Catalytic Roles and Synergetic Effects of Iron-Group Elements on Monometals and Alloys for Electrochemical Oxidation of Ammonia

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Abstract
Electrooxidation of NH3 has gained extensive attention for energy and environmental applications such as fuel cells and water purification. Pt-based precious metal alloy catalysts have been intensively studied as anode catalysts for the NH3 electrooxidation whereas applicability of earth-abundant transition metals to catalysts has not been sufficiently examined. In this study, we synthesized carbon-supported simple metal-nanoparticle, binary- and ternary-nanoalloy (NA) catalysts composed of Fe-group elements, i.e., Fe, Co and Ni, and systematically investigated catalytic performance of these catalysts for NH3 electrooxidation in alkaline media. We found that the affinity of constituent metals to nitrogen species controls overpotential and durability for the NH3 electrooxidation on Fe-group simple monometal and NA catalysts for the first time. Furthermore, each Fe-group element shows distinctive catalytic features for the NH3 electrooxidation, i.e., Ni ensures chemical stability, Fe effectively lowers overpotential and Co increases current density. The ternary FeCoNi/C shows excellent activities due to combination of all the catalytic features and synergetic effects exerted by the alloying.

Keywords: Ammonia | Electrooxidation | Fe group nanoalloys

1. Introduction
NH3 has been recognized as a possible hydrogen carrier due to its high hydrogen capacity of 17.6 wt%1-4. Furthermore, carbon-free nature and favorable transportability of fluidized NH3 originating from its liquefaction property under mild conditions allow application to a mobile and compact NH3 fuel cell to generate electric power without CO2 emission.5-12. Because NH3 has been widely used in the chemical and agricultural fields, distribution infrastructure of NH3 has been already developed, which enables delivery of quite large amounts of NH3. Thus, electrooxidation of NH3 is attracting attention in the energy field and much effort has been devoted to achieve highly efficient NH3 electrooxidation catalysts, which are applicable to an anode in a direct NH3 fuel cell. The NH3 electrooxidation is demonstrated under high NH3 concentration for the fuel cell and more easily proceeds in alkaline media than in acid as described below.

$$2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^-$$

The NH3 electrooxidation potential at 25 °C is −0.09 V vs. standard hydrogen electrode (SHE) in an aqueous solution.13 Many researchers have studied to develop highly active electrocatalyst for NH3 electrooxidation.14-17 De Voysts et al. have systematically studied electrocatalytic activities of polycrystalline precious metals such as Ru, Pd, Rh, Ir, Pt, Cu, Ag and Au for the reaction. They have revealed that both Pt and Ir catalysts
exhibit high activities and Pt is the best electrocatalyst for the reaction. Endo et al. reported that Pt–Ir and Pt–Ru binary alloy catalysts show higher NH$_3$ oxidation activities in alkaline solutions than Pt,$^{19,20}$ and several groups have also reported that precious metal based alloy catalysts exhibited high activities.$^{21–36}$ However, the high cost of precious metals is not favorable for industrial applications, which persuades us to develop less expensive and more earth abundant metal electrocatalysts, especially 3d transition metals. Several studies reported that Ni-containing materials showed catalytic activities for NH$_3$ electrooxidation.$^{37–41}$ However, the activities were much lower than those of precious metal electrocatalysts. Alloying is known as an effective strategy to improve catalytic activities for metal electrocatalysts. Recently, we successfully synthesized solid solution-type Fe-group binary and ternary nanoalloy (NA) catalysts supported on porous carbon by a two-step reduction method.$^{42,43}$ The component Fe-group elements were atomically-well mixed in a nanoparticle without phase separation and the NA catalysts provided preferable properties and novel catalytic features via synergetic effects of component metals, which are not observed for the catalysts co-supporting simple metal nanoparticles. Furthermore, the Fe-group NA catalysts exhibited high activities for electrooxidation of ethylene glycol due to their feasible affinity to the substrate molecule in alkaline media. Therefore, Fe-group NA catalysts have a possibility to show favorable catalytic activities for NH$_3$ electrooxidation in alkaline media. Furthermore, since there are few reports on 3d transition metals other than Ni, such as Fe and Co,$^{44}$ elucidation of catalytic performances of Fe-group catalysts will contribute to the development of novel alloy electrocatalysts for NH$_3$ electrooxidation.

