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Polymerizable ionic liquid derived carbon for oxygen reduction and evolution

Jian Gao ^{a,b}, Cong Shen ^a, Jianjun Tian ^a, Zhen Yin ^{a,*}, Hongbin Lu ^{c,*}, Jianyong Feng ^{d,*}, Yizhong Huang ^d, Xiaoyao Tan ^a

^a State Key Laboratory of Separation Membranes and Membrane Processes, Department of Chemical Engineering, Tianjin Polytechnic University, 399 Binshui West Road, Tianjin 300387, P. R. China

^b Tianjin Engineering Center for Safety Evaluation of Water Quality & Safeguards Technology, Tianjin Polytechnic University, 399 Binshui West Road, Tianjin 300387, P. R. China

^c Nantong Institute of Materials Engineering, 58 Chongchuan Road, Nantong 226001, P. R. China

^d School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue 639798, Singapore

* Corresponding authors.

E-mail addresses: Zhenyin233@163.com, lu_hongbin@163.com, jyfeng@ntu.edu.sg.

Abstract

A polymerizable ionic liquid is explored as the precursor to produce nitrogen-doped carbon powders. The ionic liquid is functionalized with NO₃⁻ anions, which decompose and release gases during the pyrolysis process, facilitating the formation of a carbon foam. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses show that the carbon foam is composed of curved carbon nanosheets with the maximum thickness of 70 nm. The favorable compositional (nitrogen doping to provide catalytically active sites) and morphological (curved nanosheet architecture to increase the contact area between electrolytes and catalytically active sites) characteristics make the present carbon powders a potential metal-free electrocatalyst for oxygen reduction and oxygen evolution reactions. As expected, the nitrogen-doped and curved carbon nanosheets exhibit a **considerable** activity towards the oxygen reduction reaction as well as a moderate ability for catalyzing the oxygen evolution reaction in KOH solutions.

Keywords: Nitrogen-doped carbon sheets, Oxygen evolution reaction, Oxygen reduction reaction, Bifunctional catalysts, Polymerizable ionic liquids

1. Introduction

The rapid depletion of fossil fuels and severe deterioration of ecology have stimulated extensive researches on the utilization and storage of clean and sustainable power sources. Among various power source technologies, rechargeable metal–air batteries[1] and unitized regenerative fuel cell[2] have been considered as promising power sources for future energy-demanding devices owing to their high energy densities [3, 4]. The oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) are of key importance for the rechargeable metal-air batteries and fuel cells. However, the reaction kinetics of ORR and OER are sluggish, and electrocatalysts that exhibit low overpotentials for ORR and OER are always required. Although precious metals such as Pt, Ru, Ir and their oxides have been used as such electrocatalysts[5], their high costs and/or poor stability hamper large-scale commercialization of the metal-air battery and fuel cell technologies. Correspondingly, non-precious metal catalysts (NPMCs) have been proposed and investigated to replace these precious-metal-containing electrocatalysts [6-9].

Besides the extensively studied transition-metal-based NPMCs, metal-free NPMCs have been introduced and attracting more and more attention [10, 11]. Among the metal-free NPMCs, heteroatom-doped carbon materials have gained increasing research interest for their promising catalytic activities towards the ORR and/or OER [11-13]. Previous reports have demonstrated excellent electrocatalytic activities for OER and ORR on heteroatom-doped graphenes [11, 14-16]. As an analogue to graphenes, carbon nanosheets hold great promise for electrocatalysis as well if these carbon nanosheets are well modified by heteroatom-doping and suitably assembled to form a three-dimensional interconnected porous structure.

Recently, due to their unique properties such as rich in N content, function-adjustable and non-vaporization, ionic liquids (ILs) have attracted much attention as precursors for NPMCs [17-19]. As an important type of ILs, polymerizable ionic liquids (PILs) possess the additional polymer properties after polymerization, besides the above properties of ILs. These interesting features of PILs may offer the resulting catalysts with special structures and improved catalytic performance. Therefore, the PILs can be potential precursors for NPMCs. However, the investigation of PILs as precursors for metal-free NPMCs is relatively scarce.

