

Carbon Alloy Catalysts for Polymer Electrolyte Fuel Cells: Exploration of Materials and Understanding of Mechanisms

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ABSTRACT

The launch of the fuel cell vehicle (FCV) in December 2014 has moved our society into the era of hydrogen energy. Expectations for, and demands on, this technology will first increase steadily and then explosively. Owing to the scarcity of available natural resources and considering costs, the development of cathodes using non-platinum catalysts is an important issue to be addressed for the stable and secure provision of FCVs. We have been developing carbon alloy catalysts, such as nanoshell-containing carbon and boron nitrogen (BN)-doped carbon catalysts, where catalytic activities originate from the carbon surface and not from surface metal complexes. First, we discuss the discovery of carbon materials exhibiting electrocatalytic activity followed by their application to ORR. Second, we provide experimental evidence for ORR activity originating from warped graphitic layers. Next, we describe useful methods to obtain highly active carbon alloy catalysts. Finally, we report a notable single cell performance of 0.65 W/cm² using air as the oxidant.

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Keywords : Carbon Alloy Catalysts, Oxygen Reduction Reaction, Cathode Catalysts, Polymer Electrolyte Fuel Cells

1. Introduction

Toyota commercially launched fuel cell vehicles (FCVs) in December 2014. With this release, Japan will now be pushed to construct a hydrogen station. With this launch, our society just entered the era of hydrogen energy.

Currently, platinum is used as the catalyst in a commercial FCV, which is a noble metal resource with a few deposits mined only in limited areas such as South Africa and Russia. The concentrated dependence on this resource hinders the realization of a stable and secure hydrogen society; thus, platinum surrogate catalysts have been investigated. As a method of reducing cost, reducing the amount of platinum used can be considered; however, it causes a serious problem in the cathode due to the sluggish kinetics of oxygen reduction reaction (ORR) compared to hydrogen oxidation reaction by 2–5 orders of magnitude.^{1–4} Many types of non-precious metal catalysts have been discovered, such as rhodium or ruthenium chalcogenides,⁵ metal carbides such as WC,⁶ and macrocyclic metal complexes.⁷

Carbon-based catalysts have been recognized as the most promising non-precious metal catalyst. Herein, the authors have

focused their attention on the electrocatalytic activities of carbon and discovered carbon materials exhibiting ORR activity.^{8–10} The reason for this interest stems from the fact that the properties of carbon can be designed by controlling the conditions under which they are prepared, such as starting material selection, carbonization temperature, and time. Since carbon materials that are usually obtained are kinetically stable but thermodynamically unstable, we can control the structure and properties of carbon by altering the carbonization process, which can be achieved by changing the aforementioned parameters and using catalysts to control carbonization.

Catalytic graphitization has been known in the field of carbon materials science to provide graphitic carbon at low temperatures.¹¹ In this phenomenon, carbon materials are heat-treated in the presence of some metal species such as Ni or Fe, and crystalline carbon is precipitated from metal particles, which act as solvents to dissolve carbon atoms. The carbonization process can also be altered by adding such metal species to the carbon starting materials prior to heat treatment.

The authors introduced Fe species into carbonization systems and observed an increase in the photovoltaic response of carbon/n-Si hetero-junctions¹² and an increase in heterogeneous electron transfer in the electrochemical reaction of ferricyanide anion.^{13–16} The



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Yasuo Imashiro (Administrator of R&D Center, Nissinbo Holdings Inc.)

Yasuo Imashiro is currently of Administrator of R&D Center at Nissinbo Holdings Inc. He received his M.S. from Sophia University in 1984. His research involves development of new functional carbon materials used for fuel cell cathode, hydrogen storage and hydrogen production as well as engineering of mass-production of the developed carbon materials.

He has developed and commercialized new additive for resins, glass-like carbons and electrochemical double layer capacitors. He is the director of the R&D center of the company developing novel materials and their production processes.

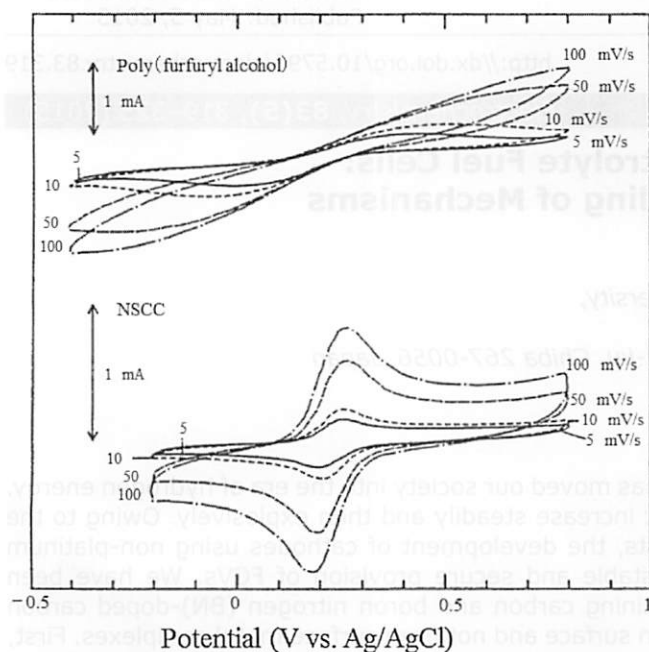


Figure 1. Cyclic voltammograms of nanoshell-containing carbons.¹³ Reprinted by permission of the publisher, The Carbon Society of Japan.