In this study, we synthesize Fe-group simple metal-nanoparticle, binary- and ternary-NA catalysts supported on carbon and examine the catalytic performances for the NH$_3$ electrooxidation. Cyclic voltammetry (CV) and chronoamperometry (CA) clarify that Ni-containing catalysts show appropriate activities for NH$_3$ electrooxidation and the catalytic performances of Fe-group catalysts depend on affinity between constituent metals and nitrogen. We first report systematic investigation of catalytic performances on Fe-group catalysts and reveal distinctive catalytic features and synergetic effects of each elements for NH$_3$ electrooxidation. The ternary NA catalyst exhibits excellent activities due to combination of all the catalytic features and synergetic effects of alloying.

2. Experimental

2.1 Sample Preparation. Carbon supported Fe-group NA catalysts composed of two or three elements, i.e., FeCo/C, CoNi/C, FeNi/C and FeCoNi/C and simple monometal catalysts, i.e., Fe/C, Co/C and Ni/C, were synthesized by the procedure reported previously.$^{42,43}$ Fe(OAc)$_2$ (OAc = acetate, Tokyo Kasei Kogyo), Co(OAc)$_2$•4H$_2$O (Wako), and Ni(OAc)$_2$•4H$_2$O (Wako) were used as metal sources. The metal sources were dissolved into a mixture of polyethylene glycol (PEG, MW = ca. 1,500, Wako) and triethylene glycol (TEG, Kishida) in a 4-necked flask. Concentration of each metal component in the solution was adjusted to be identical by controlling the amount of metal sources. The solution was vigorously stirred for 30 min at room temperature and heated up to 80 °C with Ar bubbling for 30 min. A methanol suspension of carbon black (Vulcan, XC-72R, Cabot Corporation) was added to the mixture and the suspension was stirred for 30 min at room temperature. The amount of carbon black was controlled to obtain catalysts having desired metal contents (30 wt%). An aqueous solution of NaBH$_4$ (0.6 M, 30 cm$^3$) was added to the suspension, and then the resultant mixture was stirred at 80 °C for 30 min. Black precipitate was separated from the mixture by centrifugation. The precipitates were repeatedly washed with water and acetone and dried in a vacuum overnight to obtain the catalyst precursors. The carbon-supported catalysts were prepared by treating the precursor under H$_2$/Ar (5:95) at 800 °C for 1 min.

2.2 Characterization. Powder X-ray diffraction (XRD) measurements were conducted with Cu Kα radiation (λ = 1.54059 Å) using a Rigaku Smart Lab. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed using an iCAP 6300 (Thermo Fisher scientific). Transmission electron microscopy (TEM) images of the synthesized catalysts were recorded using a JEM-2010HCKM operated at 200 kV. Bright field scanning transmission electron microscope (BF-STEM), high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) images, energy dispersive X-ray spectroscopy (EDX) analyses, and electron energy-loss spectroscopy (EELS) analysis were demonstrated using a JEM-JEM-ARM200F operated at 80 kV. For these measurements, the samples were dispersed in ethanol, dropped onto a carbon-coated Cu grid, and dried in vacuo for approximately 12 h. X-ray photoelectron spectroscopy (XPS) measurement was performed using an ULVAC-PHI PHI 5000 VersaProbe II (Al-Kα). Samples were treated at 500 °C under H$_2$ gas flowing in the pretreatment chamber (VersaPrep, ULVAC-PHI) attached to the XPS instrument which enables measurement of spectra without exposure to air. Binding energies obtained by XPS were calibrated with carbon 1s spectra on the sample at 284.6 eV.

2.3 Electrochemical Measurements. The prepared catalysts (10 mg) and commercially available Pt/C (Alfa Aesar, 20 wt%, 10 mg) were suspended in a small amount of ethylene glycol and fixed on carbon felt (KRECA Paper, 4 cm$^2$, Kureha) which was washed with acetone and dried before use. The carbon felts with catalysts were treated under N$_2$ gas at 400 °C for 30 min and successively under H$_2$ gas at 300 °C for 10 min. The carbon felt was fixed with a stainless-steel holder, and then used as a working electrode.

