a Rigaku Ultima IV X-ray diffractometer with a Cu Kα radiation source. The diffraction patterns were collected from 20° to 80° at a scanning rate of 1° min⁻¹. The morphology of the PtNi/MWCNTs was observed using a Hitachi H-7650 transmission electron microscope; SAED patterns were also obtained using the same instrument. The detailed morphology and elemental composition of the PtNi/MWCNTs were investigated by a JEOL JEM-ARM200F scanning transmission electron microscope. Atomic resolution images were acquired in BF and HAADF imaging modes of STEM. EDS elemental mapping was conducted for the same specimen area where the BF-STEM and HAADF-STEM images were acquired. The averaged EDS spectra for several tens of PtNi-NPs were also obtained by exposing the electron beam with a diameter of ~50 nm. Elemental composition ratios of NPs were evaluated from the EDS maps and spectra by using JEOL Analysis Station software. The composition of the PtNi nanoparticles was also analyzed using a Shimadzu ICPS-7510 ICP-AES.

Electrochemical Measurements. The electrocatalytic activities of the PtNi/MWCNTs were examined using a computer-controlled Hokuto Denko HZ-7000 potentiostat/galvanostat. The electrochemical measurements were conducted using a three-electrode cell at room temperature (ca. 298 K) with a glassy carbon rotating disk electrode (GC-RDE). A Pt mesh, Ag/AgCl electrode, and 0.1 M HClO₄ aqueous solution were used as the counter electrode, reference electrode, and electrolyte, respectively. Each PtNi/MWCNT sample was dispersed in an i-propanol solution with a weight concentration of 1.48 g L⁻¹. A 10 μL aliquot was dropped onto a GC rotating disk electrode (surface area, 0.196 cm²) with a diameter of 5 mm and dried naturally. Finally, the GC disk was covered with 10 μL of Nafion i-propanolic solution (0.1 wt %) to fix the PtNi/MWCNT sample with a thin Nafion layer. All potential values were reported with respect to a reversible hydrogen electrode (RHE). Voltammetric experiments were conducted at a rate of 10 mV s⁻¹ between 0.050 and 1.20 V (vs RHE) at room temperature. Prior to the experiments, the working electrode was electrochemically cleaned using 40–100 potential sweeps between 0.050 and 1.20 V at a scan rate of 50 mV s⁻¹ under a N₂ atmosphere until the cyclic voltammograms (CVs) were stabilized. The electrolyte was deaerated using N₂ or O₂ bubbling for at least 30 min.

ECSA of the Pt nanoparticles was determined using the hydrogen adsorption/desorption Coulombic charge under a nitrogen atmosphere, as shown in the cyclic voltammogram, after subtracting the double layer charge current. The ECSA value was calculated using the equation

\[
\text{ECSA} = \frac{Q_{\text{H}} \times 10^{2}}{210 \times M_{\text{Pt}}}
\]

where \(Q_{\text{H}}\) (mC) is the charge of hydrogen adsorption/desorption. Additionally, \(M_{\text{Pt}}\) (mg) is the mass of Pt on the GC working electrode. The average value of the charge associated with a hydrogen adsorption/desorption monolayer formed on smooth polycrystalline Pt is 210 μC cm⁻².⁵⁷

The ORR performances of the specimens were investigated using rotating disk electrode linear sweep voltammetry (RDE-LSV) in the anodic direction with a sweep rate of 10 mV s⁻¹ under an O₂ atmosphere and the revolution speed was 1600 rpm. The ORR performance at the RDE is discussed from the current density at 0.90 V.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02951.

TG measurement results for metal precursors (Figure S1); particle size distributions of nanoparticles (Figures S2 and S5); TEM images (Figure S4), BF-STEM and HAADF-STEM images (Figures S3, S6, and S7), EDS mappings (Figures S3, S6, and S7), and SAED patterns (Figure S8) of the PtNi/MWCNTs; summary of PtNi/MWCNTs prepared in [N1,1,1,3][Tf²N] with Pt(acac)₂, Ni(acac)₂, and MWCNT (Table S1) (PDF)

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Notes
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