Preparation of Ordered Intermetallic Compounds and Their Application in Electrocatalytic Reactions

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Atomically ordered intermetallic compounds

Fuel cells catalyst

CO₂ reduction

co-Catalyst for photocatalysts
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Development of novel metal catalysts with high catalytic activity and selectivity is one of the most crucial research topics in the field of environmental and energy technologies. In general, the development of metal catalysts involves the addition of a second element to the active sites, such as Pt and Pd. Among the various metallic alloys, our focus has been specifically on a class of alloys, known as “intermetallic compounds,” which exhibit long range atomic order. This study aims to review the electrooxidation of formic acid, oxygen reduction reactions using atomically ordered intermetallic compounds such as Pd₃Pb and PdCu₃, high selectivity or catalytic reaction selectivity associated with additive element species, and CO₂ reduction reactions. Furthermore, various factors related to the electrocatalytic oxygen reduction reaction in acidic environments and electrooxidation of formic acid over Pd-based ordered intermetallic compounds have been discussed. The study also examines the photocatalytic activity of intermetallic co-catalysts toward the decomposition of volatile organic compounds using intermetallic co-catalysts. Finally, the electrocatalytic conversion of CO₂ over Sn- and Pd-based electrocatalysts has been discussed. The review and the ensuing discussions are presented in the backdrop of previous studies conducted in this field and is anticipated to provide important insights for the accelerated development of highly active advanced catalysts.

Key words
Ordered intermetallic Compounds; Fuel cell catalysts; photocatalysts; CO₂ reduction reaction
1. Introduction

Heterogeneous catalysts, particularly metal materials, are significantly important for energy conversion process, synthesis of organic compounds, and chemical industry. Above all, the demand for electrochemical energy conversion has been increasing. Generally, electrocatalysts are required to promote electrochemical reactions. The mainstream of the development of metallic electrocatalysts is alloys that aim at enhancing the electrocatalytic activity of elemental metals by adding a secondary element to the active metals such as Pt and Pd. Until now, several efforts have been made for the development of these alloys,\textsuperscript{1-2} including core–shell structures\textsuperscript{3-4} and electrocatalysts that show superior activity and selectivity for various electrochemical reactions. A new approach is required to understand the factors governing electrocatalytic selectivity and activity, and to create catalysts that are more selective, active, and durable.

Structurally ordered intermetallic compounds have significantly different chemical and physical characteristics compared to random alloys, and they contain distinct crystal structures with highly ordered atomic arrangements and crystal structures that are different from the constituent elements.\textsuperscript{5-6} Therefore, intermetallic compounds often exhibit different chemical and physical properties from their constituent elements. Owing to their unique properties, they have been studied for applications such as
superconductivity materials,\textsuperscript{7} shape memory alloys,\textsuperscript{8} and plating materials. However, many of them are bulk materials, and their application to catalysts, which requires a high surface area (i.e., nanoparticle materials), has been limited because they are difficult to prepare. With recent technological advances in inorganic materials, research on intermetallic compound catalysts is growing.

To date, several studies have been conducted on the application of intermetallic compounds as catalysts. For example, alumina supported atomically ordered intermetallic compounds of PtCu were reported for preferential oxidation of CO in excess hydrogen and oxygen.\textsuperscript{9} The study suggested that the role of Cu atoms adjacent to Pt in PtCu intermetallics is to act as O\textsubscript{2} adsorption sites and therefore function as active sites in this catalytic reaction. In another study,\textsuperscript{10} atomically ordered PtPb intermetallic compound were shown to exhibit improved electrocatalytic activity toward formic acid oxidation. In addition, in-situ Fourier transform infrared spectroscopy data revealed that adsorbed CO species do not form on the surface of intermetallic compounds in the oxidation of formic acid.\textsuperscript{11} In order for CO poisoning to occur on the Pt surface, two or more adsorption sites are required (known as the third body effect\textsuperscript{12}). In this case, Pt-CO bond is difficult to form on atomically ordered surface because of the secondary element adjacent to Pt. In the latter case, the catalytic role of intermetallic compound is to modify the electronic and
crystal structure of the active site (i.e., Pt and/or Pd). Therefore, the second element in the intermetallic compounds does not “directly” serve as the active site, but rather modifies the active site structures such as Pt and Pd. Our research is focused on catalysts with the latter function.