Herein, a facile fabrication scheme is developed to produce nitrogen-doped and curved carbon nanosheets in one step with a functionalized PIL hydrolyzed vinyl imidazolium nitrate as the precursor. The desirable nitrogen doping effects and curved nanosheet structure of the resultant carbon powder render it a good metal free electrocatalyst for oxygen reduction and oxygen evolution reactions.

2. Experimental

2.1 Preparation of the nitrogen-doped and curved carbon nanosheets

The PIL hydrolyzed vinyl imidazolium nitrate was prepared by adding HNO_3 (65%) dropwise into equal molar of vinyl imidazole under stirring. The mixture was stirred for an hour at room temperature and two hours in a water bath of $50\text{ }^\circ\text{C}$, respectively, to obtain a viscous liquid. The obtained liquid was submitted for proton nuclear magnetic resonance (^1H NMR, shown in Fig. S1a in the ESI) check to confirm its structure. The liquid was then used as the precursor and pyrolyzed at $560\text{ }^\circ\text{C}$ for an hour to get a carbon foam (CN_1) as shown in Fig. S2 in the ESI. The detailed heating process is shown in Fig. S3 in the ESI. The IL will polymerize during the heating process since the cation is equipped with $\text{C}=\text{C}$ group, and the polymerization can be confirmed with ^1H NMR as shown in Fig. S1b in the ESI. The preparing process is shown schematically in Fig. 1. The CN_1 was submitted for several physical characterizations such as SEM, TEM, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). For comparison, a control sample CN_2 was prepared with IL hydrolyzed methylimidazolium nitrate that possesses a similar structure but is non-polymerizable. Sample CN_3 was also prepared under similar conditions with hydrolyzed vinyl imidazolium phosphate, which is polymerizable but not functionalized with NO_3^- anion that can release gases.

Fig. 1 Schematic illustration of the preparation for the electrocatalyst CN_1 .

2.2 Electrochemical characterization

All electrochemical measurements were conducted in a three-electrode configuration at room temperature. The potential, measured against an Hg/HgO electrode, was converted to potential versus reversible hydrogen electrode (RHE) according to $E_{\text{RHE}} = E_{\text{Hg}/\text{HgO}} + 0.955$. To prepare the working electrode, 5 mg of catalyst samples were dispersed in an aqueous solution containing 0.9 ml of ethanol and 0.1 ml of 5 wt% Nafion under sonication for 30 minutes. The obtained homogeneous catalyst ink (10 μl) was dropped onto a mirror-polished glassy carbon electrode. The mass loading was 0.25 mg cm^{-2} unless otherwise noted. For comparison, The Pt/C (60%) working electrode was

prepared using a procedure similar to that of CN₁. The loading amounts of Pt/C and Pt are 0.25 and 0.15 mg cm⁻², respectively.

A 0.1 M KOH aqueous solution saturated with oxygen was used as the supporting electrolyte unless otherwise stated. For the linear sweep voltammetry (LSV) tests, the scanning rate is 10 mV s⁻¹ in the range of 0-1.2 V_{RHE} unless otherwise stated.

Electrochemical impedance spectroscopy (EIS) was measured with the electrolyte saturated with O₂ at 0.77 V_{RHE}. The frequency range for CN₁ and CN₂ was from 0.001 and 0.01 to 100 000 Hz, respectively, with an amplitude of 0.005 V at room temperature.

To evaluate the electrochemical active surface areas, cyclic voltammetry (CV) tests were performed in a 0.1 M KOH aqueous solution saturated with nitrogen as the supporting electrolyte at various scanning rates ranging between 10-500 mV s⁻¹ in the range of 0-1.2 V_{RHE}, and lines were fabricated by plotting the closed area of the CV curves vs. the scanning rates. The slope of the line can be used to evaluate the electrochemical active surface area, which is proportional to the slope [20]. More detailed information about the electrochemical tests is presented in section 2 of the ESI.

