

Facile Synthesis of Metal-free N-doped Carbon Porous Materials by Microwave Co-condensation and Their Electrocatalytic Performances during Oxygen Reduction Reaction in DMFC

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Abstract

Metal catalysts supported on carbon porous materials (CPMs) are widely used as electrocatalysts for direct methanol fuel cell (DMFC) due to their excellent electrocatalytic properties. However, detailed incorporation procedure, cost (particularly noble metals), and electrocatalytic performance (activity and stability) of the metals invoked during fabrication of the supported M-CPM electrocatalyst normally limit their applications in terms of scale-up synthesis and commercialization of the fuel cell stacks. As such, R&D of non-noble metal and/or metal-free electrocatalysts has attracted great research attentions. Among them, nitrogen-doped carbon materials are known to be favorable for four-electron transfer reaction during oxygen reduction reaction (ORR). Typically, N-doped CPMs synthesized via conventional precipitation routes are normally drawback by the low N loading (< 3 wt%) and undesirable electronic properties, which in turn, leading to lower limiting currents. Herein, a novel synthesis method to overcome these drawbacks by means of a microwave-assisted self-assembly process is reported. This is achieved by first preparing various carbon-silicate (C-Si) composites by co-condensation method using melamine-formaldehyde resin oligomer (MFRO) as the primary carbon source, triblock copolymer surfactant (P123) as the soft template, and sodium silicate as the hard template. The resultant Si-C composites were

further subjected to graphitization at high temperature ($\geq 700^{\circ}\text{C}$) to obtain the high N-doped ($\geq 7\text{ wt\%}$) CPMs after removal of the silica template by acid treatment. It was found that thermal treatment by microwave provides not only a homogeneous environment with practically no thermal gradient, it also speeds up the energy penetration throughout the target source materials to benefit formation of carbon structure, hence, substantially reduces the processing time. The N-doped carbons so fabricated were found to possess higher specific surface areas ($\geq 500\text{ m}^2/\text{g}$) by at least two-fold compared to those synthesized by conventional hydrothermal method. In addition, these highly N-doped CPMs also exhibit superior electrochemical activities, excellent stabilities and durabilities, and resistance to MeOH crossover, during ORR even in the absence of a novel metal catalyst, surpassing the commercial Pt-C electrocatalysts commonly used in DMFCs.

Keywords: N-doped carbon, Co-condensation, Microwave, cathodic catalyst, fuel cells, Oxygen reduction reaction

1. Introduction

The electrocatalysts of alkaline direct methanol fuel cells (DMFCs) at anode and cathode, which normally employ novel metal (Pt or Ru) catalyst supported on carbon substrates, take over more than 50% of the membrane

electrolyte assembly (MEA) cost of a fuel cell stack. As such, R&D aiming to reduce the cost of the catalysts while improving the electrocatalytic activity and stability of the performance has drawn much research attention.

To apprehend these goals, one of the strategies is to replace the novel metals by non-precious metals or to prepare metal-free electrocatalysts by doping the carbon support with a Group V element, such as nitrogen [1-3]. A recent study showed that, when pyrolyzed at elevated temperatures, metal–nitrogen chelate complexes tend to decompose into metallic species. During the pyrolysis treatment, the metal also facilitates incorporation of pyridinic (N6) and quarternary (NQ) nitrogen groups onto the carbon matrix, which showed electrocatalytic activity during oxygen reduction reaction (ORR) [4,5]. However the role of nitrogen species in these N-doped carbon substrates is still not well understood [6].

Microwave-assisted synthesis has been recognized as a convenient and highly efficient route for the fabrication of nano-materials such as mesoporous silicas and carbons. As compared to the conventional chemical synthesis by hydrothermal route, microwave heating is normally capable of not only greatly shorten the synthesis time but also largely improve the overall performances.

We report herein a facile synthesis route to fabricate metal-free N-doped carbon porous materials (NCPMs) by microwave co-condensation method. These novel NCPM materials were characterized by a variety of analytical and spectroscopic techniques, such as N₂ adsorption-desorption isotherms, X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) etc. and their electrocatalytic performances during oxygen reduction reaction (ORR) were evaluated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and rotating disk electrode (RDE) voltammetry measurements.