We have developed several catalysts centered on nanosized intermetallic compounds, applied to fuel cell catalysts, co-catalysts for photocatalysts, electrochemical CO₂ reduction reactions, and plating films. This comprehensive study reviews both theoretical calculations and experimental work on atomically ordered intermetallic compound catalysts for electronic energy conversion, photocatalysis, and conversion of CO₂. This study is divided into three major sections. Section 2 introduces factors related to the electrocatalytic oxygen reduction reaction (ORR) in acidic environments and electrooxidation of formic acid over Pd-based ordered intermetallic compounds. Section 3 discusses the photocatalytic activity toward the decomposition of volatile organic compounds using intermetallic co-catalysts. Finally, electrocatalytic conversion of CO₂ over Sn- and Pd-based electrocatalysts is discussed in Section 4.
2. Preparation of Pd-based ordered intermetallic compounds and their application to fuel cell catalysts

The preparation of nanosized electrocatalysts for cathodic ORR and anodic oxidation of small organic compounds, such as formic acid, in direct fuel cells is important. Bimetallic electrocatalysts based on Pt and Pd have been extensively used to develop fuel cells with low or zero Pt content. Moreover, to develop commercially viable polymer electrolyte fuel cells (PEFCs), it is imperative to use active electrocatalysts. Herein, we have examined various nanoscale Pd-based bimetallic and core–shell electrocatalysts for the ORR and formic acid oxidation in PEFCs. We also discuss theoretical and experimental methods that are used to enhance the activity of these electrocatalysts.

2.1. ORR on PdCu₃ intermetallic compound

The ORR is one of the key electrochemical reactions for fuel cell applications and metal–air batteries and, therefore, has been investigated over the last several decades. Pt-group metals, in particular Pt, still have great potential as electrode materials because of their high performance in ORR and durability in acidic environments. To enhance the electrocatalytic activity of Pt, various approaches such as alloying effects, strong metal-
support interactions,\textsuperscript{26-29} grain boundary effects,\textsuperscript{30} and interfacial geometric interactions\textsuperscript{31} have been used. Electrocatalytic activity toward ORR should correlate with the electronic state of the metal surface. The d-band center, obtained from XPS and/or density functional theory (DFT) calculations, is an index for determining the activity of ORR.\textsuperscript{32-33} The d-band center value corresponds to the catalyst–oxygen binding strength. When the d-band center position is near the Fermi level, oxygen molecules and reaction intermediates, such as O$_2^-$ and OH$^-$, are strongly adsorbed on the active sites. Conversely, when the d-band center is far from the Fermi level, the activation of the oxygen molecules is poor. Therefore, the ideal ORR activity should proceed well under the optimal value of the d-band center. Pt has an optimal value for the d-band center for ORR in pure metal elements,\textsuperscript{34} and oxygen can be reduced to H$_2$O via a four-electron transfer on the Pt surface. However, there are several concerns for the commercialization of Pt-based materials: (i) high cost as well as Pt resources are required and (ii) poor tolerance to methanol caused by methanol crossover. Therefore, it is necessary to significantly develop alternative materials, such as other precious metals.

Among the precious metals, Pd has attracted significant attention as an alternative candidate for the ORR because its physicochemical characteristics are similar to those of Pt (i.e., the same crystal structure, and both belong to the same group in the periodic table).
In addition, Pd can electrochemically reduce oxygen via a four-electron transfer without any by-products such as H$_2$O$_2$.$^{35-36}$ Recently, Pd has become more expensive metal than Pt. However, historically, Pt has been more expensive than Pd; therefore, we still believe that Pt-free catalysts should be explored. In the electrocatalytic ORR in acidic media over pure Pd, the electrocatalytic activity is lower than that of pure Pt owing to the high d-band center value of pure Pd metal. Therefore, to develop Pd-based electrocatalysts that show superior activity toward ORR, it is necessary to modify the electronic state of the Pd surface by alloying with secondary elements.
Figure 1. (A) Schematic illustration (top and side views) of the electrochemical dealloying process of PdCu₃. (B) Binding energy of oxygen, oxygen adsorption sites, and
average distances between catalyst surface and oxygen. Reproduced with permission.\textsuperscript{14} Copyright 2018, The Royal Society of Chemistry.