3. Results and Discussion

The SEM images of CN₁ derived from the PIL are shown in Fig. 2a and Fig. 2b. A chaotic sheet structure for CN₁ can be observed as indicated by Fig. 2a, consistent with its foam-like appearance. Fig. 2b is the higher magnification SEM image of CN₁, which exhibits the flower-like curved sheets with the maximum thickness of around 70 nm. Fig. 2c presents a representative TEM image of the CN₁ where thin and curved nanosheets can be observed. The curved nanosheets are believed to increase effective catalyst area by forming an open and porous structure [21], making more active sites accessible to the reacting species. Additionally, the interconnected nanosheets are helpful to afford a good electric conductivity, a desirable merit for electrocatalysis, when these powders are assembled into an electrode form. In comparison, the SEM image for CN₂ (derived from the non-polymerizable ionic liquid) is presented in Fig. 2d, for which only irregular bulk films with the thickness of over 9 μm can be observed. This structure makes it difficult for the active sites to be exposed. For a quantitative comparison, we have measured the electrochemical surface areas of CN₁ and CN₂ according to the reported method[20] based on the slope of the CV closed area-scanning rate line. As shown in Fig. 2e, CN₁ exhibits an electrochemical surface area that is 63 times that of CN₂. The corresponding CV curves for CN₁ and CN₂ are presented in Fig. S4a and Fig. S4b, respectively, in the ESI.

The sharp difference in morphology between CN₁ and CN₂ suggests the importance of selecting

suitable IL cations as precursors to produce carbon based catalysts with interconnected porous structures. When an IL with polymerizable cations is selected, the cations polymerize during the pyrolysis process to form the skeleton which then induces the emergence of sheet-like graphite. When a non-polymerizable IL is used as the precursor, the carbonization process may be uncontrollable, resulting in irregular bulk particles/films as shown in Fig. 2d. The NO_3^- anions used as counterions to the polymerizable cations (hydrolyzed vinyl imidazole) decompose and release gases during the pyrolysis process, leading to the formation of a carbon foam with a curved sheet structure. The functionalization of PIL with NO_3^- is pivotal to the formation of curved nanosheets. If NO_3^- is replaced by H_2PO_4^- that does not release gases during the pyrolysis process, only bulk carbon particles are obtained as shown in Fig. 2f.

Fig. 2 (a, b) SEM images of CN_1 , (c) TEM image of CN_1 , (d) SEM image of CN_2 , (e) closed area of CV as a function of scanning rate, (f) SEM image of CN_3 .

As the hydrolyzed vinyl imidazole cation contains N elements inherently, the nitrogen doping in carbon can be fulfilled simultaneously with the formation of the curved nanosheet structure. Therefore, the NO_3^- anion functionalized PIL applied here is an efficient precursor for the production of nitrogen-doped and curved carbon nanosheets in one step, rendering the preparing process simple and easy to perform. X-ray diffraction peaks at around 24.4° and 42.6° confirm the existence of thin graphite sheets in CN_1 (Fig. 3a), and the broadenings of these peaks are probably due to the nitrogen doping effects [14].

To investigate the chemical composition and the nature of chemical bonding of constituent elements in the obtained sample CN_1 , the XPS measurements were performed. Based on the XPS survey spectrum shown in Fig. 3b, the as-prepared sample CN_1 possesses C, N and O elements. The contents for C, N were found to be 75.4% and 14.6%, respectively. The XPS spectrum for N 1s is