2. Experimental

The synthesis of highly N-doped carbon porous materials (NCPMs) is achieved by first preparing the melamine-formaldehyde resin oligomer (MFRO), which was achieved by mixing 50 mL formalin (37 wt% formaldehyde solution) with 40.8 mL deionized water, then,

adjusting the pH of the solution to 8.4 ~ 8.6 by NaOH solution. Subsequently, 30 g of melamine (C₃H₆N₆) was added to the above solution and stirred for 2 h at 60 °C to obtain the polymerized MFRO (Fig. 1a). Subsequently, various carbon-silicate (C-Si) composites were synthesized by co-condensation method (Fig. 1b) using the MFRO as the primary carbon source, triblock copolymer surfactant P123 (poly(ethylene glycol)–poly (propylene glycol)–poly (ethylene glycol)) as the soft template, and sodium silicate (Na₂SiO₃) as the silicon source (hard template). Typically, this was achieved by first mixing the above MFRO solution with a P123 solution (ca. 6 g P123 dissolved in 60 mL deionized water) and kept under stirring at 60 °C for 2.5 h, followed by adding 2.24 mL of acetic acid. The resultant solution was mixed with another solution containing 13.5 g of Na₂SiO₃ dissolved in 150 mL deionized water. The mixture solution was then stirred at a desirable temperature x ($x = 60, 80$, and 100) °C for a duration of y ($y = 1, 6$, and 24) h in a microwave (denoted as “mw”) oven or heat water reactor (“ht” for hydrothermal) to obtain various C-Si composites with different textural and electrochemical properties.

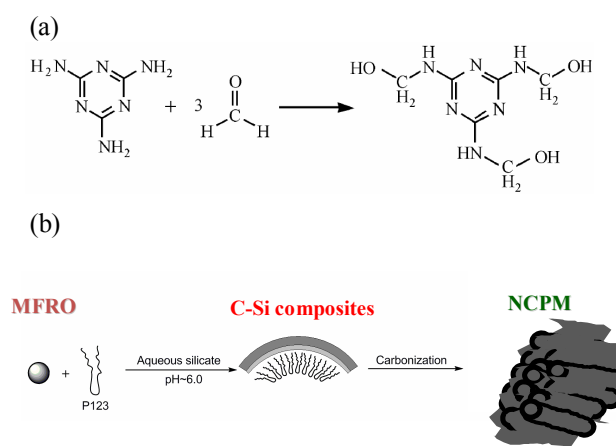


Fig. 1. Illustrations of (a) polymerization of MFRO from melamine and formaldehyde, and (b) synthesis route for NCPM via co-condensation method.

The resultant Si-C composites were further subjected to graphitization at high temperature (900°C) to obtain the highly N-doped NCPMs after removal of the silica template by acid treatment. The NCPMs so prepared are

hereafter denoted as NPCM-ht-*x-y* and NPCM-mw-*x-y*.

These NCPMs were applied as cathodic electrocatalyst for direct methanol fuel cell (DMFC) and their catalytic performances during ORR were evaluated by CV, LSV, and RDE voltammetry tests. Typically, this was carried out by first preparing the glass carbon electrodes (5.0 mm in diameter): ca. 1 mg of grinded catalyst sample was dispersed in 0.5 mL of solvent by sonication. Then, ca. 20.0 μ L of suspended catalyst were pipetted onto the glassy carbon electrode surface along with ca. 20 μ L of electrolyte (1 wt% Nafion). The resultant electrode was allowed to dry at room temperature (298 K) for 0.5 h in a desiccator before measurement.

For analysis of RDE voltammetry data, the number of transferred electron (n^*) per oxygen molecule involved during the ORR reaction may be derived from the Koutecky–Levich first-order equation:

$$J^{-1} = J_k^{-1} + J_{dl}^{-1} = J_k^{-1} + B^{-1} \omega^{-1/2} \quad \text{Eq.(1)}$$

where, $B = 0.62n^*FC_0D_0^{2/3}\nu^{-1/6}$; $J_k = n^*FkC_0$, J is the measured current density, J_k is the kinetic current density, J_{dl} is the diffusion-limiting current density, F is the Faraday constant (96485 Cmol^{-1}), C_0 is the bulk concentration of O_2 , D_0 is the diffusion coefficient of O_2 in the KOH electrolyte, ν is the kinetic viscosity of the electrolyte, and ω is the angular velocity of the disk ($\omega = 2\pi f$; f is the linear rotation frequency). Herein the following values were adopted for the derivation of n value: $C = 1.2 \times 10^{-3} \text{ mol L}^{-1}$, $D = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ in 0.1 M KOH solution [7].