All electrochemical measurements with a three-electrode system were conducted using a galvanostat/potentiostat (VersaSTAT4, Princeton Applied Research, AMETEC Inc.). A coiled Pt wire and Hg/HgO electrode (RE-6A, BAS Co. Ltd.) with a 1 M KOH aqueous solution were used as a counter and reference electrode, respectively. CV measurements were performed in an aqueous solution of 1 M KOH electrolyte (80 cm$^3$) with or without 1 M NH$_3$ under Ar atmosphere using a single compartment glass cell with the working, reference and counter electrodes. CA measurements were conducted using a two-compartment electrochemical cell with a piece of proton conducting membrane (Nafion®, NRE-212, Sigma-Aldrich) as a separator which was placed between the anode and cathode cell under Ar atmosphere. Aqueous solutions (anode: 50 cm$^3$ of 1 M
KOH and 1 M NH₃, cathode: 50 cm³ of 1 M KOH) were introduced into the cells and the working/reference and counter electrodes were placed inside the cathode and anode cell, respectively. All potentials were measured against the Hg/HgO reference electrode, which has a potential of 0.098 V vs. the standard hydrogen electrode (SHE), and finally converted to a potential referring to the reversible hydrogen electrode (RHE).

After electrochemical measurements, the reaction solution was analyzed using ICP-AES to determine the amounts of metal ions dissolved from the catalysts. The amount of NH₃ and products by NH₃ electrooxidation in the solution was measured using an ion chromatograph. The gaseous components in the headspace of the anode cell were analyzed using a gas chromatograph (Shimadzu corporation, GC-8A).

3. Results and Discussion

3.1 Structural and Morphological Properties of Simple Monometal and NA Catalysts. Figure 1 shows XRD patterns for the synthesized Fe-group NA catalysts and their Rietveld profiles together with those for simple monometal ones. Rietveld analyses provided detailed structural parameters for the prepared samples (Table S1). No peaks derived from oxides were observed for any catalyst (Figure S1). The XRD pattern for Fe/C was reproducible by the superposition of diffractions from α- and γ-Fe phases, which are characterized with body-centered-cubic (bcc) and face-centered-cubic (fcc) structures, respectively. The Co/C and Ni/C showed a diffraction pattern from an fcc phase. The XRD pattern for FeCo/C was assigned to a bcc structure and the other alloy samples showed XRD patterns attributable to an fcc structure. TEM images of the prepared catalysts indicate that nanoparticles are well dispersed on the carbon support for all samples (Figure 2A and Figure S2). The average diameter of nanoparticles on the support was found to be in the range of 25 to 52 nm. ICP-AES measurements revealed that metal contents and molar ratios for the constituent metal elements were similar to those in the starting materials (Table S2).

 Elemental distributions in each nanoparticle of the ternary FeCoNi NA were investigated in detail by STEM-EDX and EELS measurements. Figure S3 shows a BF-STEM image of the FeCoNi/C and STEM-EDX elemental maps for Fe, Co, Ni, oxygen and carbon. Each metal element was uniformly distributed over the single particle, and white particles were observed in an overlay of the elemental maps (Figure S3(E)), indicating the formation of solid-solution FeCoNi NAs as reported previously42,43 although inhomogeneous distribution of constituent element was partially confirmed. The signal from oxygen was also observed all over the FeCoNi NAs (Figure S3(F)). Considering that signals from carbon and Fe-group metals were overlapped on the oxygen signal in EDX spectra, distribution of oxygen was indeterminable from the STEM-EDX mapping result. Thus, we conducted the EELS measurement to investigate precise distribution of oxygen on the FeCoNi particles. A HAADF-STEM image of the FeCoNi/C and EELS maps for Fe, Co, Ni revealed the uniform distribution of metal elements (Figure 2). It was noted that oxygen signals were predominately observed around the periphery of the FeCoNi particles. The results revealed that the surface of the FeCoNi particle was slightly oxidized due to exposure to air, whereas most of the FeCoNi NAs were in a metallic state.