application of carbon to the oxygen reduction reaction (ORR) led to our current study on carbon alloy catalysts for fuel cell cathodes,^{17,18} which are examples of catalytic carbonization. We have also developed boron nitrogen-doped carbon. The catalytic activities of our carbon catalysts were achieved by introducing heterogeneity; hence, we named these carbon alloy catalysts after the definition of a carbon alloy proposed by Tanabe and Yasuda.¹⁹

This paper gives a background on our carbon alloy catalysts from its discovery to the state-of-art.

2. Carbon Alloys Exhibiting ORR Catalytic Activity

2.1 Discovery of electrochemically active carbon¹³

First, nanoshell-containing carbon (NSCC) was prepared by adding ferrocene to poly(furfuryl alcohol), a starting polymer of glass-like carbon, to be carbonized. The obtained NSCC exhibited a reversible response to the redox reaction of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$, as shown in Fig. 1; the rate of heterogeneous charge transfer was as high as that of a platinum electrode.¹³ From transmission electron microscopy and X-ray diffraction (XRD) results, NSCC was observed to contain shell-like carbon particles having a diameter of 20–50 nm, and the shells consisted of stacked graphitic layers; such a structure is termed as a nanoshell (NS),¹⁸ as coined by Ozaki et al. This study commenced subsequent studies on carbon alloy catalysts used in cathodes of fuel cells.

2.2 Nanoshell-containing carbon (NSCC)

The detailed structure of an NS has been described in this section. Figure 2 shows typical transmission electron microscopy (TEM) images of an NS. The sizes of NSs were approximately 20–30 nm in diameter [Fig. 2(a)]. An enlarged picture of the fringe of the NS structure in Fig. 2(b) clearly exhibited stacked graphitic layers. The central and left-hand side parts of the picture correspond to the graphite layered structure and hollow space, respectively. X-ray studies revealed that the material contains a turbostratic structure, which is a type of a carbon structure without the ABAB stacking sequence of a perfect graphite crystal. Such NS structures are known to be produced by some catalytic action of transition metal species;

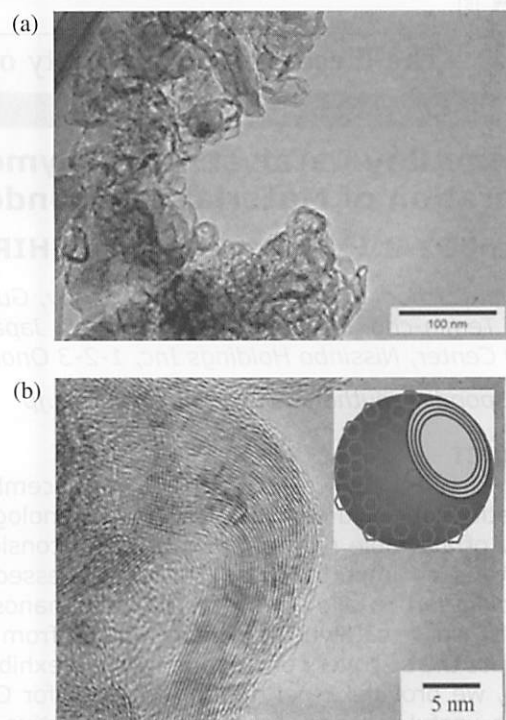


Figure 2. Typical images of NS. (a) low-magnification. (b) high-magnification. Reprinted by permission of the publisher, The Carbon Society of Japan.

namely, Fe was used as the catalyst in this case (as described in the above paragraph). Only limited metal species such as Fe, Co, and Ni can promote the formation of an NS structure. Figure 2(b) shows the inset of a model of the NS structure, a part of the surface of which is truncated to stress the hollow inside.