3. Results and discussion

Table 1 summarized the textural and electrochemical properties of various NCPMs. For samples prepared via microwave treatment, it is found that the specific (BET) surface area increase with increasing heating duration (y), likely due to the crosslinking of MFRO with silica precursor to form a hybrid skeleton. A higher specific surface area of the substrate should be more preferable for a higher dispersion of active sites. By comparing the NCPMs prepared under the same microwave heating time ($y = 6$ h),

it is found that NPCM-mw-80-6 possesses a higher surface area than NPCM-mw-60-6, however, upon increasing the treatment temperature (x) to 100 $^\circ\text{C}$, a sharp decrease in surface area was observed. This indicates that, while the reaction rate of MFRO to resins may be increase by lifting the heating temperature, one should also maintain the reaction rate to ensure a homogeneous mixing of the MFRO with the silica precursor to form a hybrid skeleton by keeping the system under a moderate temperature. Similar conclusion may also be drawn for the NPCM-mw- x -1 series samples with $y = 1$ h.

Table 1. Textural properties and electrochemical performances of various NPCMs**

| Sample | BET (m^2/g) | N (wt%) | V_o (V) | n^* | J_k (mA/cm^2) | ζ (S/cm) |
|---------------|----------------------------------|------------|--------------|-------|--------------------------------------|-------------------|
| NCPM-mw-60-1 | 178 | 10.4 | -0.21 | 4.5 | 5.7 | 1.02 |
| NCPM-mw-60-6 | 380 | 10.1 | -0.19 | 4.4 | 11.3 | 0.89 |
| NCPM-mw-80-1 | 233 | 10.0 | -0.19 | 3.8 | 10.6 | 3.03 |
| NCPM-mw-80-6 | 517 | 11.5 | -0.12 | 4.8 | 11.5 | 1.60 |
| NCPM-mw-100-1 | 210 | 11.0 | -0.18 | 4.7 | 12.2 | 0.50 |
| NCPM-mw-100-6 | 246 | 10.9 | -0.17 | 4.3 | 15.4 | 0.51 |
| NCPM-ht-60-24 | 240 | 12.3 | -0.22 | 3.4 | 11.3 | 0.70 |

** Carbonization temperature: 900 $^\circ\text{C}$; ht: hydrothermal method; mw: microwave heat treated; N: nitrogen content; V_o : onset potential; n^* : average number of electrons transferred during ORR; J_k : limiting current density; ζ : electrical conductivity

Moreover, NPCM samples prepared via microwave synthesis route appear to possess high N content (ca. 10 ~ 11 wt%) as compared to those prepared via conventional precipitation routes (normally < 3 wt%) [2]. Moreover, the N content of the NCPMs so prepared seems to be independent neither on the duration (y) nor on the temperature (x) of the microwave treatment. Rather, it is dictated by the final carbonization (or graphitization) temperature, as concluded in our earlier study [8]. In this context, the role of N content may be excluded for the discussion below regarding to the electrocatalytic performances of the NCPMs.

The results obtained from electrocatalytic tests by CV, LSV, and RDE voltammetry, namely, the onset potential (V_o), kinetic current density (J_k), and number of transferred electron during ORR (n^*) are also summarized in Table 1 along with the electrical conductivity data. While all

sample show the preferred 4-electron transfer mechanism during ORR, suggesting a more efficient electron transfer and excluding the existence of hydrogen peroxide radicals, whose presence prone to attack the carbon support and the proton-exchange membrane, leading to an undesirable degradation of the fuel cell [9,10]. Among all NCPM examined, NCPM-mw-80-6, which possesses highest surface area (nearly by two folds compared to the others) and electrical conductivity exhibits not only the best onset potential (-0.12 V) but also satisfactory limiting current density.