The combination of experiments and theoretical calculations is a powerful tool for determining not only high-performance catalysts for the ORR, but also for guiding novel electrocatalysts. For example, it is difficult to understand the key factor responsible for the high electrocatalytic performance obtained in the case of Pd–M random alloys (e.g., M = Fe, Co, Ni, and Cu), which have been commonly reported. In contrast, the atomically ordered intermetallic structure allowed us to understand the key factors and create novel electrocatalysts that show high electrocatalytic activity owing to their ordered structure. Therefore, there are two advantages to creating atomically ordered intermetallic compounds: (i) They can be expected to realize a higher electrocatalytic activity and durability, and (ii) their electrocatalytic performance can be predicted from theoretical calculations. First, we performed DFT calculations on ordered intermetallic PdCu\textsubscript{3} structures to achieve a higher electrocatalytic ORR performance compared to conventional Pt electrocatalysts. Figure 1A shows the process in which stable Cu-free surface is formed in the electrochemical environment (this structure will be denoted as “dealloyed PdCu\textsubscript{3}”). This structure is a key factor in achieving high electrocatalytic
activity toward the ORR. In fact, surprisingly, DFT calculations (Figure 1B) indicate that the dealloyed PdCu₃ structure has significantly lower oxygen binding energy than conventional Pt as well as pure Pd metal. According to our calculation results, the oxygen binding energy (4.36 eV) in dealloyed PdCu₃ is comparable to that of Pt–Ni alloy catalysts, which is well known as superior ORR catalysts in the literature.⁷ The mass activity of dealloyed PdCu₃ toward ORR at 0.9 V is 0.047 A mg⁻¹, which is lower than that of pure Pt. The difference between the ORR activity and DFT calculations is considered to be due to the difference in the number of oxygen adsorption sites. Further research efforts, both experimental and theoretical, are required to develop high-performance electrocatalysts in the Pd-based alloys.

In the case of ORR in alkaline media, we synthesized various Pd-based alloy (i.e., Pd-M; M = Fe, Co, and Ni) electrocatalysts and then electrochemically dealloyed them to enhance the ORR activity. The Pd–M nanoparticles after electrochemical dealloying had a core–shell-type structure with Pd₃M as the core and Pd as the shell.⁸ A core–shell-type-structured Pd₃M nanoparticle exhibited an enhanced electrocatalytic activity compared to that before the dealloying process. Moreover, the electronic state, which relates to catalytic activity, was estimated based on both DFT calculations and experimental results.
2.2. Electrochemical oxidation of formic acid over Pd₃Pb nanoparticles

