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Recent progress in solution plasma-synthesized-carbon-supported catalysts for energy conversion systems

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Carbon-based materials have been widely utilized as the electrode materials in energy conversion and storage technologies, such as fuel cells and metal-air batteries. In these systems, the oxygen reduction reaction is an important step that determines the overall performance. A novel synthesis route, named the solution plasma process, has been recently utilized to synthesize various types of metal-based and heteroatom-doped carbon catalysts. In this review, we summarize cutting-edge technologies involving the synthesis and modeling of carbon-supported catalysts synthesized via solution plasma process, followed by current progress on the electrocatalytic performance of these catalysts. This review provides the fundamental and state-of-the-art performance of solution-plasma-synthesized electrode materials, as well as the remaining scientific and technological challenges for this process. © 2018 The Japan Society of Applied Physics

1. Introduction

Carbon materials have been widely considered as catalyst support materials because of their intrinsic properties including a diverse porous structure, low density, resistance to acidic and basic environments, and amenability to synthesis or modification by various manufacturing methods.1–3 For electrochemical systems such as metal air battery or fuel cell, graphitic carbon and carbon nanotubes/nanofibers have often been used as electrode materials because of their light weight and electron-conducting properties.4–6 Recently, the application of mesoporous carbons as cathode materials for energy conversion devices has also been reviewed extensively due to their porous nature and high surface area.7,8 Porous carbon materials can be classified according to their pore diameter as microporous (<2 nm), mesoporous (2–50 nm), and/or macroporous (>50 nm). Among these mesoporous carbon materials have attracted much attention owing to their remarkable porosity for oxygen diffusion. Previous studies have already shown that mesoporous carbon offers an effective transmission path for reaction substrates with a moderately accessible surface area.9,10

The oxygen reduction reaction (ORR) is the most important reaction in energy applications including metal air batteries11 and fuel cells.12 In these systems, ORR occurs at the cathode and is considered to be the rate-determining step of an electrochemical device.13 ORR in aqueous solutions often occurs by two main pathways: the direct four-electron reduction pathway from O2 to H2O and the two-electron reduction pathway from O2 to hydrogen peroxide (H2O2).14,15 In non-aqueous aprotic solvents and/or in alkaline solutions, the one-electron reduction pathway from O2 to superoxide (O2−) can also occur.16,17 In order to speed up the reaction, a cathode ORR catalyst is required and often plays the most crucial factor in maximizing the overall performance of energy conversion systems. At the current stage of technology, noble metal catalysts, in particular, platinum (Pt)-based nanoparticles supported on carbon materials (Pt/C), have long been regarded as the most efficient catalysts for ORR because of their excellent catalytic activity.18–20 However, they suffer from serious problems in their further development and practical commercialization due to their high capital cost and limited natural supply. Extensive researches over the past several decades has focused on developing alternative catalysts, including Pt-alloy catalysts,21 non-noble metal catalysts,22–24 and non-metal based heteroatom-doped carbon catalysts.25,26

A variety of preparation routes have been reported for the synthesis of carbon-based catalysts. Conventional methods include chemical vapor deposition,27,28 solvothermal synthesis,29,30 and flame pyrolysis.31 However, most of the currently available approaches usually require either multiple processes or a metal catalyst source for the growth and formation of carbon materials. Metal nanoparticle catalysts or heteroatom-doped carbon can be either prepared in situ or through post-treatment.32 Recently, plasma in liquid method has been accepted as a capable synthesis route for carbon-based materials including carbon nanotubes (CNTs),33 nanoparticles,34 metal nanoparticles supported on carbon35 and nitrogen-doped carbon materials36,37 mainly due to the recent development of various plasma sources operated from low to atmospheric pressures. During plasma discharge, various types of electrons and radicals are generated and this unique plasma–liquid system provides a fast reaction for material synthesis.38 Among various types of plasma discharge in a liquid, the solution plasma process (SPP) is categorized as a specific glow discharge which can occur in various combination of solvents and solutes, in both aqueous and non-aqueous solutions.39 SPP provides novel plasma–liquid interfaces that initiate multiple physical and chemical processes. These unique interactions promote carbon aggregation in different manners from conventional synthesis routes, and eventually form mesoporous carbon with interconnected pore channels in different directions on both the meso- and macrometer length scales. Over the past decade, SPP has been widely utilized for carbon nanomaterial synthesis ranging from mesoporous carbon nanoparticles40,41 to graphite nanosheets.42 This review provides the current status of research on carbon-supported catalysts synthesized and their corresponding ORR catalytic activities, as well as
the application on energy conversion devices. The scientific and technical challenges as well as perceptive opinions on the present issues of SPP-synthesized-carbon-supported catalysts will be discussed.

2. Physical properties of carbon-catalysts synthesized by SPP

SPP is a non-equilibrium plasma process which occurs with a discharge voltage, current, and frequency in the range of 1 kV, $1 \times 10^3$ A, and $10^3$–$10^4$ kHz, respectively. A bipolar power supply with a controllable pulse and resting time can limit the energy input into the liquid media, which makes SPP significantly different from conventional arc discharge. A general model of SPP is composed of a batch reactor, a pair of electrodes and a bipolar power supply, as shown in Fig. 1(a). There are two major reactions that occur within SPP: (1) chemical reactions at the plasma–gas–liquid interface [Fig. 1(b)] and (2) physical reactions caused by electrode evaporation and sputtering [Fig. 1(c)]. During carbon synthesis, plasma discharge is carried out within a solution of a carbon-containing precursor (e.g., benzene), while the main reactions present at plasma/gas/ and gas/liquid interfaces. In this section, the carbon synthesis mechanism via SPP and the mesoporous properties of the as-prepared carbon will be discussed.