NSCC consists of not only NS structures but also an amorphous component, which was formed without the influence of transition metal catalysts during carbonization. (002) XRD patterns exhibited two diffraction lines—sharp and broad lines—confirming the multicomponent nature of this material.¹⁶ Detailed structural analysis by electron diffraction, TEM, and XRD revealed that the sharp and broad components corresponded to NS and amorphous structures, respectively.¹⁸ The development degree of NS, f_{sharp} , was estimated by the ratio of the scattering intensity of NS to the total intensity of (002) diffraction. The f_{sharp} value depended on the types of metal catalysts and carbonization temperature. Figure 3 shows the relationship between E_{O_2} and f_{sharp} , where E_{O_2} represents the potential corresponding to an ORR current density of $-10 \mu\text{A}/\text{cm}^2$.²¹ Fe and Co were found to be effective catalysts to produce carbon with higher E_{O_2} values; however, Ni was not effective. The type of ligand is also a factor that influences ORR activity; e.g., the phthalocyanine ligand was more effective in producing active carbon than acetylacetonate or pentadienyl ligand, both of which do not contain any N atoms. Both series of ligands with and without nitrogen atoms exhibited maximum activities at certain f_{sharp} values.

2.3 BN-doped carbon alloy catalysts

BN-doped carbon is another type of a carbon alloy that we discovered.^{9,22,23} Figure 4 shows the ORR voltammograms of BN-doped carbon prepared by carbonizing mixtures of a furan resin with melamine, a nitrogen dopant, and a trifluoroborane-methanol complex, a boron dopant. BN-doped carbon, denoted by BN_x ($x = 1-3$), exhibited higher ORR activities than those of carbon with singly doped nitrogen, N1 and N2, and boron B1. The N1s X-ray photoelectron spectroscopy (XPS) spectra of BN-doped carbon exhibited the presence of B–N–C moieties.

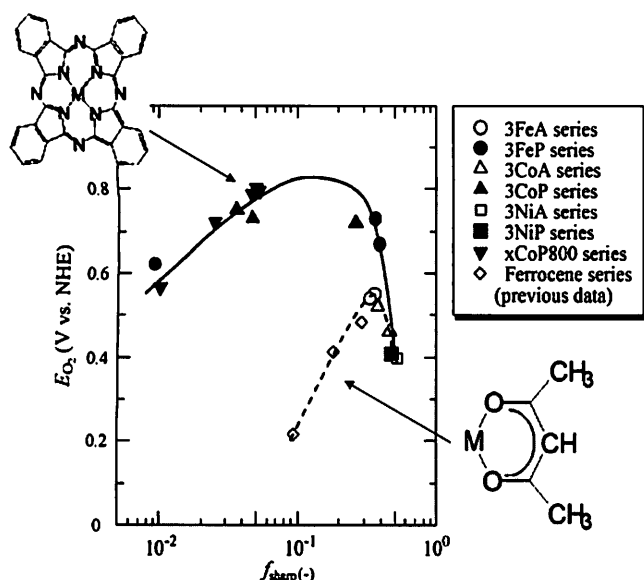


Figure 3. Dependence of ORR activity on the development of NS structure.²⁰ Reprinted by permission of the publisher, Elsevier Scientific.

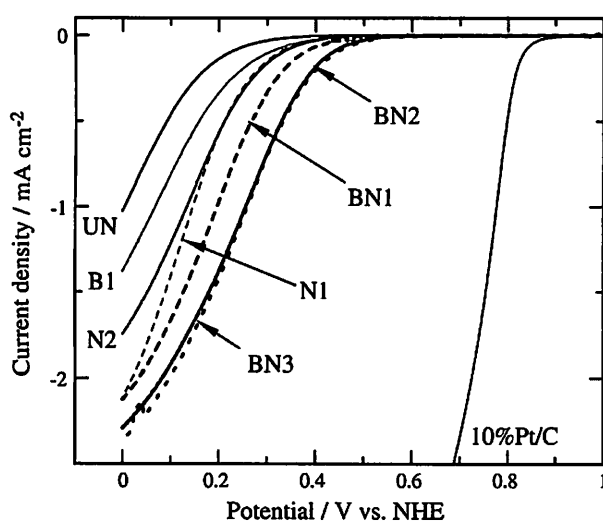


Figure 4. (Color online) ORR voltammograms of N, B, and BN-doped carbons.²² Reprinted by permission of the publisher, Elsevier Scientific.

The ORR activity of the aforementioned BN-doped carbon has been demonstrated to depend on the amounts of the nitrogen species located in the peripheral part of graphitic layers such as pyridine-type or pyrrole/pyridone-type carbon, referred to as N_{edge} .²² A comparison of the ORR activities of BN- and N-doped carbon with the same N/C ratio indicated that the former exhibited higher activity than the latter. If the amount of the N atoms, $N_{\text{B-N-C}}$, included in the B–N–C moieties is considered as a parameter to be added to N_{edge} , the ORR activity exhibited a continuous curve against the summation of N_{edge} and $N_{\text{B-N-C}}$. This finding suggested that the active sites formed by BN-doping are the same as those formed by N-doping, indicating that the carbon atoms influenced by the heteroatoms form active sites for ORR.