presented in Fig. 3c. The peaks at 398.2, 400.4 and 401.1 eV can be attributed to pyridinic, pyrrolic and graphitic, respectively.[1] The relative atomic percentages of pyridinic, pyrrolic and graphitic are 51.3%, 26.9%, and 21.73%, respectively. Particularly, the pyridinic N, and pyrrolic N are believed to function as active sites.[22] The XPS spectrum for C 1s is shown in Fig. 3d. The peaks at 284.6, 285.8 and 287.2 eV can be assigned to C-C carbon, C-O and/(or) C-N carbon and C-O-C carbon, respectively.[23] The XPS results imply that the CN₁ catalyst is doped with nitrogen, and this is consistent with the XRD results. For the stronger electronegativity of N, the charge will be redistributed, which is helpful to enhance the catalytical performance.[24, 25] Therefore, the XRD and XPS characterizations of CN₁ imply that the heteroatom-doping in carbon nanosheets has been realized, with N atoms on the desirable structural sites for maximum electrocatalytic efficiency.

Fig. 3 (a) XRD pattern of CN₁, (b) XPS survey spectrum of CN₁, (c) N 1s XPS spectrum of CN₁, and (d) C 1s XPS spectrum of CN₁.

To evaluate the electrocatalytic activity of the nitrogen-doped and curved carbon nanosheets, CN₁ was subjected to ORR measurements. The LSV curve at 1600 rpm in Fig. 4a confirms the electrocatalytic performance of CN₁, with an onset potential of 0.92 V_{RHE}. This value is comparable to those of Pt/C catalysts[11] and outperforms some previously reported metal-free ORR catalysts.[26-29] In comparison, CN₂ derived from the non-polymerizable IL shows dramatically decreased performance, with the onset potential being negatively shifted by approximately 120 mV

to 0.8 V_{RHE}. The higher onset potential of ORR usually means a higher electrocatalyst activity. Therefore, it implies that the introduction of functional group of NO₃⁻ in PILs indeed helpful to prepare NPMCs with superior catalytic performance toward ORR.[30]

Fig. 4 (a) LSV curves for ORR in O₂-saturated electrolyte on CN₁ and CN₂ at 1600 rpm, (b) current-time chronoamperometric response of CN₁ and CN₂ at 0.65 V_{RHE}, (c) EIS for CN₁ and CN₂, (d) EIS for CN₁, (e) EIS for CN₁ for CN₂, (f) Z'- $\omega^{-1/2}$ line.

The ORR stability for CN₁ and CN₂ was examined using chronoamperometry at 0.65 V_{RHE} in the O₂-saturated 0.1 M KOH aqueous solution without rotating. The current-time curves presented in Fig. 4b exhibit a 68% decay of current density for CN₂ during the 3600 s test while the loss for CN₁ is only 27%. This stability test also shows the superiority of CN₁ derived from polymerizable IL over CN₂ derived from non-polymerizable IL.

The EIS for CN₁ and CN₂ at 0.77 V_{RHE} clearly show that both the reduced film resistance and

charge transfer resistance for CN₁ compared with CN₂ (see Fig. 4c), consisting with the three-dimensional interconnected porous structure in CN₁ for exposing catalytic active sites, enhancing mass transport and affording a good electric conductivity. For clearance, the EIS for CN₁ and CN₂ are presented in Fig. 4d and Fig. 4e, respectively.

The ion diffusion coefficients for the samples ($D \text{ cm}^2 \text{ s}^{-1}$) were investigated according to eq. (1),[31] where A is the surface area of the electrode, which is $0.196 \times 10^{-4} \text{ m}^2$. N is the number of the electrons per molecule attending the electron transfer reaction, and this is the same for CN₁ and CN₂. F is the Faraday constant (96485 C mol^{-1}). C is the concentration of active ions, which is also the same for CN₁ and CN₂. R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$). T is the testing temperature, and σ is the slope of the line $Z' - \omega^{-1/2}$ shown in Fig. 4f derived from Fig. 4d and Fig. 4e. Since all the parameters in eq. (1) are of the same values except σ , the relationship between CN₁ and CN₂ can be evaluated according to the σ values for CN₁ and CN₂. Based on Eq. (1), the relationship between the D for CN₁ and CN₂ can be described with eq. (2). As shown in Fig. 4d, the σ for CN₂ is around 100 times that of CN₁. Therefore, the D for CN₁ can be estimated to be around 10000 times that of CN₂. The above results imply that the PIL is more effective than the non-polymerizable one in producing efficient carbon-based electrocatalysts.