2.1 Synthesis of carbon material via SPP

Kang et al. has applied aromatic organic benzene as a carbon precursor to synthesize carbon nanosphere (CNSs) via SPP with various repetition pulse frequencies from 25 to 65 kHz. Typically, 500 mg of CNSs was obtained from 100 ml of benzene with 20 min. of treatment. The average diameters of the CNSs were from 20 to 100 nm when the pulse frequency of the bipolar power supply was adjusted from 25 to 65 kHz. In Figs. 2(a)–2(f), the morphologies showed that the CNSs synthesized at 25–50 kHz consisted of continuous short-range graphite with a turbostratic structure. X-ray diffraction (XRD) patterns illustrated that CNSs synthesized at 25–50 kHz had a low graphitization degree, while the CNSs synthesized at 65 kHz consisted of graphite sheets with a two-dimensional regular and ordered structure in basal planes. Raman study further agrees with the above

Fig. 1. (Color online) (a) Schematic of typical SPP, (b) chemical reaction in SPP, and (c) electrode sputtering in SPP.

Fig. 2. TEM/HRTEM image of CNSs synthesized at (a–c) 25 kHz and (d–f) with 65 kHz. Reproduced with permission from Ref. 40. © 2013 Royal Society of Chemistry.
results, as the 2D band around 2600–2750 cm$^{-1}$, which corresponded to the D band's second order, was only observed in the CNSs synthesized at 65 kHz. All the results confirmed that the transition from amorphous carbon to nanocrystalline graphite have occurred by increasing the repetition pulse frequency, which eventually, by increasing the energy input.

The authors have further developed a new class of porous carbon black with a hierarchical structure, named the carbon nanoballs (CNBs), which was generated by bottom-up synthesis based on SPP.41) The structural characterization revealed that CNBs have an excellent meso-macro hierarchical pore structure, with an average diameter of 14.5 nm and a total pore volume of 1.1 cm$^3$/g. Commercial carbon ketjen black (KB) has a much larger surface area of 1251 cm$^3$/g and a pore volume of 2.5 cm$^3$/g, while it exhibits a smaller mean pore size of 6.5 nm. The CNBs are aggregated, forming interconnected pore channels in different directions on both the meso- and macrometer length scales. The pore structures of CNBs and KB were investigated and demonstrated by the N$_2$ adsorption–desorption method in Fig. 3(a), where the integral curves of the pore size distribution are shown in Fig. 3(b). The pore volume in the 2–10 nm diameter range of CNBs was not observed, whereas in the large pore region, i.e., pores $>$10 nm, a drastic increase in the pore volume is observed. Therefore, it can be assumed that CNB has large pore volume in the meso-macro range. In contrast, KB has a large pore volume in the region smaller than 50 nm. These characteristics clearly indicated that CNBs consist of a meso-macropore hierarchical structure while KB consists of a micro-mesopore hierarchical structure framework. In a lithium-air battery test, the discharge capacity of CNBs reached 3600 mAh/g, which exceeded the capacity of KB by 30–40% under the same discharge condition. The excellent discharge capacity was contributed to the co-existence of a high pore volume and a meso-macro hierarchical porous structure.

3. Electrocatalytic activity of metal-based catalysts supported on carbon synthesized by SPP

As mentioned in the previous section, both chemical reactions and physical processes are simultaneously occur in SPP. The formation of carbon materials often occurs in plasma/gas and gas/liquid interfaces, while various types of metal nanoparticles can be easily generated by electrode sputtering during plasma discharge. In the following section, we seek to give a clear image of the synthesis route and its electrocatalytic activity for metal-based catalysts supported on carbon materials prepared by SPP.

3.1 Metal catalysts supported on carbon materials via electrode sputtering

Novel metal-based catalysts, in particular within the nanosize region, have been widely studied for their remarkable electrocatalytic activity. Terashima et al. reported the introduction of bimetallic platinum and gold (PtAu) nanoparticles on a commercial carbon material (Ketjen Black EC600 JD) via solution plasma sputtering.47) The average diameter of the PtAu nanoparticles was 5.7 nm with a relative standard deviation of 3.6 nm [Figs. 4(a) and 4(b)] where the composition ratio between Pt and Au was found to depend on the plasma discharge conditions. The electrocatalytic activities of the PtAu/C in an O$_2$-saturated aprotic electrolyte (1 M
LiClO$_4$(PC-EC) showed two reduction peaks at 3.45 and 2.95 V vs Li/Li$^+$, which were similar to those of bulk metallic Pt and Au, respectively. The electrochemical performance of PtAu/C was further investigated in a Li–air battery cell under a discharge current density of 0.1 mA/cm$^2$ and the discharge capacity was approximately 2000 mAh/g, which was considerably higher than that of a pure carbon electrode (1500 mAh/g) [Fig. 4(c)].