3.2 Surface Chemical States of the FeCoNi/C NAs. We conducted XPS measurements for FeCoNi/C NAs to investigate oxidation states of the catalyst surface. We elucidated that the surface of FeCoNi NAs was partially oxidized since the spectra of Fe 2p, Co 2p and Ni 2p were found to include peaks derived from Fe⁰, Fe⁺, Co⁰, Co⁺ and Ni⁰ (Figure S4) similar to previous reports45,46 which is consistent with the discussion for STEM-EELS maps. Complicated spectra due to coexistence of metallic and oxidative states of the metals made it difficult to elucidate electronic states of NAs in the analysis. We then conducted XPS experiment for the FeCoNi/C NAs without exposure to air after H₂-reduction treatment (Figure 3, Figure S5). No peaks assignable to metal oxides were observed in any region of the spectra in Figures 3Aa, 3Ba and 3Ca, suggesting that the H₂ treatment completely removes oxide layers on the FeCoNi NA surface. Noted that deconvoluted Fe 2p₁/₂, Co 2p½ and Ni 2p½ XPS spectra for the H₂-treated FeCoNi NA were similar to those for the simple metal catalysts after H₂ reduction treatment (Figure S5). The results indicate that electronic states of the NA were hardly changed by the

**Figure 1.** XRD patterns for A) Fe/C, B) Co/C, C) Ni/C, D) FeCo/C, E) CoNi/C, F) FeNi/C and G) FeCoNi/C (black dot). Diffraction patterns reproduced by the Rietveld method are described in colored lines.

**Figure 2.** A) BF- and B) HAADF-STEM images for the FeCoNi/C NA catalyst, STEM-EELS maps of C) Fe (blue), D) Co (red), E) Ni (green) and F) oxygen (orange) inside the red square depicted in A.)
alloying. Furthermore, we measured Fe 2p, Co 2p and Ni 2p XPS spectra for FeCoNi NAs after immersing in an aqueous solution of 1 M KOH in the presence of NH₃ for 10 min (Figures 3Ab, 3Bb and 3Cb). XPS spectra for all metal elements were shifted to higher energy region compared to those for FeCoNi NAs exposed to air (Figure S4). Deconvoluted Fe 2p3/2, Co 2p3/2 and Ni 2p3/2 peaks located at 710.9, 781.5 and 856.5 eV, respectively, for the FeCoNi NAs after immersing in aqueous solution are assignable to Fe³⁺, Co²⁺ and Ni²⁺ species for their metal hydroxides. The results indicate that further surface oxidation proceeds and surface metal hydroxides of FeCoNi NAs form in an aqueous NH₃ solution before electrooxidation. Therefore, catalytic performances of the synthesized NA catalysts would predominantly originate from metal hydroxides on the surface of nanoparticles.

3.3 Electrochemical Performances of Monometal and NA Catalysts. Catalytic performances for the NH₃ electrooxidation were investigated by CV measurements. Figure 4 shows the voltammograms observed on Fe-group and Pt/C catalysts in a potential range from −0.25 to 1.3 V vs. RHE in 1 M KOH aqueous solution with and without 1 M NH₃. All catalysts showed characteristic anodic peaks at different potentials. The Pt/C, which is the most active monometal electrocatalyst for the NH₃ electrooxidation, showed no obvious anodic peak in the absence of NH₃, indicating that the Pt/C is durable in a KOH aqueous solution within the potential range in this study. The Pt/C showed the onset potential at 0.6 V vs RHE in the presence of NH₃ (Figure 4H), which is attributable to NH₃ oxidation. The anodic peaks on monometal and NA catalysts were also observed in the presence of NH₃. It was noted that the anodic peaks on Fe/C, Co/C and FeCo/C catalysts were also observed in the absence of NH₃, which were possibly assigned to occurrence of corrosion or dissolution of metals. Table S3 provides the amount of metal ions dissolved in the solutions after the reaction, which were determined using ICP-AES. We found that 5.68% of Co ion was dissolved into the solution from Co/C, indicating that the anodic peaks observed on Co/C are mainly attributable to electrodissolution of Co nanoparticles in the presence of NH₃. Although the amount of Fe ions dissolved in the solution was 0.72%, which was one-eighth the amount of the Co ions, the current density on Fe/C in the absence of NH₃ was similar to that on Co/C. The results suggest that self-oxidation of Fe mainly contributes to the anodic current observed on Fe/C, but the influence from the Fe dissolution is of limited significance. The anodic peak observed on FeCo/C was explainable by considering both electrodissolution and self-oxidation of metals. Thus, we conclude that anodic peaks observed on Fe/C, Co/C and FeCo/C do not originate only from NH₃ electrooxidation and these three catalysts are inactive or less active for NH₃ electrooxidation. Meanwhile, no anodic peak was observed on Ni-containing catalysts, i.e., Ni/C, FeNi/C, CoNi/C and FeCoNi/C, in the absence of NH₃, whereas apparent oxidation peaks emerged in the presence of NH₃, indicating that NH₃ electrooxidation proceeds on the four catalysts. These results suggest that alloying Ni into Fe or Co eliminates catalytic degradation originating from Fe oxidation on FeNi/C or Co dissolution on CoNi/C and enhances stability of the NA catalysts for NH₃ electrooxidation in alkaline media.