The electrooxidation of formic acid in direct formic acid fuel cells has attracted significant attention because of its high energy density. Pd metal electrocatalysts are a better benchmark than pure Pt for the electrooxidation of formic acid. This is because pure Pd provides a direct pathway, \((\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-)\), with slight CO poisoning, which is produced by the reduction of CO₂ rather than dehydration of formic acid, whereas pure Pt provides an indirect pathway (\(\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}, \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-\)). However, there is still room for improvement in the catalytic performance of Pd. It is necessary to control the surface structure of Pd at the atomic level to develop high-performance electrocatalysts. We prepared atomically ordered intermetallic Pd₃Pb nanoparticles and estimated their electrocatalytic activity toward formic acid oxidation. Figure 2A shows the atomic resolution scanning transmission electron microscopy (STEM) images of the prepared ordered intermetallic Pd₃Pb. The arrangement of the Pb and Pd atoms is well-ordered, as observed by z-contrast (i.e., the Pb atoms exhibit brighter dots than Pd atoms). The electrocatalytic activity toward formic acid oxidation is shown in Figure 2B. In the case of the Pt catalyst, two oxidation peaks that correspond to the direct and indirect pathways were observed, thus indicating that Pt has low catalytic activity. For the Pd electrocatalyst, the main oxidation (direct pathway)
and shoulder peaks (CO oxidation pathway) were observed. In addition, although it was not mentioned in a previous study, a small peak was observed at approximately +0.1 V (vs. RHE) on only the pure Pd catalyst, while Pd₃Pb did not exhibit this particular peak. This is not due to the range switching in the potentiostat. In fact, a similar phenomenon has been observed in other studies. It is considered that CO₂ molecules or intermediates are desorbed from the Pd surface for the CO₂ reduction reaction. It is well known that HCOOH is decomposed to H₂ and CO₂ at ambient temperature on pure Pd, and CO₂ molecules can be electrochemically reduced to HCOOH on the Pd surface at almost zero overpotentials. In addition, observed peak at +0.1 V at pure Pd electrocatalyst could not be observed on the atomically ordered intermetallic Pd₃Pb surface. Recently, we conducted electrochemical tests for the CO₂ reduction reaction using Pd and atomically ordered intermetallic Pd₃Pb. Formate could be detected on the pure Pd surface in the low potential region; however, it could not be (or poor) generated on the Pd₃Pb surface. The details of this observation will be provided in the next study. Thereafter, the prepared atomically ordered intermetallic Pd₃Pb (after electrochemical treatment) showed a significantly higher mass activity toward formic acid oxidation, compared to electrocatalysts reported by several previous studies. This electrochemical phenomenon could be explained by the CO binding strength on the Pd- or Pd₃Pb- surface based on the
d-band center value. The CO binding strength was measured by both theoretically calculated density of state spectra and hard X-ray photoelectron spectroscopy.

Figure 2 (A) High-resolution STEM images of an ordered intermetallic Pd₃Pb nanoparticle before and after electrochemical treatment. (B) Anodic sweep
voltammogram for formic acid oxidation and CO stripping test. Theoretically calculated and experimentally obtained d-band center values for the surfaces of Pd and ordered intermetallic Pd₃Pb. Reproduced with permission.⁰¹³ Copyright 2017, American Chemical Society.

3. Photocatalytic decomposition of volatile organic compounds over intermetallic PtPb-loaded WO₃ photocatalyst

Even in photocatalysts with low activity, such as WO₃, organic compounds can be decomposed by loading Pt on the photocatalyst surface, as reported by Abe et al.⁴² Oxygen reduction via a multi-electron transfer can be conducted on the surface of the Pt co-catalyst. To develop novel co-catalyst-loaded photocatalysts that exhibit highly active and selective materials, the electrochemical ORR activity is considered to be a key parameter in the decomposition of volatile organic compounds. Since the ORR should be conducted on the surface of a co-catalyst, the development of the co-catalysts for photocatalysis is important to prepare highly active catalysts. Atomically ordered intermetallic PtPb exhibits a high performance for a four-electron transfer ORR and electrochemical oxidation of small organic compounds such as formic acid and
methanol$^{9,11}$ We believe that the use of a high-performance catalyst for electrochemical reactions is an effective strategy. In one of our studies, we prepared WO$_3$-photocatalyst-supported atomically ordered intermetallic PtPb nanoparticles with excellent photocatalytic activity toward the decomposition of acetic acid, as shown in Figure 3. The prepared PtPb/WO$_3$ catalyst showed significantly higher photocatalytic activity than the Pt-loaded WO$_3$ and pure WO$_3$ photocatalysts. Interestingly, the photocatalytic decomposition of acetic acid on intermetallic PtPb nanoparticle co-catalysts proceeds through a mechanism different from that of the Pt co-catalyst. This result indicates that the reaction selectivity in the photocatalysts depends on the co-catalyst.$^{16}$
Figure 3. Decomposition of acetic acid over Pt/WO$_3$ and PtPb/WO$_3$ with respect to time. Inset: low- and high- magnification TEM images of ordered intermetallic PtPb/WO$_3$ surface. Reproduced with permission.$^{16}$ Copyright 2016, Elsevier.