To unravel the possible reasons for the above behavior observed in NCPMs, we performed additional XPS study to explore the nature of the N species that may present in these novel metal-free electrocatalysts. It is well-known that there are four typical types of N species [11], which may be identified by their corresponding binding energies observed from the XPS spectrum, namely pyridinic-N (N6;

BE $\sim 398.5 \pm 0.3$ eV), pyrrolic-N (N5; BE $\sim 400.5 \pm 0.3$

eV), quaternary-N (NQ; BE $\sim 401.3 \pm 0.3$ eV), and

oxidized pyridinic-N⁺-O⁻ (NX; BE $\sim 402-405 \pm 0.3$ eV), as shown in Fig. 2. Among them, N6 and NQ are commonly referred as primary electrochemical active sites [4,6,12].

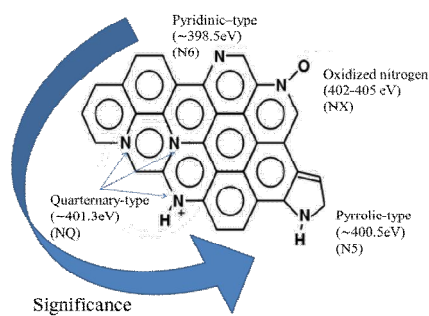


Fig. 2. Plausible types of N species that may incorporated in graphitized carbon structure.

Figure 3 shows the XPS spectra obtained from assorted NCPM-mw(ht)-x-y samples. The major types of N species

derived from the XPS spectra are summarized in Table 2. Owing to the fact that the content of oxidized pyridinic-N⁺-O⁻ (NX) is typically less than 1-5% (close to the limit of experimental error), it may be ignored for the discussions below. It is found that a treatment temperature more than 60 °C is preferred for the preparation of NCPM

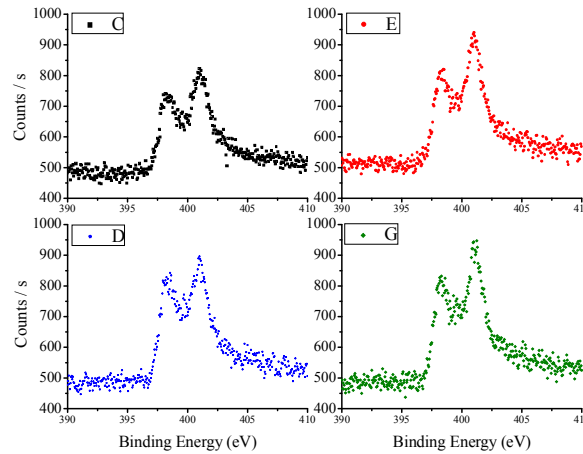


Fig. 3. XPS spectra of various NCPMs samples.

Table 2. Distribution of various N species in various NCPMs.

| Sample | N6 (atom%) | N5 (atom%) | NQ (atom%) |
|---------------|---------------|---------------|---------------|
| NCPM-ht-60-24 | 36.0 | 28.4 | 35.6 |
| NCPM-mw-60-1 | 44.7 | 28.4 | 26.9 |
| NCPM-mw-80-1 | 47.8 | 29.2 | 23.0 |
| NCPM-mw-100-1 | 42.6 | 30.2 | 27.2 |
| NCPM-mw-60-6 | 42.7 | 25.5 | 31.8 |
| NCPM-mw-80-6 | 47.3 | 28.9 | 23.8 |
| NCPM-mw-100-6 | 42.7 | 23.3 | 34.0 |

with reasonable textural and electrocatalytic properties. While the amount of N6 species do not seem to depend on the treatment temperature of NCPM, the amounts of N5 and NQ seem to increase slightly with increasing temperature. Moreover, the amount of NQ species in the sample prepared by hydrothermal process (NCPM-ht-60-24) appears to be higher than those prepared by microwave heating. On the contrary, the amount of N6 seems to be less for NCPM-ht-60-24 compared to NCPM-mw-x-y, indicating that samples prepared by microwave heating promote formation of N6 at the expense of NQ and *vice versa* for hydrothermal heating process. The formation of NQ (or graphitic N) species should affect the pristine graphitization level, which in turn, leading to a lower electrical conductivity of the carbon substrate (*cf.*

Table 1).