The Ni/C exhibited an anodic peak for the NH₃ electrooxidation at 0.95 V vs RHE with onset potential at 0.49 V vs RHE, resulting in 0.58 V of overpotential calculated from the potential for NH₃ electrooxidation. Some groups have reported that metallic Ni does not show catalytic activities but Ni(OH)₂
Figure 5. Cyclic voltammograms observed on Ni/C (green), FeNi/C (purple), NiCo/C (orange) and FeCoNi/C (black) in 1 M KOH aqueous solution in the presence of 1 M NH₃. Scan rate: 10 mV/s; Counter electrode: Pt wire; Reference electrode: Hg/HgO in 1 M KOH.

is active for the NH₃ electrooxidation. Since the XPS results suggested the formation of Ni(OH)₂ on the surface of nanoparticles, the observed activities for Ni/C are attributed to the surface Ni(OH)₂. The amount of Ni ions dissolved from Ni/C during the reaction was determined (Table S3). In general, Ni shows the lowest oxophilicity among the Fe-group elements, which is consistent with the results that no Ni species were observed for FeCoNi/C in the XPS measurement (Figure S4). The most part of the surface on Ni nanoparticles in Ni/C became hydroxide in the reaction solution, whereas a part of the surface probably remained as metallic Ni, which was dissolved during CV cycles. Unlike the case of Fe/C and Co/C, we could observe an obvious anodic peak on Ni/C in the presence of NH₃ but not without NH₃. Therefore, we believe the effect from the dissolution of Ni on the surface is limited and the activities of Ni/C for NH₃ electrooxidation is discussable. The Ni-containing NA catalysts showed distinctive catalytic activities, which are different from that on Ni/C, i.e., maximum current densities and onset potentials depend on the constituent metals. Comparing current densities between Ni/C and CoNi/C and between FeNi/C and FeCoNi/C, Co-containing NAs catalysts showed higher current densities (Figure S5, Table S4). The charge calculated from the amount of Co ions dissolved in the solution was a few percent of that composed of the entire anodic current and the decrease in current ascribed to the Co dissolution was very small compared to the increase brought by the inclusion of Co into catalysts. This result indicates that the contribution of the Co dissolution to the anodic current is negligible. Therefore, the results suggest that the inclusion of Co into nanoparticles enables enhancement of the catalytic activities for NH₃ electrooxidation. The Ni-containing binary NA catalysts showed lower onset potentials, i.e., 0.18 V vs RHE on FeNi/C and 0.29 V vs RHE on CoNi/C compared to 0.49 V vs RHE observed on the Ni/C, which originate from the alloying of Fe or Co with Ni. These results indicate that the onset potentials on the NA catalysts are influenced by the constituent metals and the overpotential are lowered in the order of Fe < Co < Ni. Especially, we found that alloying with Fe can effectively lower overpotential for the NH₃ electrooxidation. The order of overpotential can be connected to the adsorption energy of nitrogen on metals, which depends on d band center energy of the metals and correlates with the affinity to nitrogen (Table S5). Bonding strength between metals and nitrogen relates to the filling of the anti-bonding states formed between the metal d states and nitrogen states. Calculation and experimental studies have suggested that metals having lower energy d band exhibit more filled anti-bonding states, leading to weaker bond strength. Since the energy of the d band center is located at higher energy level in the order of Fe, Co, Ni, the adsorption energy for an ammonia molecule increases in the order of Fe, Co, Ni. This finding accords to the computational study that onset potentials for the NH₃ electrooxidation are determined by the affinity between nitrogen and metal.

