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 provision of FCVs. We have been developing carbon alloy 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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application of carbon to the oxygen reduction reaction (ORR) led to our current study on carbon alloy catalysts for fuel cell cathodes, 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.

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 carbon

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 \( \text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-} \), as shown in Fig. 1; the rate of heterogeneous charge transfer was as high as that of a platinum electrode. 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), 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 graphene 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; 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. Detailed structural analysis by electron diffraction, TEM, and XRD revealed that the sharp and broad components corresponded to NS and amorphous structures, respectively. The development degree of NS, \( f_{\text{NS}} \), was estimated by the ratio of the scattering intensity of NS to the total intensity of (002) diffraction. The \( f_{\text{NS}} \) value depended on the types of metal catalysts and carbonization temperature. Figure 3 shows the relationship between \( E_{\text{O}_2} \) and \( f_{\text{NS}} \), where \( E_{\text{O}_2} \) represents the potential corresponding to an ORR current density of \(-10 \mu\text{A/cm}^2\). Fe and Co were found to be effective catalysts to produce carbon with higher \( E_{\text{O}_2} \) 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 acetylacetone 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 \( f_{\text{NS}} \) values.

2.3 BN-doped carbon alloy catalysts

BN-doped carbon is another type of a carbon alloy that we discovered. 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 BNx (\( x = 1–3 \)), 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.
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. 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, \( N_{B-N-C} \), included in the B–N–C moieties is considered as a parameter to be added to \( N_{\text{edge}} \), the ORR activity exhibited a continuous curve against the summation of \( N_{\text{edge}} \) and \( N_{B-N-C} \). 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. 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, \( N_{B-N-C} \), included in the B–N–C moieties is considered as a parameter to be added to \( N_{\text{edge}} \), the ORR activity exhibited a continuous curve against the summation of \( N_{\text{edge}} \) and \( N_{B-N-C} \). 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.

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

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-M catalysts. The difference in the characteristics between NSCC and N-M catalysts are as follows: (1) The ORR activity of N-M catalysts diminishes by acid leaching; however, the ORR activity of NSCC is maintained or increased by the same treatment. (2) Both N and metal species are required for the preparation of N-M; however, they are not required for the preparation of NSCC. (3) The formation of an NS structure inhibits ORR activity in the case of N-M catalysts; however, ORR activity is not inhibited in the case of NSCC.

Recently, Singh et al. have discriminated the differences between the N-M and N-doped carbon catalysts. In their study, acid leaching decreased the activity of N-M catalysts, but it did not affect the ORR activity of N-doped carbon. They also reported that both the N-M and N-doped catalysts exhibited different performance: N-doped catalysts exhibited a longer lifetime than N-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.

These two recent studies suggested the presence of two types of catalytic carbon: N-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-M catalysts.

We have studied the effects of acid washing conditions on the ORR activity of NSCC. 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-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 Electrochemical 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, \( \Delta E_p \), 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 \( f_{\text{sharp}} \) (Fig. 6), indicative of the promotion effect of NSCC on the heterogeneous electron transfer. On the other hand, the maximum ORR activity was observed at a potential of \(-10\, \mu A/cm^2\) at certain \( f_{\text{sharp}} \) 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 \( f_{\text{sharp}} \) from that of ferricyanide can be attributed to the oxygen adsorption step.

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\(_2\)O\(_2\). 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\(_2\)O\(_2\) 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.

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. 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, (2) carbon nano-onions produced by the heat-treatment of nanodiamond, 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 solid crystal states (mesophase); this material carbonizes at the heat-treatment temperature, forming highly oriented graphitic carbon. A mixture of fullerenes, C\(_{60}\) and...
C\textsubscript{70} (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. O\textsubscript{2}-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.


4.1 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.\textsuperscript{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).
To achieve this, poloxine 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. 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. 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. 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. 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.
4.3 Recent advances in carbon alloy catalysts for PEFC

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/cm² with a carbon loading of 1.0 mg/cm² 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. 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 University (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.

References