Figure 4 displays the CV curves of various NCPMS during. Clearly, the oxygen reduction peak at around -0.26 V can be inferred for all samples. Moreover, the ORR peak intensity is larger for sample prepared by microwave than that by hydrothermal route. The may be

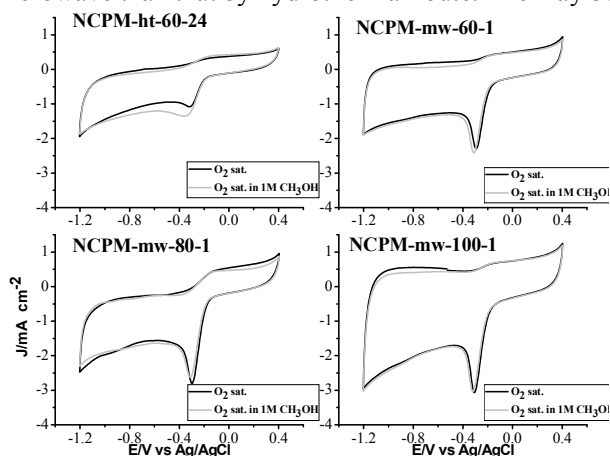


Fig. 4. Cyclic voltammograms of various NCPM samples during ORR.

ascribed due to the more abundant N6 in the substrate, whose presence is anticipated to promote ORR activity. The durability of the electrocatalyst is one of the major concerns in fuel cell technology. To assess the stability of NCPM, two samples (NCPM-mw-80-6 and NCPM-ht-60-24) were further tested at a constant voltage of -0.26 V for 18000 s in a 0.1 M KOH solution saturated with O_2 at a rotation rate of 1600 rpm together with a commercial catalyst JM-10 (Johnson-Matthey, 10%Pt/XC-72). Remarkably, the corresponding current-time (*i-t*) chronoamperometric response of the metal-free NCPM-mw-80-6 catalyst exhibits a satisfactory stability resembling that of JM-10 catalyst loaded with 10%Pt (Fig. 5). For the NCPM-mw-80-6, a very slow attenuation after a fast decrease of 10% within the initial 5000 s, and a high relative current of 69.8% still persisted after 18000s. In contrast, the NCPM-ht-60-24 showed a gradual decrease with a current loss of approximately 59.8 % after 18000s. These results suggest that while the durability of NCPM-mw-80-6 is less than that of JM-10, it is far superior compared to that of the NCPM-ht-60-24.

4. Conclusions

We have successfully developed a facial synthesis route to prepare metal-free, highly N-doped carbon porous materials (NCPMs) through microwave-assisted heating. The novel NCPMs electrocatalysts so fabricated were found to have good electrocatalytic activity and durability comparable to commercial carbon supported Pt

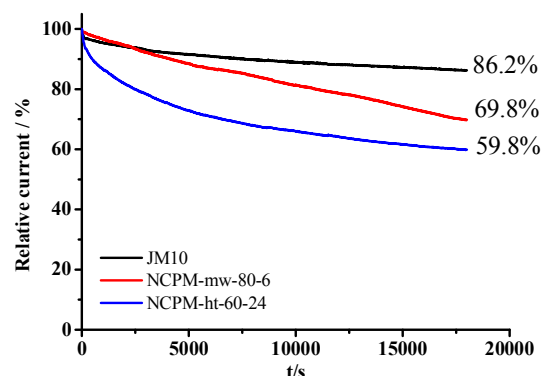


Fig. 5. Current-time (*i-t*) chronoamperometric response of NCPM-mw-80-6, NCPM-ht-60-24, and JM-10 on modified GC electrodes at -0.26 V in O_2 -saturated 0.1 M KOH at a rotation rate of 1600 rpm.

catalysts. Moreover, since the NCPMs do not contain any metal, the critical issue of methanol cross-over during DMFC operation is also resolved. These unique electrochemical properties together with the inexpensive reactants and simple procedures involved during material preparation, making these NCPMs excellent candidates for future practical and cost-effective applications as cathodic electrocatalysts for DMFCs.

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