3.2 One-step synthesis of metal catalysts supported on mesoporous carbon

Kang et al. demonstrated the simultaneous synthesis of metal and carbon nanoparticles by discharging in pure benzene with a pair of gold/platinum electrodes, as shown in Fig. 5(a). SPP applied to benzene produced active species including C, CH, and C$_2$ during molecule dissociation, atomic and molecular excitation. The reactions of these radicals at the gas/liquid interface generated nanosize mesoporous carbon nanoparticles ranged between 20–30 nm. At the same time, gold/platinum nanoparticles of 2–5 nm synthesized through electrode sputtering were supported or embedded into the carbon matrix [Figs. 5(b) and 5(c)]. Since the carbon matrix was amorphous in nature, the catalyst was treated at 900 °C under argon atmosphere in order to enhance its conductivity. From a cyclic voltammetry experiment, Au/C and Pt/C under O$_2$-saturated 1 M H$_2$SO$_4$ illustrated sharp and clear reduction peaks at 1.2–1.4 V (Ag/AgCl) and 0.1–0.5 V (Ag/AgCl), respectively, which are similar to those of bulk Au and Pt materials [Figs. 5(d) and 5(e)].

Non-noble metal catalysts have been synthesized by applying iron/copper electrode in pure benzene via SPP. Unlike noble metals with lower chemical reactivity, Fe and Cu were easily oxidized and formed a composite alloy in the form of CuFe$_2$O$_4$. Bimetallic FeCu catalysts supported on mesoporous carbon showed electrocatalytic activities in an alkaline-based electrolyte (0.1 M KOH), and exhibited slightly higher activity than a single Fe/C or Cu/C catalyst. The catalytic activity, however, was still inferior to that of noble metal catalysts.
4. Electrocatalytic activity of heteroatom-doped carbon catalysts

One of the most attractive features of SPP is its ability to design and tune the carbon matrix in a single process. By selecting the starting precursor, the carbon matrix could contain single or multiple heteroatoms, whose structure and density are highly dependent on the original precursor. Compared with metal catalysts, the heteroatom-doped carbon has advantages in terms of long-term stability and durability since the catalyst itself was embedded within the carbon matrix. Conventional heteroatom-doped carbon catalysts are synthesized either by direct pyrolysis of heteroatom-containing precursors or post-treatment of synthesized carbon nanomaterials with desired dopant species. SPP has been utilized as a novel in situ synthesis route for nitrogen-doped, boron-doped, oxygen-doped, as well as halogen-atom-doped carbon catalysts by rationally selecting an appropriate organic precursor containing the desired heteroatom dopant, as shown in Fig. 6(a). The state-of-the-art heteroatom-doped carbon catalysts synthesized by SPP and their corresponding electrocatalytic activity are discussed as follows.

4.1 Nitrogen-doped carbon catalysts

Nitrogen-doped carbon materials (N-doped carbon) as non-metal catalysts have been intensively researched and are considered as the most promising alternatives to noble Pt catalysts for fuel cell applications. Theoretically, doping of electronegative N atoms reduces the electron density of the adjacent C atoms and polarizes the C atoms. As a result, carbon atoms become positively charged C(δ+) by the charge delocalization and promote the adsorption of O$_2$ molecules. The improved catalytic performance has been attributed to changes in the O$_2$ chemisorption mode that effectively weaken the O–O bonding, facilitating ORR at the metal-free N-doped nanocarbon electrodes. Generally, five major bonding states of nitrogen can be observed: pyridinic, pyrrolic, amino, graphitic, and oxide-type nitrogen [Fig. 6(b)]. Up to date, the role of each nitrogen bonding type and its corresponding relationship in terms of ORR activity are still unclear. Besides simply doping nitrogen atoms into the carbon matrix, the nitrogen-binding configuration is of importance for designing efficient catalysts. In the following sections, we summarize the research on SPP-synthesized N-doped carbon catalysts, as well as on tuning the chemical states of N-doped carbon.