Some mechanisms of the NH₃ electrooxidation have been proposed by several groups. The most accepted mechanism for the NH₃ electrooxidation in alkaline media, which was proposed by Maurer and Gerischer, is described in eqs (1)–(6).

\[
\begin{align*}
\text{NH}_3^{(aq)} & \rightarrow \text{NH}_3^{\text{rad}} & (1) \\
\text{NH}_3^{\text{rad}} + \text{OH}^- & \rightarrow \text{NH}_4^{\text{rad}} + \text{H}_2\text{O} + \text{e}^- & (2) \\
\text{NH}_2^{\text{rad}} + \text{OH}^- & \rightarrow \text{NH}_2^{\text{rad}} + \text{H}_2\text{O} + \text{e}^- & (3) \\
\text{NH}_x^{\text{rad}} + \text{NH}_y^{\text{rad}} & \rightarrow \text{N}_x\text{H}_y & (4) \\
\text{N}_2\text{H}_y^{\text{rad}} + (x + y)\text{OH}^- & \rightarrow \text{N}_y + (x + y)\text{H}_2\text{O} + (x + y)\text{e}^- & (5) \\
\text{NH}_x^{\text{rad}} + \text{OH}^- & \rightarrow \text{N}_x + \text{H}_2\text{O} + \text{e}^- & (6)
\end{align*}
\]

NH₃ reacts with OH⁻ adsorbed on the surface of the nanoparticles and is progressively dehydrogenated to form surface adsorbed NH₃ rad. Then the NH₃ rad species dimerize into N₂H₂ rad, which is followed by subsequent dehydrogenation to give the final product, i.e., N₂. The fully dehydrogenated N₂ produced at reaction (6) is a poisonous species fixed on the electrode surface and prevents further adsorption of NH₃ due to its high adsorption strength, which causes decrease of catalytic performances. Experimental and theoretical studies have suggested that formation of N₂ through dimerization of NH₃ rad species does not occur in the NH₃ electrooxidation. Metals that strongly adsorb nitrogen species have a high affinity to nitrogen, resulting in a low energy barrier for dehydrogenation reactions and a low overpotential in NH₃ electrooxidation. Thus, higher affinity between metal and nitrogen results in a lower onset potential for NH₃ electrooxidation whereas it also leads to poisoning on the catalyst due to the irreversible adsorption of N₂ rad, which causes decrease of reaction rate. The adsorption energy of nitrogen on metals is related to affinity to nitrogen, which is consistent with the order of onset potential observed in this study. Therefore, we can conclude that the onset potential on Fe-group catalysts is determined by affinity between metals and nitrogen.

We conducted CA experiments under the application of 0.5 V vs RHE to further investigate catalytic performances of Ni-containing NA catalysts (Figure 6). All catalysts showed an anodic current for the NH₃ electrooxidation with formation of N₂ (Figure S6). Current densities were relatively stable in the
The affinity to nitrogen and higher affinity provides lower onset potential and more rapid decrease of current densities due to faster poisoning. This work is the first systematic experimental study that reveals catalytic performances of Fe-group metal catalysts for the NH₃ electrooxidation. The potential dependence of the product selectivity is significant to elucidate a reaction mechanism, which would be a next challenge.