The size distribution of graphitic layers in carbon can be obtained by analyzing the (11) XRD peak of carbon by the Diamond's analysis.²⁴ N-, B-, and BN-doping resulted in the formation of smaller graphitic layers, as shown in Fig. 5. Since the size of the

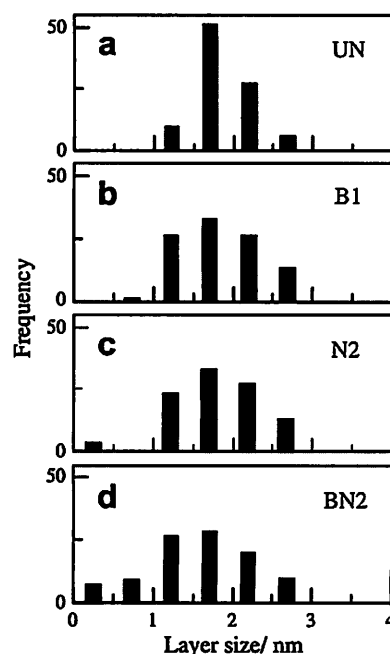


Figure 5. Distribution of L_n size.²² Reprinted by permission of the publisher, Elsevier Scientific. Reprinted by permission of the publisher, Elsevier Scientific.

graphitic layers was obtained by XRD analysis, the detected size represented the coherent region of the graphitic layers. This means that the formation of smaller sizes of graphitic layers does not simply indicate the formation of edge sites but also the formation of warped graphitic layers.

The abovementioned BN-doped carbon was prepared by altering the carbonization process by introducing compounds including N or B atoms. Other methods of BN-doping into carbon materials are possible. One of the methods we examined involves the sequential doping of N followed by B on the surfaces of carbon such as carbon black. The nitrogen doping method employed by us was ammoxidation, which involves heat-treatment using appropriate ratios of ammonia and oxygen diluted by nitrogen. Boron doping was performed on N-doped carbon by heating it in a mixture gas flow of BCl_3 and N_2 at elevated temperatures. BN-doped carbon prepared by the sequential doping of N and B was also found to exhibit ORR activities higher than that of original carbon black.²⁵ A study measuring the ORR activity of the N- and BN-doped carbon in electrolytes with different pH indicated that the enhancement of the local pH in the vicinities of the active sites is one of the factors that influence ORR activities. A mechanochemical method, the ball milling of carbon black in the presence of hexagonal boron nitride (h-BN) powder, can also be used to introduce N and B into the carbon material.²³

3. Active Sites of Carbon Alloy Catalysts

3.1 Comparison of catalytic features of carbon alloys with other non-Pt catalysts

Most of the ORR catalysts reported thus far have been prepared by introducing metallic elements such as Fe and Co as well as N atoms at elevated temperatures. The introduction of metal species and N atoms are crucial for the ORR activity of carbon materials. Many researchers believe that the surface metal–nitrogen complexes, such as Fe-N_x , are active sites for ORR.²⁶ Other candidates for the ORR active sites are the edge sites formed by N-doping; the electronic state of the carbon atoms, located at the periphery of the zigzag edge, is altered by the nearest N atoms in three-coordinated

forms located in the “valley” site of zigzag edges of graphene,²⁷ and the carbon atoms are positively charged because of the introduction of graphitic N atoms.²⁸

NSCC is prepared by carbonizing a precursor polymer in the presence of transition metal complexes as an NS-forming catalyst. This resembles the preparation of N_4 -M catalysts. The difference in the characteristics between NSCC and N_4 -M catalysts are as follows: (1) The ORR activity of N_4 -M catalysts diminishes by acid leaching; however, the ORR activity of NSCC is maintained or increased by the same treatment.^{29,30} (2) Both N and metal species are required for the preparation of N_4 -M; however, they are not required for the preparation of NSCC.^{31,32} (3) The formation of an NS structure inhibits ORR activity in the case of N_4 -M catalysts; however, ORR activity is not inhibited in the case of NSCC.^{31,33,34}

Recently, Singh et al. have discriminated the differences between the N_4 -M and N-doped carbon catalysts.³⁵ In their study, acid leaching decreased the activity of N_4 -M catalysts, but it did not affect the ORR activity of N-doped carbon. They also reported that both the N_4 -M and N-doped catalysts exhibited different performance: N-doped catalysts exhibited a longer lifetime than N_4 -M catalysts. The same results have also been reported by Chung et al., who studied the order of preparation of catalysts; they found two types of carbon with different persistence toward endurance tests.³⁶ These two recent studies suggested the presence of two types of catalytic carbon: N_4 -M-type carbon and other types of carbon. The features described in (1)–(3) indicate that the catalytic mechanism of NSCCs is different from that of N_4 -M catalysts.

We have studied the effects of acid washing conditions on the ORR activity of NSCC.³⁷ The ORR activity of NSCC did not change even when the surface metal content was diminished to a level below the detection limit of XPS ($< 0.1\%$ in atomic ratio). On the other hand, the ORR activity of N_4 -M catalysts changed with the amount of metals: As detected by XPS, the optimal surface contents were reported to be 0.5–2%. The discussion here confirms our opinion that the ORR activity of NSCC originates from some specially arranged carbon structures and not from surface metal species.