4.1.1 N-doped carbon catalysts synthesized by C–N precursor. The first report regarding the in situ SPP synthesis of N-doped carbon was by Kim et al., who synthesized the catalyst by using pyrrole (C$_4$H$_4$NH) as a C–N precursor. During the discharge, weak intensities of N$_2$ and CN were detected in addition to major emission peaks of C$_2$, CH, and H [Fig. 7(a)]. The formation of the N-doped carbon matrix was possibly formed by the combination of CN and C$_2$ radicals. The nitrogen contents of as-prepared catalysts and those after heat treatment (at 900 °C) were 12.28 and 3.91 wt %, respectively. The N-doped carbon catalyst exhibited an ORR onset potential of $-0.18$ V (Ag/AgCl) in O$_2$-saturated 0.1 M KOH, which was more positive than that of the pure carbon matrix [$-0.22$ V (Ag/AgCl)] [Fig. 7(b)]. Other SPP-synthesized N-doped carbon catalysts have been formed by discharging under various types of nitrogen-containing organic precursors in order to tailor the content and bonding states of nitrogen. Panomsuwan et al. synthesized N-doped carbon from acrylonitrile (C$_3$H$_3$N) and tailored the nitrogen bonding state through varying the post-heating treatment from 500 to 900 °C. The nitrogen content decreased from 3.18 to 0.93 at. % with increasing annealing temperatures, where the surface elemental composition showed that the N-doped carbon catalyst mainly existed in the form of nitrile-N (~62%). When increasing the annealing temperature, the content of nitrile-N and pyrrolic-N substantially decreased, while that of pyridinic-N and graphitic-N pro-
gressively increased when the annealing temperature increased to 800–900 °C. N-doped carbon with annealing treatment at 800 °C exhibited the most positive onset potential of −0.14 V (Ag/AgCl) and the largest current density of 3.48 mA cm⁻² at −0.6 V. The electron transfer number (n) was estimated to be 3.15 at −0.5 V. The same group also carried out a similar study by applying cyano-aromatic molecules with various C:N ratios, such as benzonitrile (C₇H₅N), 2-cyanopyridine (C₆H₄N₂), and cyanopyrazine (C₅H₃N₃) as a single source precursor for N-doped carbon catalysts.⁵⁶) The total nitrogen doping contents of the catalysts prepared from benzonitrile (NCNP-1), 2-cyanopyridine (NCNP-2), and cyanopyrazine (NCNP-3) were, respectively, 0.63, 1.94, and 1.85 at. %. CV measurements in an alkaline electrolyte illustrated that NCNP-3 displayed the most positive ORR onset potential of −0.143 V, followed by NCNP-2 of −0.166 V and NCNP-1 of −0.182 V (Ag/AgCl) [Fig. 7(c)]. The current density of NCNP-3 at −0.5 V (−3.79 mA cm⁻²) was close to that of NCNP-2 (−3.91 mA cm⁻²), where both calculated n values of NCNP-2 and NCNP-3 were above 3 at potential of −0.4 V [Fig. 7(d)]. The electrocatalytic activities of N-doped carbons were evaluated in acidic electrolyte. The ORR activity order of the catalysts in terms of both onset potential and current density exhibited a similar tendency to their activity in an alkaline solution. The onset potentials of the LSV curves were determined to be 0.103, 0.158, 0.217, and 0.234 V (Ag/AgCl) for CNP, NCNP-1, NCNP-2, and NCNP-3, respectively [Figs. 7(e) and 7(f)]. However, they were still inferior to those for 20% Pt/C.

4.1.2 Enhancement of conductivity in N-doped carbon catalysts. One of the major challenges regarding of SPP-synthesized carbon-based catalysts is to change the carbon matrix crystallinity from amorphous to graphite to improve the conductivity. Thus, all catalysts require post-heating treatment in order to increase the conductivity and be applicable as electrode materials. However, the content of nitrogen...
is generally reduced after heat treatment. Panomsuwan et al. prepared a composite material of N-doped carbon nanoparticles (NCNPs) on carbon nanofibers (CNFs).\(^5^7\) CNFs were dispersed in 2-cyanopyridine (CNP) and subjected to SPP, where the NCNPs were directly produced from the CN precursor and attached to the CNF surface [Fig. 8(a)]. The conductive nature of the CNFs eliminated the post-heating process. Also, after surface modification of the CNFs, the specific surface area increased from 47.4 to 159.8 m\(^2\) g\(^{-1}\) with a meso- and macroporous structure. The nitrogen content of the composite was 0.51 at.\%, and the nitrogen atoms were predominantly bonded as graphitic-N (63–67\%). From linear sweep voltammetry (LSV) measurement, the original CNFs exhibited a two-step reduction process, where the first and second onset potentials were found to be \(-0.21\) and \(-0.64\) V (Ag/AgCl) in 0.1 M O\(_2\)-saturated KOH, respectively. The onset potential of the NCNP–CNF composite became more positive and reached \(-0.14\) V (Ag/AgCl) [Fig. 8(b)]. The calculated \(n\) values were, respectively, 2.16 and 3.54 for the CNFs and NCNP–CNF composite at \(-0.4\) V (Ag/AgCl). The enhanced ORR activity of NCNP–CNF composite can be mainly attributed to the synergistic contributions of NCNPs and CNFs. In the NCNP–CNF composite, the NCNPs provided a high surface density of ORR active sites (i.e., pyridinic N and graphitic N) with meso- and macroporosity, while the CNFs served as highly conductive paths for charge transport.

Other approaches to enhance the conductivity of the carbon matrix have been conducted by Hyun et al. They investigated the effect of the repetition frequency of the bipolar power supply on a N-doped carbon matrix.\(^5^8\) They applied N-methyl-2-pyrrolidone (C\(_2\)H\(_3\)NO) as a precursor and synthesized N-doped carbon with higher frequencies up to 200 kHz. Interestingly, the morphology of the synthesized N-doped carbon appeared as a planar nanosheet (NCNS), which consisted of 3–5 graphene layers [Fig. 8(c)]. The resistivity of the NCNS was measured as 0.065 \(\Omega\) cm, which was 3–4 orders of magnitude higher than other SPP-synthesized carbon materials (1 \(\times\) 10\(^3\) \(\Omega\) cm).\(^5^9\) The ORR catalytic activity was estimated in a 0.1 M KOH electrolyte, where the onset ORR potential was observed to be \(-0.17\) V (Ag/AgCl) and was significantly higher than that of bulk graphite [Fig. 8(d)]. The NCNS enhanced the electrocatalytic activity even with small amount of nitrogen within the carbon matrix (1.3 wt \%).