4. Electrocatalytic reduction of CO$_2$

The electrochemical reduction of CO$_2$ is a challenging approach that reduces CO$_2$ and is helpful in solving resource depletion problem. However, the CO$_2$ reduction reaction on electrocatalysts requires significantly high overpotentials because CO$_2$ molecules are the most stable compounds in carbon-based molecules. In the CO$_2$ reduction reaction, protons (H$^+$) in the aqueous electrolyte solution are involved in the reaction; however, the low reduction efficiency owing to the competition and simultaneous progress of the H$^+$ reduction reaction is also an important problem. Therefore, to allow the CO$_2$ reduction reaction to proceed with high efficiency, it is important to develop a catalyst with a low overpotential and high selectivity for the CO$_2$ reduction reaction. As a pioneering work in the electrochemical CO$_2$ reduction reaction, Hori et al. reported the relationship between the electrocatalytic selectivity toward the CO$_2$ reduction reaction and the type of metal electrocatalysts.$^{43}$ Precious metals such as Ag, Au, and Pd exhibit CO selectivity;
non-precious metals such as Sn, Pb, and Bi exhibit formate selectivity; and metals such as Pt, Fe, Ni, and Co are non-active metals. Only Cu exhibits selectivity for organic compounds through the transfer of more than six electrons. In addition, the selectivity and activity of the electrocatalytic CO$_2$ reduction reaction depend on the structure of the electrocatalysts, that is, morphology, size, and crystal structure; therefore, it is important to design the corresponding electrocatalysts.

4.1. CO$_2$ reduction reaction over intermetallic Cu$_6$Sn$_5$ nanoparticles with a SnO$_2$ shell

Sn metal is a unique electrocatalyst for the CO$_2$ reduction reaction because of its relatively high formate selectivity. Moreover, it is a non-noble metal with low toxicity. Interestingly, SnO$_2$, rather than Sn metal, exhibits high selectivity as an electrocatalyst toward formate formation in the CO$_2$ reduction reaction. The electrocatalytic selectivity toward formate formation in the CO$_2$ reduction reaction can be increased by controlling the surface structure of SnO$_2$. Recently, Sn- and Sn-based electrocatalysts with high selectivity toward formate and/or CO production, such as Sn-based alloys and core–shell-type structures, have been reported. In a recent study, we prepared an atomically
ordered intermetallic core–shell structure with Sn$_5$Cu$_6$ as the core and SnO$_2$ as the shell. In this core–shell material, Sn$_5$Cu$_6$ has a Ni-As-type structure, as shown in Figure 4A. It was obvious that the Sn shell layer was coated on the intermetallic Sn$_5$Cu$_6$ nanoparticles. We believe that this core–shell structure is key to enhancing the electrocatalytic selectivity toward the CO$_2$ reduction reaction. We have attempted to test the potential dependence of faradaic efficiency of H$_2$, HCOOH, and CO in the CO$_2$ reduction reaction. The prepared intermetallic Sn$_5$Cu$_6$-core–SnO$_2$-shell exhibits superior electrocatalytic selectivity toward formate formation in a low reduction potential region ( $>$ −0.4 V), thus indicating that formate could be produced at a significantly low overpotential. This electrocatalytic phenomenon was considered by measuring the local structure of the Sn$_5$Cu$_6$-core–SnO$_2$-shell. Figure 4A-B shows X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements at beamline 01XU in Spring-8. From the XANES profiles, the oxide component exists in the prepared materials, as expected from other characterizations. Importantly, according to the EXAFS profiles, the Sn–Sn atomic distance in SnO$_2$ on the surface of the Sn$_5$Cu$_6$ core was calculated to be 3.09 Å, representing compressions of 4.9% compared to that of the prepared Sn nanoparticles (3.25 Å), as shown in Figure 4. We considered that this compressive strain, caused by the formation of an intermetallic compound core,
contributes to the high electrocatalytic performance toward the formation of formate in the CO₂ reduction reaction.