Unique catalytic behaviors were observed for the ternary FeCoNi/C catalyst, which showed the highest current density among the Ni-containing catalysts in the CA experiment. From the CV results in Figure 4, the CoNi/C showed higher current density than that of FeCoNi/C, suggesting that NA catalysts with larger Co ratio were expected to show higher current density. However, the FeCoNi/C showed higher current density than that of CoNi/C in the CA measurement. The activities of FeCoNi/C originate from synergetic effects by alloying. Theoretical calculation study suggested that catalytic activities of Co are higher than those of other transition metal catalysts including Pt. However, the activation energy for nitrogen-nitrogen bond formation described in eq (4) is significantly higher on Co than on Pt, leading to low activities on Co for the NH₃ electrooxidation. It is noted that Co-containing NA catalysts achieved an atomically-well-mixed structure in this study. Therefore, Fe and Ni atoms adjacent to Co can probably facilitate nitrogen-nitrogen bond formation and enhance catalytic activities as synergetic effects. In addition to effects of alloying with Co, it should be noted that catalytic properties on ternary FeCoNi/C catalyst reflect all characteristics of each constituent metal for the NH₃ electrooxidation. The FeCoNi/C showed comparable onset potential (0.21 V vs RHE) to that of FeNi/C (0.18 V vs RHE), which are lower than those of CoNi/C (0.29 V vs RHE) and Ni/C (0.49 V vs RHE) in Figure 4, indicating effects of Fe to lower overpotential. We observed no changes in structural and electronic properties from XRD and XPS measurements before and after the CA measurement (Figure 3c and Figure S7) and negligible dissolution of metal ions into the solution (Table S3). The results indicate that the FeCoNi catalyst has good stability due to alloying with Ni. Therefore, we concluded that the ternary FeCoNi/C catalyst exhibited excellent catalytic performances for the NH₃ electrooxidation by synergetic effects of catalytic roles of all Fe-group metals.

The findings in this study will help to synthesize novel electrocatalysts for NH₃ electrooxidation. The potentials for NH₃ electrooxidation on Fe-group NA catalysts were found to depend on the metal composition, e.g., peak potentials on one-to-one bimetallic alloys are intermediate of those observed on component pure metals and the potential varies according to the metal composition, which means that NH₃ electrooxidation reflects the slight difference in chemical interactions between a reactant molecule and a binding site on Fe-group NAs. Because Fe, Co and Ni are classified as Fe-group metals, binding energies and binding forms of reactants on the Fe-group NAs are not extremely different compared to those observed on the NAs including noble metals. For example, an Fe-group metal alloy including a precious metal, which has a low affinity to nitrogen, perhaps catalyzes reactions via different mechanisms. The potential shift on the Fe-group NA catalysts for NH₃ electrooxidation can be predicted by the affinity of the constituent metals.
metals to nitrogen and the composition ratio of the constituent metals. On the other hand, current density is influenced by various factors in the entirety of the reaction, such as adjacent elements, adsorption of reactants, transition state of intermediates, and so on, which are hardly predicted on the complex NA system in this study. We will examine the relationship between current density and characteristics of catalysts for NH₃ electrooxidation.

4. Conclusion

We synthesized a series of Fe-group simple monometal, binary and ternary NA catalysts supported on carbon and systematically investigated their catalytic performances for NH₃ electrooxidation. The Ni-containing catalysts showed activities for the NH₃ electrooxidation whereas the Fe/C, Co/C and FeCo/C were less active due to self-oxidation and dissolution. We first found that affinity of constituent Fe-group metals to nitrogen is considerably related to the catalytic performances for the NH₃ electrooxidation, i.e., the catalysts having higher affinity show lower overpotentials and vice versa more rapid decrease of current densities due to surface N₂ formation. Furthermore, each Fe-group element exhibits distinctive catalytic features for the NH₃ electrooxidation, i.e., Ni ensures chemical stability, Fe effectively decreases the overpotential and Co increases the current density. The ternary FeCoNi/C achieved the excellent catalytic performances originated from synergistic effects of the catalytic roles. This work will contribute to rational catalyst design using Fe-group elements.

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Supporting Information

Structural parameters from Rietveld analyses, the amount of metal ions dissolved, heat of formation of M-N, results of the CV and CA measurements, XRD patterns, XPS spectra, TEM images, BF-STEM images and STEM-EDX are described in Supporting information. This material is available on https://doi.org/10.1246/bcsj.20210007.

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