### 4.1.3 Tunable nitrogen bonding state in N-doped carbon catalysts.

The conventional method for the selective synthesis of C–N bonding states mostly involved bottom-up synthesis using chemical vapor deposition (CVD), followed by post-annealing with the temperature varied from 550 to 1000 °C.\(^3^2\) However, these methods consist of complex processes with a high temperature and pressure, which make the approach not economically favorable. Li et al. successfully tailored the bonding state of nitrogen via SPP in order to further probe in detail the relationship between each C–N bonding state and electrochemical performance. They reported two types of N-doped carbon catalysts prepared by linear and heterocyclic precursors.\(^6^0\) Surface analysis demonstrated that the relative percentage of amino-N was significantly higher when linear structural acrylonitrile was applied as a precursor (AN). In contrast, pyridinic-type nitrogen bonding preferentially occurred in carbon synthesized from heterocyclic structural pyrazine (PZ). The atomic percentages of the nitrogen content in carbon synthesized from pyrazine and acrylonitrile were 8.58 and 2.97 at.\%.

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**Fig. 8.** (Color online) (a) TEM images of NCNP–CNF composite. (b) LSV curves on an RRDE in an O\(_2\)-saturated 0.1 M KOH solution at a scan rate and rotation speed of 10 mV s\(^{-1}\) and 1600 rpm, respectively, where the ring potential was fixed at 0.5 V. (c) TEM images of NCNS, (d) LSV of NCNS in 0.1 M KOH electrolyte at scan rate and rotation speed of 10 mV s\(^{-1}\) and 1600 rpm, respectively. Reproduced with permission from Ref. 57, copyright 2016 American Chemical Society and Ref. 58. © 2014 Royal Society of Chemistry.
respectively. From electrochemical analyses, PZ exhibited a higher current density, where AN demonstrated a more positive ORR onset and peak potential. The result agreed with some studies that suggested that amino-N might act as an electron-donating group in N-doped carbon and thus result in higher ORR activity than other nitrogen bonding.\textsuperscript{61,62} A similar study carried out by the same group further tuned the nitrogen bonding state through different combinations of precursors and additives.\textsuperscript{63} Four types of catalysts were synthesized as follows: catalysts synthesized by pure pyridine and acrylonitrile were denoted as PD and AN, where samples with 7 mM of anthracene introduced to each precursor were referred to as PDA and ANA, respectively. The dominant peak was found to be amino-N in the carbon catalysts synthesized from acrylonitrile precursor, where the addition of small amount of anthracene (7 mM) enhanced the formation of graphitic-N by 30–40% [Fig. 9(a)]. From electrochemical measurement, the current density was proportional to the content of graphitic-N while a higher percentage of amino-N shifted the ORR onset potential to a more positive value [Fig. 9(b)]. In that study, the onset potential and electron transfer number were respectively $-0.206 \text{V (Ag/AgCl)}$ and 3.7.

### 4.1.4 N-doped carbon catalysts with iron N\(_4\)-macrocyclic structure

Transition metal N\(_4\)-macrocycles (M–N\(_4\)-macrocycles) have shown promising results as future ORR catalysts. In particular M–N\(_4\)-macrocycles with a combined iron and N\(_4\) structure showed higher ORR catalytic activity than other macroyclic ligands.\textsuperscript{64,65} Kim et al. successfully incorporated N\(_4\)-macrocylics and Fe–N\(_4\)-macrocycles by utilizing phthalocyanine macroyclic ligands as precursors via SPP.\textsuperscript{66} Comparing the two catalysts, the cathodic peak current corresponding to ORR activity slightly shifted from $-0.19 \text{V (Ag/AgCl)}$ to $-0.17 \text{V (Ag/AgCl)}$ when the active site changed from the N\(_4\) to Fe–N\(_4\) macrocyclic structure, while the current density increased by approximately 30% in the presence of iron. The calculated $n$ values of the ORR reaction in the N\(_4\) and Fe–N\(_4\)-structured carbon were 3.25 and 3.98, respectively. Hyun et al. prepared Fe–N\(_4\)-incorporated carbon nanosheets (FP-NCNs) via SPP with the same precursor (iron phthalocyanine) but a higher repetition frequency of the bipolar power supply.\textsuperscript{67} The morphology changed from pure nanoparticles (FP-CNPs) to nanosheets (FP-NCNs) when the repetition frequency of the bipolar power supply increased from 20 to 200 kHz [Figs. 10(a) to 10(c)]. The nitrogen doping contents were estimated to be 0.3, 1.0, and 2.3 at. % for FP-CNPs, FP-CPNs after heat treatment at 700 °C, and FP-NCNs, respectively. A narrow scan of N 1s spectra revealed that the Fe–N component was absent for heat-treated catalysts, where FP-NCNs exhibited higher amounts of pyridinic-N and graphitic-N than FP-NCPs [Fig. 10(d)], while all possible nitrogen bondings in carbon matrix was schematically demonstrated in Fig. 10(e). The ORR onset potential of FP-NCNs was $-0.062 \text{V (Ag/AgCl)}$ and is comparable to that of commercial 20 wt% Pt/C $[-0.064 \text{V (Ag/AgCl)}]$ in an alkaline electrolyte [Fig. 10(f)]. The calculated $n$ values of FP-NCNs were very close to 4 at $-0.4 \text{V (Ag/AgCl)}$, which indicated that the electrocatalytic activity of the catalyst was similar to that of the state-of-the-art 20 wt% Pt/C catalyst in 0.1 M KOH. However, the catalysts showed limited ORR catalytic activity in 0.5 M H\(_2\)SO\(_4\). In term of stability, FP-NCNs were found to be superior to Pt/C in both alkaline and acidic electrolytes [Fig. 10(g)].