3.2 Electrocatalytic nature of NSCC

The electrochemical activities of NSCC were compared for two reactions: the redox reaction of ferricyanide ion and ORR. The peak separation between the oxidation peak and the reduction peak, ΔE_p , in cyclic voltammograms for the redox reaction of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ decreased with the development of NS structures, as evaluated by f_{sharp} (Fig. 6), indicative of the promotion effect of the NS to heterogeneous electron transfer.¹⁶ On the other hand, the maximum ORR activity was observed at a potential of $-10 \mu A/cm^2$ at certain f_{sharp} values. The differences in the dependence of the electrochemical catalytic activity of NSCC suggest the difference in the rate determining steps of these two reactions. The ORR mechanism includes oxygen adsorption and subsequent electron transfer. The different dependence of ORR activity on f_{sharp} from that of ferricyanide can be attributed to the oxygen adsorption step.³⁸ This inference indicates the abundance of active sites on the intermediately developed NSs.

The presence of the active sites on the NS was proved by purifying NSCC with H_2O_2 .³⁹ The multi-component nature of NSCC has been mentioned in the previous sections: NSCC consists of an amorphous carbon moiety and NS carbon. NS was selectively extracted by utilizing the difference of these two components against oxidation. The oxidation by H_2O_2 exposed the NS surface, resulting in an increase in the ORR activity. The high-temperature heat-treatment of the purified carbon removed surface defects on the exposed NS carbon, resulting in the loss of ORR activity. These experimental results proved that the surface defects formed on the NS structures are responsible for the ORR activity of NSCC.

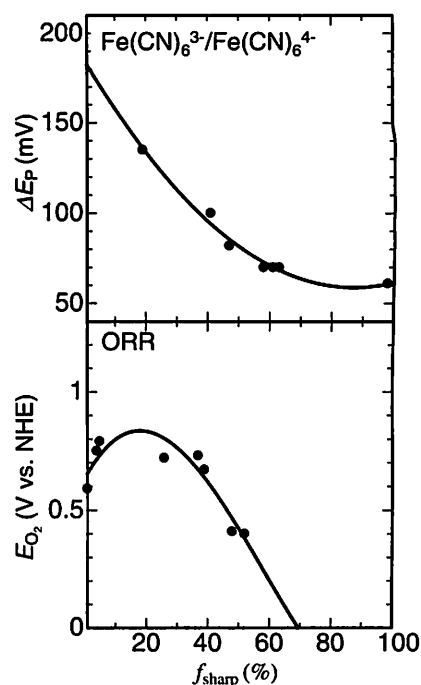


Figure 6. Comparison of correlations between electrocatalytic activities and f_{sharp} values for the redox reaction of ferricyanide anion (upper) and ORR (below).

3.3 Defective structure in graphitic layers as active sites for ORR

A comparison of TEM images also provides evidence for the contribution of surface defects to ORR. Figure 7 shows the TEM images of NSCC with different ORR activities. Figures 7(a) and (b) correspond to NSCC with higher and lower ORR activities, respectively. As shown in Fig. 7(a), NSCC with higher ORR activity exhibited an NS structure with small particles with an average particle size of approximately 30 nm; many edges and warped graphitic layers were observed in the magnified image (a-2). On the other hand, NSCC with lower ORR active sites exhibited larger NS structures with particle diameters of greater than 50 nm and smooth surfaces. Such less active NSCC was obtained by using Ni as the nanoshell-forming catalyst. The comparison between NSCC of varying activity and results of NS purification together proved the importance of defects of the carbon structure on the promotion of ORR.

Turbostratic carbon is a carbon structure without the stacking regularity of graphitic layers, which can be detected by XRD: broad (002) diffraction and extinction of three-dimensional diffraction were observed. In his book, (Late) Prof. Sugio Otani stated that the turbostratic structure is not merely losing the stacking regularity of the graphitic layers but is a structure composed of non-planar graphitic layers induced by the existence of a pentagonal or heptagonal ring structure in the hexagonal plane.⁴⁰ His description provides evidence for the possibility of such warped graphitic structures forming active sites for ORR.

We have conducted experimental studies to confirm the above possibility by using three carbon materials: (1) carbon with disordered stacking, induced by fullerene,⁴¹ (2) carbon nano-onions produced by the heat-treatment of nanodiamond,⁴² and (3) fullerene soot with warped graphitic layers. Herein, we describe the results of case (1).