Figure 4. (Upper) XRD profile for the carbon-supported nanoparticles. (Lower) (A) XANES spectra of Sn K-edge over (a) Sn foil, (b) Sn/C, and (c) SnOₓ–Sn₅Cu₆. (B) Fourier transform of the Sn K-edge EXAFS spectra. Reproduced with permission. Copyright 2019, The Royal Society of Chemistry.
4.2. CO$_2$ reduction reaction over various Pd-based alloys

As remarkable electrocatalysts for the CO$_2$ reduction reaction, Pd and Pd-based materials have attracted significant attention owing to their electrocatalytic properties. Pure Pd exhibits high faradaic efficiency for both formate (at lower reduction potentials) and CO (at a high reduction potential) formation.$^{52}$-$^{53}$ It is important to control the electrocatalytic selectivity of the Pd metal. Several Pd- and Pd-based alloy catalysts have been reported every year. For example, He et al. first reported that a single atom of Pd electrocatalyst for the CO$_2$ reduction reaction shows superior activity and selectivity because it can suppress PdH formation, which is essential in Pd- and Pd-based alloys.$^{54}$ Other studies on the alloying effect of Pd in the electrocatalytic CO$_2$ reduction reaction in a KHCO$_3$ aqueous electrolyte solution have been reported. Until now, Pd–B,$^{55}$ Pd–Pt,$^{56}$ Pd–Ag,$^{57}$ and Pd–Bi$^{58}$ alloys have been explored in order to enhance the faradaic efficiency for formation of CO and HCOOH. In our recent study, we demonstrated the preparation of different Pd electrocatalysts and investigated their electrocatalytic selectivity toward the CO$_2$ reduction reaction. At a potential of −0.1 V (vs. RHE), the Pd–Zn alloy electrocatalyst exhibited a significantly superior faradaic efficiency of 99.4%, which is the highest value in recently published reports. In addition, we considered that
the electrocatalytic selectivity toward CO$_2$ reduction depends on the atomic radius of the second element with Pd.$^{59}$ That is, smaller atomic radius of the second element than that of Pd results in formate selectivity, whereas larger atomic radius of the second element than that of Pd results in CO selectivity. We also considered the factors responsible for the enhancement of catalytic activity from the viewpoint of electronic states. Therefore, we believe that this work should be a design guideline for the CO$_2$ reduction reaction of Pd-based bimetallic alloys with excellent performance. At present, we are attempting to prepare Pd-based atomically ordered intermetallic compounds that show selectivity toward organic compounds such as CH$_4$, C$_2$H$_5$, and CH$_3$OH.
Figure 5. Schematic illustration of electrocatalytic selectivity toward CO₂ reduction reaction. The electrocatalytic selectivity depends on the secondary element of Pd in Pd-based alloys. Reproduced with permission. Copyright 2020, American Chemical Society.

5. Conclusion

The atomically ordered intermetallic compounds and/or bimetallic alloy electrocatalysts developed by us were explored and discussed in three parts: (1) A combination of experiments and theoretical calculations of Pd-based materials for electrocatalytic ORR
and formic acid oxidation, (2) photocatalytic activity for the decomposition of acetic acid over intermetallic PtPb co-catalyst for photocatalysis, and (3) electrocatalytic CO₂ reduction reaction over Sn- and Pd-based materials. The combination of theoretical calculations and experiments allowed us to determine the design guidelines for creating a highly active electrocatalyst for the ORR. Although atomically ordered PdCu₃ nanomaterials with electrocatalytic performance for ORR higher than that of conventional Pt catalysts have not yet been achieved, DFT calculations have shown PdCu₃ core–shell compounds as promising electrocatalysts. In the case of photocatalysts, we first applied ordered intermetallic compounds as co-catalysts. In addition, using our synthesis techniques, alloy nanoparticles were deposited only onto the reduction sites of the photocatalyst, and our prepared material exhibited superior photocatalytic activity toward the decomposition of various organic compounds. In the electrochemical CO₂ reduction reaction, we clarified the conditions under which formic acid selectivity can be enhanced in Sn-based materials. In addition, a significantly higher faradaic efficiency for formate formation was found on the bimetallic Pd–Zn alloy compared to that on a conventional Pd catalyst. This faradaic efficiency value of Pd–Zn is a record value in recent literature. We also considered the dependence of the electrocatalytic selectivity on the type of second materials with Pd in Pd-based alloys. We believe that our work will accelerate the
development of highly active catalysts.

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