The precursor, nitrogen content, morphology, ORR onset potential, and calculated electron transfer number of each reported SPP-synthesized N-doped carbon catalyst are summarized in Table I. Most of the catalysts showed promising results in 0.1 M KOH; however, the electrocatalytic activity in acidic media still requires further improvement. Although the ORR onset potential is still lower than that of Pt/C, N-doped carbon demonstrated high stability with the addition of methanol and high durability over a longer operation time.

### 4.2 Other heteroatom-doped carbon catalysts

Incorporating heteroatoms within the carbon matrix can induce defects due to differences in atomic radius, bond length, and electronegativity, which results in electron modulation to tune the chemical activities of carbon material.\textsuperscript{68} Extensive theoretical and experimental studies have demonstrated that breaking the symmetry of either the atomic charge or spin densities of the sp\(^2\)-hybridized carbon structure by doping heteroatoms can create the active sites favorable
for O₂ adsorption to facilitate the ORR process, regardless of whether the dopants are electron-rich (e.g., nitrogen, oxygen, fluorine) or electron-deficient (e.g., boron and phosphorus) atoms. In the previous section, we demonstrated the successful synthesis of N-doped carbon via SPP. The basic principle of SPP has also been widely used to develop a large variety of other heteroatom-doped (e.g., B, P, O, F, Cl, Br, I) carbon catalysts as efficient metal-free ORR catalysts.

4.2.1 Boron-, phosphate-, and oxygen-doped carbon catalysts. Boron and phosphorus can induce uneven charge within the carbon matrix since the electronegativity of boron and phosphorus is comparatively lower than that of carbon. In comparison with nitrogen, B and P exhibit a different ORR mechanism. Substitution of these atoms in the carbon network might lower the Fermi level of the carbon matrix and then tune the properties of oxygen chemisorption and electrochemistry, which results in the adsorption of oxygen on the B or P dopant. On the other hand, incorporating oxygen could break the electroneutrality of sp² carbon because the dopant is electron-rich, thus leading to the activation of carbon π electrons for effective utilization by O₂. A theoretical study by first-principles density-functional theory (DFT) calculations suggested that oxygen doping could modify the π conjugation of carbon nanotubes and impact the near-infrared band gaps.

Kim et al. reported the successful synthesis of B- and P-doped carbon by SPP. B- and P-carbon catalysts were prepared, respectively, by mixing benzene with phenylboronic acid (C₆H₇BO₂) and phenylphosphonic acid (C₆H₇PO₃). The dominant active sites of B- and P-doped carbon were expected to be B–C and P–C bondings, respectively. From electrochemical study, the P-doped carbon showed a slightly higher ORR activity than the B-doped carbon. Since the same research group also reported superior electrocatalytic activity by dual doping of B–N and P–N bondings, detailed information is provided in Sect. 4.2.3. Panomsuwan et al. have synthesized B-doped carbon (BCNP) with an alternative precursor, triphenyl borate (C₁₈H₁₅BO₃). The boron content was approximately 0.67 at. %, and various bonding states including BC₂O, BCO₂, and B₂O₃ were observed [Fig. 11(a)]. Compared with the results obtained by Kim et al., the catalysts exhibited a significant amount of
oxide species. BCNP exhibited an onset potential and current density of −0.18 V (Ag/AgCl) and 3.15 mA cm\(^{-2}\), respectively, in O\(_2\)-saturated 0.1 M KOH electrolyte [Figs. 11(b) and 11(c)].

Table I. Summary of precursor, nitrogen content, morphology, ORR onset potential, and calculated electron transfer number of each reported SPP-synthesized N-doped carbon catalyst.