Mesophase pitch is a type of pitch composed of polycyclic aromatic hydrocarbons in liquid crystal states (mesophase); this material carbonizes at the heat-treatment temperature, forming highly oriented graphitic carbon. A mixture of fullerenes, C_{60} and

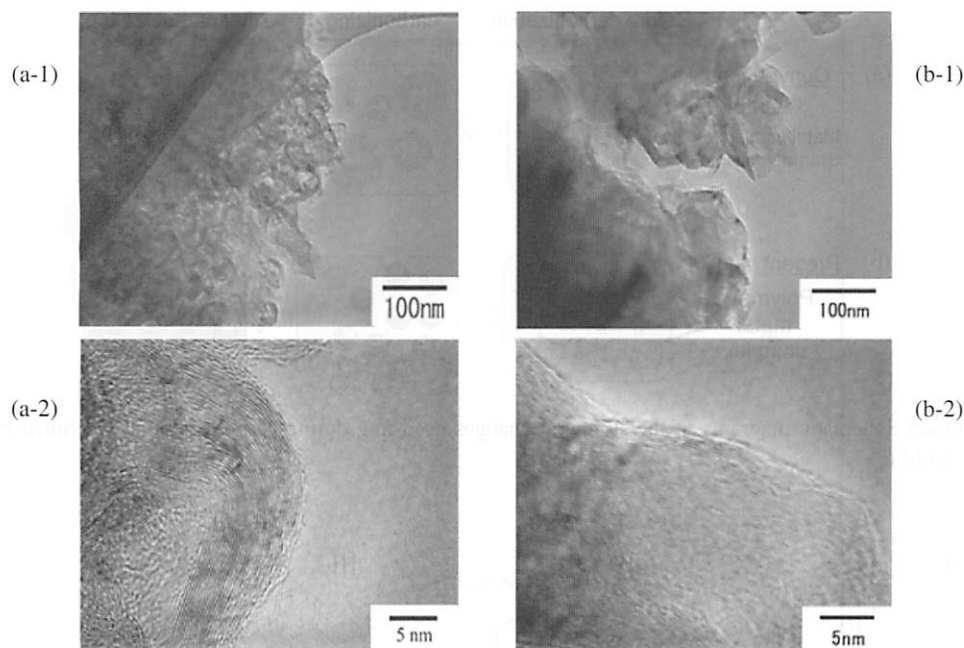


Figure 7. TEM images of (a) an active NSCC and (b) an inactive NSCC. Reprinted by permission of the publisher, The Carbon Society of Japan.

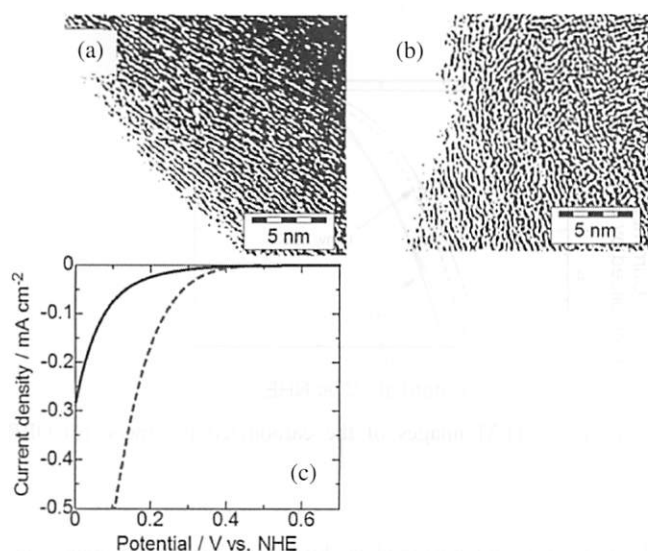


Figure 8. (Color online) TEM images of carbons prepared without FM (a) and with FM (b). (c) ORR voltammograms.⁴¹ Solid line and broken line represent the voltammograms for the pitch-derived and the FM-pitch-derived carbons, respectively. Reprinted by permission of the publisher, The Carbon Society of Japan.

C₇₀ (FM), was added to the pitch, and the mixture was carbonized at 1000°C. Figure 8 shows TEM images showing the effects of the addition of FM to the pitch. Figure 8(a) shows TEM images of the carbonized pitch prepared in the absence of FM. From upper-left to lower-right in the image, oriented layers of the graphitic structure were observed. On the other hand, carbon prepared in the presence of FM exhibited disorder in the graphitic layers [Fig. 8(b)]. Figure 8(c) shows a comparison of the ORR voltammograms of these two types of carbon. The carbon prepared in the presence of FM exhibited ORR activity higher than that of the carbon prepared in the absence of FM. O₂-adsorption and temperature-programmed desorption measurement revealed that the carbon prepared in the presence of FM exhibited oxygen uptake (0.18 mmol/g) higher than that of the carbon prepared in the absence of FM (0.12 mmol/g).

The results obtained here concluded that the disorders introduced into the stacking structure of carbon form the oxygen adsorption sites and promote ORR activity.

The above conclusion also explains the results mentioned in the previous sections about NSCC and BN-doped carbon. In the case of NSCC, the defects observed on the active NS surface adsorb oxygen to promote ORR. On the other hand, in the case of BN-doped carbon, the defects induced by doping, which were detected by a decrease in the coherent length, play the same role as the active sites of NSCC.