<table>
<thead>
<tr>
<th>Precursors (heat treatment temperature)</th>
<th>Nitrogen content (at. %)</th>
<th>Morphology</th>
<th>Onset potential(^{a}) (0.1 M KOH)</th>
<th>Electron transfer number</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrole/dodecane (900 °C)</td>
<td>3.91</td>
<td>Nanosphere</td>
<td>−0.18 V</td>
<td>N/A</td>
<td>54</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>4.78</td>
<td>Nanosphere</td>
<td>−0.22 V</td>
<td>2.42</td>
<td>55</td>
</tr>
<tr>
<td>Acrylonitrile (800 °C)</td>
<td>1.43</td>
<td>Nanosphere</td>
<td>−0.14 V</td>
<td>3.15</td>
<td>55</td>
</tr>
<tr>
<td>Benzonitrile (800 °C)</td>
<td>0.63</td>
<td>Nanosphere</td>
<td>−0.182</td>
<td>2.36</td>
<td>56</td>
</tr>
<tr>
<td>2-Cyanopyridine (800 °C)</td>
<td>1.94</td>
<td>Nanosphere</td>
<td>−0.166</td>
<td>3.04</td>
<td>56</td>
</tr>
<tr>
<td>Cyanopyrazine (800 °C)</td>
<td>1.85</td>
<td>Nanosphere</td>
<td>−0.143</td>
<td>3.02</td>
<td>56</td>
</tr>
<tr>
<td>Benzonitrile (800 °C)</td>
<td>0.63</td>
<td>Nanosphere</td>
<td>0.158</td>
<td>3.05</td>
<td>56</td>
</tr>
<tr>
<td>2-Cyanopyridine (800 °C)</td>
<td>1.94</td>
<td>Nanosphere</td>
<td>0.217</td>
<td>3.12</td>
<td>56</td>
</tr>
<tr>
<td>Cyanopyrazine (800 °C)</td>
<td>1.85</td>
<td>Nanosphere</td>
<td>0.234</td>
<td>3.13</td>
<td>56</td>
</tr>
<tr>
<td>2-Cyanopyridine with CNFs</td>
<td>0.51</td>
<td>Nano composite</td>
<td>−0.14</td>
<td>3.54</td>
<td>57</td>
</tr>
<tr>
<td>N-methyl-2-pyrrolidone</td>
<td>1.3</td>
<td>Nanosheet</td>
<td>−0.17</td>
<td>N/A</td>
<td>58</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>2.97</td>
<td>Nanosphere</td>
<td>−0.23</td>
<td>N/A</td>
<td>59</td>
</tr>
<tr>
<td>Pyrazine</td>
<td>8.58</td>
<td>Nanosphere</td>
<td>−0.26</td>
<td>N/A</td>
<td>60</td>
</tr>
<tr>
<td>Acrylonitrile/anthracene</td>
<td>2.54</td>
<td>Nanosphere</td>
<td>−0.206</td>
<td>3.7</td>
<td>61</td>
</tr>
<tr>
<td>Phthalocyanine (700 °C)</td>
<td>N/A</td>
<td>Nanosphere</td>
<td>−0.19</td>
<td>3.25</td>
<td>66</td>
</tr>
<tr>
<td>Iron phthalocyanine (700 °C)</td>
<td>N/A</td>
<td>Nanosphere</td>
<td>−0.17</td>
<td>3.98</td>
<td>66</td>
</tr>
<tr>
<td>Iron phthalocyanine</td>
<td>2.3</td>
<td>Nanosheet</td>
<td>−0.062                 (0.5 M H(_2)SO(_4))</td>
<td>4.03</td>
<td>67</td>
</tr>
<tr>
<td>Iron phthalocyanine</td>
<td>2.3</td>
<td>Nanosheet</td>
<td>0.38 V</td>
<td>N/A (0.5 M H(_2)SO(_4))</td>
<td>67</td>
</tr>
</tbody>
</table>

\(a\) Potential is presented as (V vs Ag/AgCl).

Fig. 11. (Color online) (a) High-resolution XPS B 1s spectrum with deconvolution of BCNP (b) CV curves of CNP and BCNP in N\(_2\)-(dashed line) and O\(_2\)-saturated 0.1 M KOH solutions (solid line) at a scan rate of 50 mV s\(^{-1}\). (c) LSV curves of CNP, BCNP, and 20% Pt/C on an RRDE in an O\(_2\)-saturated 0.1 M KOH solution at a scan rate of 10 mV s\(^{-1}\) and a rotation speed of 1600 rpm. (d) High-resolution XPS C 1s spectrum with deconvolution, (e) CV curves of O\(_2\)-saturated 0.1 M KOH solutions at a scan rate of 50 mV s\(^{-1}\), (f) LSV curves on an RRDE in an O\(_2\)-saturated 0.1 M KOH solution at a scan rate of 10 mV s\(^{-1}\) and a rotation speed of 1600 rpm for BZ100, BZ90+DO10, BZ70+DO30, and BZ50+DO50. Reproduced with permission from Ref. 75. © 2015 Elsevier. Reproduced with permission from Ref. 76. © 2014 Royal Society of Chemistry.

The correlation between the physicochemical properties and the electrocatalytic activity of oxygen-containing nanocarbon was examined by Ishizaki et al.\(^{76}\) The catalyst was synthesized from a mixed solvent of benzene and 1,4-dioxane...
with various ratios. Surface analysis revealed that the O/C atomic ratio increased from 0.044 to 0.227 with increasing 1,4-dioxane ratio from 0 to 50%. The binding state of oxygen was attributed to carboxyl and carbonyl groups. From the report, the ORR electrocatalytic activity is not proportional to oxygen content. In contrast, the best result in terms of ORR activity was found at a 9:1 ratio of benzene : 1,4-dioxane. The authors suggested that besides surface functional groups, structural defects also seem to play a significant role in influencing electrocatalytic activity [Fig. 11(d)]. The onset ORR potential and calculated $n$ value of O-doped CNPs ranged from $-0.19$ to $-0.2$ V (Ag/AgCl) and 2.9 to 3.1 at $-0.6$ V (Ag/AgCl), respectively, in an O$_2$-saturated 0.1 M KOH electrolyte [Figs. 11(e) and 11(f)].