4. Material Design of High-performance Carbon Alloy Catalysts

4.1 Control of metal dispersion for uniform-sized NSs

The aim of preparing more active NSCC is to control the diameter of NS at 20–30 nm. The role of Fe or Co is to produce NS structures; however, the mechanism of NS formation is not fully understood. Metal complexes such as phthalocyanines or ferrocene decompose at elevated temperatures, resulting in the formation of metal particles. Reactive carbon species formed in the carbonized organic compounds dissolve into metal particles since smaller metal particles are unstable and can easily dissolve carbon atoms. Supersaturated carbon atoms deposit from the metal particles as more structurally organized carbon moieties or NS. The studies conducted thus far have revealed that the optimum size of NS for ORR activity ranges from 20 to 30 nm. Controlling the size of NS is an important requirement for the preparation of active NSCC.

For this purpose, polymeric metal complexes can be used. Figure 9(a) shows the distribution of metal atoms and their changes during carbonization. We used a phenol–formaldehyde resin as the NSCC precursor together with phthalocyanines. Phthalocyanines are insoluble in all solvents, and their complexes exist as microcrystallites in polymer matrices.⁴³ The inhomogeneous dissolution of the metal complexes leads to the formation of non-uniformly distributed NS particles, where some parts are very small, while other parts are very large. The uniform distribution of the metal cations or complexes in the polymer matrices was expected to form NS particles with a uniform size of ~20 nm in diameter, as shown in Fig. 9(b).

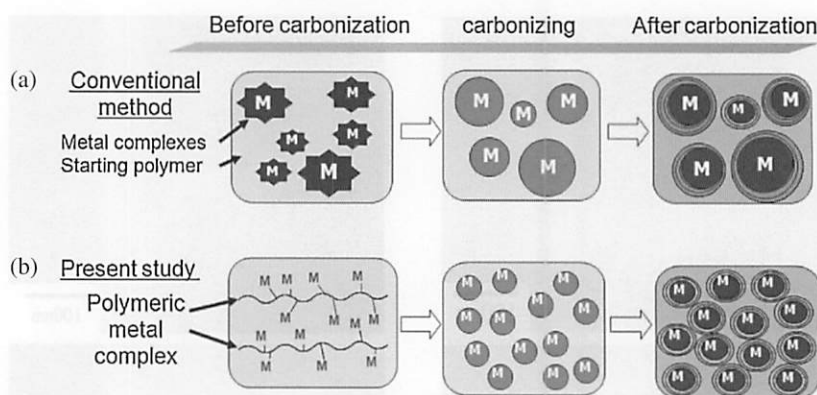


Figure 9. (Color online) Schematic diagrams of the structural changes occurring during carbonization.⁴⁴ Reprinted by permission of the publisher, Elsevier Scientific.

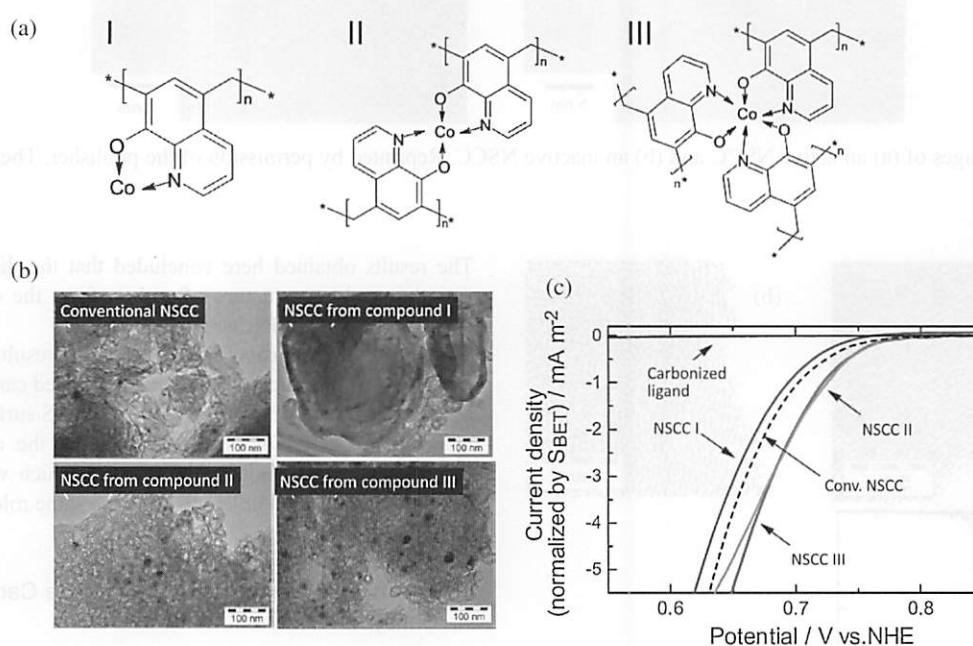


Figure 10. (Color online) (a) Structures of cobalt coordinated poly(oxines). (b) TEM images of the carbonized polymers. (c) ORR voltammograms of the obtained carbons.