4.2.2 Halogen-doped carbon catalysts. Very recently, halogen-doped carbon materials have emerged as one of the promising choices as ORR catalysts.\textsuperscript{77–80} Interestingly, the electroactivity of halogen-doped carbon materials is not directly related to the electronegativity of halogen atoms and seems to be more complex than the relationships for B-, N-, and P-doped carbon. Ganomsuwan et al. have applied a mixture of toluene and trifluorotoluene as precursors for F-doped carbon.\textsuperscript{81} The doping percentage of F could be controlled by the ratio of the two precursors, where the highest F content of 4.52 at. % was achieved when pure trifluorotoluene was applied. The major bonding state of F-doped carbon was attributed to ionic C–F followed by semi ionic C–F bonds. F-doped carbon showed an onset potential of $-0.22$ V vs Ag/AgCl and an electron transfer number of 2.29 at $-0.5$ V (Ag/AgCl) in an O$_2$-saturated 0.1 M KOH electrolyte. The same group also conducted research compared the effects of various halogen dopants on ORR activity.\textsuperscript{82} The F-doped (F-CNPs), Cl-doped (Cl-CNPs), and Br-doped (Br-CNPs) catalysts were synthesized by mixing benzene with hexafluorobenzene (C$_6$F$_6$), hexachlorobenzene (C$_6$Cl$_6$), and hexabromobenzene (C$_6$Br$_6$), respectively [Fig. 12(a)]. The results revealed that halogen doping did not play a significant role in shifting the onset potential for ORR, while a slight enhancement in the diffusion-limited current density was observed at high overpotentials. The ORR activity decreased in the order of F-CNPs > Br-CNPs > Cl-CNPs [Figs. 12(b) and 12(c)]. The insufficient ORR activity of SPP-synthesized halogen-doped CNPs might originate from a low degree of graphitization and the low content of ionic and/or semi-ionic bonds. Compared to other previous reports in which were halogen-doped carbon catalysts synthesized by a post-treatment process, it is expected that halogen atoms were mostly incorporated into the surface and edges of carbon matrices. In contrast, SPP incorporates halogen atoms in both the surface and bulk of carbon particles, which might cause undesired electronic arrangement and consequently inhibit the further enhancement of ORR activity.

4.2.3 Multiple heteroatom-doped carbon catalysts. Co-doping of carbon with more than one heteroatom has been demonstrated to potentially generate a synergic effect to enhance the catalytic activity toward ORR.\textsuperscript{83,84} Dual doping of B–N and P–N was first performance by Kim et al.\textsuperscript{74} This study compared both single-(B-, P-, N-doped) and dual-doped (B–N, P–N doped) carbon catalysts and illustrated superior ORR catalytic activity by dual-doped catalysts. First of all, the dominant sites changed from single to dual doping: the major bonding of B-doped (BCNPs) and P-doped (PCNPs) catalysts was attributed, respectively, to B–C and P–C bonds, where the...
most predominant bonding of B–N (BNCNPs) and P–N (PNCNPs) shifted to B–N and P–O, respectively [Figs. 13(a) and 13(b)]. The highest electrocatalytic activity was found to be that of PNCNPs, and descended in the order of BNCNPs > NCNPs > PCNPs > BCNPs [Fig. 13(c)]. A later research studied by Lee et al. further tuned the framework of B–N-doped carbon into coupling and uncoupling structures.85) Catalysts with the B–N uncoupling structure exhibited a more positive onset potential and higher cathodic current density the B–N coupling catalysts in a 0.1 M KOH electrolyte [Figs. 13(c) and 13(d)]. The results suggest that a higher amount of direct bonding between nitrogen and boron in B–N coupling led to compensation of the electroneutrality and thus the electronegativity on conjugated carbon was reduced. Thus, higher delocalization of electrons in the carbon framework can enhance the ORR activity.

The precursor, dopant, ORR onset potential, and calculated electron transfer number of various SPP-synthesized heteroatom-doped carbon catalyst are summarized in Table II. Although all the electrochemical activity of heteroatom-doped carbon catalysts were still not comparable to that of 20% Pt/C, for which the onset potential was −0.08 V (Ag/AgCl) and the highest current density was 4.54 mA cm⁻² at −0.60 V (Ag/AgCl) in an alkaline electrolyte, heteroatom-doped catalysts exhibited higher tolerance in methanol oxidation and durability compared to Pt/C.

5. Conclusions and outlook

From the above discussions, we have summarized the recent advances and present research on carbon-supported materials synthesized by the solution plasma process (SPP) and their corresponding performance as electrocatalysts. SPP provides unique plasma–liquid interfaces where multiple physical and chemical processes occur and initiates fast reactions. By critical design of the reactions between the precursor and electrode materials, various types of nanomaterials can be formed directly via SPP. In particular, metal-free carbon-based catalysts have been intensively reported.

SPP has been successfully utilized as a novel in situ single synthesis route for nitrogen-doped, boron-doped, oxygen-doped, as well as multiple-doped carbon catalysts by rationally selecting appropriate organic precursors containing desired heteroatom dopants. Also, the morphology of synthesized carbon can be varied from nanoparticles to nanosheets, depending on the input energy of the system. Most of the catalysts showed promising results in terms of oxygen reduction reaction (ORR) activity in an alkaline electrolyte, in which Fe–N₄-incorporated carbon nanosheets exhibited the most superior electrocatalytic activity, comparable to that of commercial 20 wt % Pt/C catalyst. Moreover, the metal-free catalysts demonstrated greater stability with the addition of methanol and higher durability over a longer operation time.

Although many achievements on heteroatom-doped carbon catalysts have been reported, the ORR activity is still less positive compared to that of commercial 20 wt % Pt/C, especially in an acidic electrolyte. Since the effect on ORR activity induced by heteroatom-doped carbon catalysts is still debatable, many studies have focused on the selective synthesis of specific bonding configurations in order to further probe in detail the relationship between various types of bonding states and electrochemical performance. More
detailed studies are required to understand the process and finally to elaborately tune the specific reactions in order to tailor the structural and bonding properties, which is of importance for designing efficient catalysts.

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