To achieve this, polyoxine was used as the candidate polymer to realize the above idea, the structure of which is shown in Fig. 10(a). Kannari et al. have conducted the polycondensation of oxine with formaldehyde and coordinated Co cation to oxine coordination sites, formed by O and N atoms.⁴⁴ The carbonization of this precursor gave an NS having a diameter of 30 nm, larger than expected; however, a more uniform size distribution was obtained, as can be observed in Fig. 10(b). The NSCC thus prepared exhibited higher ORR activities with a uniform size distribution than that of a conventionally prepared NSCC, as shown in Fig. 10(c).

Takigami et al. have expanded this idea to use humic acid as a precursor, because it is rich in ion-exchangeable functional groups.⁴⁵ Humic acid exchanged with Co exhibited ORR activity higher than that exhibited by a conventionally prepared NSCC. Interestingly, the carbon material obtained from Co-exchanged humic acid did not produce NS structures; understanding the ORR mechanism of such carbon requires a more detailed understanding of the ORR catalyzed by carbon materials.

4.2 Modification of carbonization

Controlling the carbonization process is central to the preparation of functional carbon materials, since the structure, and hence

the properties, are governed by kinetic processes. Of course, the carbonization process can be altered by the use of metal species. Maie et al. have subjected partially carbonized polymers to mechanical treatment for altering the carbonization process by adding stress to the polymer matrix of the NSCC precursor.^{43,46} The combined treatment of the partial carbonization of the precursor and ball-milling was found to be effective for increasing ORR activity. The serial treatments also increased the remaining nitrogen content in the carbon, and further efforts to understand the enhancement of ORR activity are currently being undertaken in our laboratory.

Another method for controlling the carbonization process that is being undertaken in our laboratory is the use of a heterogeneous interface for influencing the carbonization of NSCC precursors. Kobayashi et al. have coated carbon black, Ketjen Black, with a cobalt–poly(vinyl pyridine) complex and carbonized it.⁴⁷ Maie et al. have introduced graphite oxide into an NSCC precursor. They observed an enhancement in the ORR activity depending on the graphite oxide content. Thus, recognizing that carbonization is a kinetic process broadens the spectrum of methods available for preparing carbon materials with desirable properties.⁴⁸

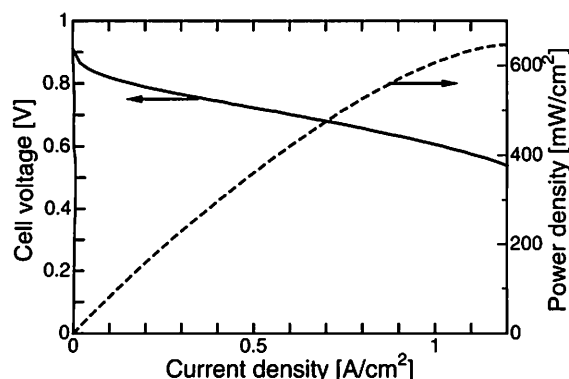


Figure 11. Polarization curves of the latest carbon alloy catalyst obtained for H_2/air condition. Reprinted by permission of the publisher, The Carbon Society of Japan.

4.3 Recent advances in carbon alloy catalysts for PEFC⁴⁹

Recently, Nisshinbo Holdings Inc. and the Gunma University carbon group have together developed highly active carbon alloy catalysts for ORR during their study toward the development of practical carbon alloy catalysts, based on the knowledge on carbon alloy catalysts for ORR. Figure 11 shows the single cell performance of the recently developed carbon alloy catalysts. We succeeded in obtaining carbon alloy catalysts exhibiting a maximum power generation of 650 mW/cm^2 with a carbon loading of 1.0 mg/cm^2 on the cathode; notably, such high performance was observed using air, not pure oxygen, as the oxidant, as has been reported by other research groups.⁴⁹ The detailed report is now being prepared for publication.

5. Conclusion

This paper has described the history and the state-of-art of carbon alloy catalysts for ORR. Of note, the key in designing carbon alloy catalysts is to recognize that carbonization is a kinetic process; hence, understanding and control of the reaction are essential. We would like to conclude this paper by citing words from the book of the Late Emeritus Professor Sugio Otani, Gunma University⁵⁰ (the original sentence is in Japanese).

Making carbon from organic compounds involves the elimination of elements other than carbon and the alignment of carbon atoms as designed by researchers. One can say, “You can prepare carbon materials simply by heating or burning organic substances”; there is no difficult science involved in that. He or she is absolutely correct. Heating or burning organic substances will yield carbon materials; however, whether the carbon materials thus obtained will meet the desired goal is questionable. In this case, the material is not designed but is formed accidentally.

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