$$D = 0.5 * \left(\frac{RT}{AN^2R^2C\sigma} \right)^2 \quad (1)$$

$$D_{CN1} = (\sigma_2/\sigma_1)^2 * D_{CN2} \quad (2)$$

The number of apparent electrons transferred (n) was studied with RDE technology at various rotate rates, and the LSV curves are presented in Fig. 5a. It reveals a typical increase in current with an increase of rotational speed as expected due to the thinner diffusion layer at higher rotational speeds. A group of lines called Koutecky-Levich plots shown in Fig. 5b were fabricated by plotting of i^{-1} versus $\omega^{-1/2}$ at various potentials. The Koutecky-Levich plots shown in Fig. 5b demonstrate a linearity at each electrode potential, indicating a first-order reaction kinetics with respect to the concentration of dissolved O₂.

The slope of the Koutecky-Levich plots was used to calculate the n via eq. (3) and (4), where i and i_k is the measured current density and the kinetic current densities, respectively. B is the reciprocal of slope of Koutecky-Levich plots, n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96485 C mol^{-1}), C₀ is the bulk concentration of O₂ ($1.1 \times 10^{-3} \text{ mol L}^{-3}$), D₀ is the diffusion coefficient of O₂ in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and γ is the kinetic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$). The constant 0.2 is adopted when the rotation speed is expressed in rpm.[32] The calculated n is 3.16~4.01. This value is comparable with that of other N doped carbon materials, which are in the range of 3.2~4.01.[17, 33] The result implies that the ORR

on the sample is via a four-electron pathway, which is desired for power sources.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B\omega^{1/2}} \quad (3)$$

$$B = 0.2nFC_0D_0^{2/3}\gamma^{-1/6} \quad (4)$$

For comparison, the LSV curves for CN₁ and commercial Pt/C (60%) are presented together in Fig. 5c. The performance of CN₁ is lower comparing with the state-of-art Pt/C ORR catalyst. However, the much lower price and higher methanol tolerance of CN₁ shown in the following part render the prepared carbon a promising alternative catalyst.

Fig. 5 (a) Polarization curves for ORR in O₂-saturated 0.1 M KOH on the CN₁ catalyst with a scanning rate of 10 mV s⁻¹ at various rotational speeds, (b) Koutecky-Levich plots, (c) Polarization curves for ORR on CN₁ and Pt/C (d) methanol tolerance tests of CN₁ and Pt/C.

The above experiments show that the PIL hydrolyzed vinyl imidazolium nitrate is a promising precursor for metal-free NPMs. Besides the parameters such as the onset potential, the number of apparent electrons transferred and conductivity, the methanol tolerance is another important factor to evaluate a ORR catalyst. In direct methanol fuel cells, the fuel of methanol in the anode sometimes permeates through the polymer membrane to the cathode and seriously affects the cathode catalysis process (ORR). Therefore, it is important to consider and investigate the methanol tolerance for newly developed electrocatalysts. Thus, the methanol tolerance of CN₁ was measured by LSV in the presence of methanol (20000 ppm). As indicated by Fig. 5d, no obvious changes in the LSV profile are observed for CN₁ upon addition of methanol into electrolytes, whereas a strong negative response

for the commercial Pt/C catalyst is detected. Similar found was also reported by others.[34] Thus, the CN₁ developed here demonstrates a good methanol tolerance and thereby a promising potential in practical applications.

Fig. 6 (a) The OER activities of CN₁ in N₂-saturated 0.1M KOH at a scanning rate of 10 mV s⁻¹ with a rotational rate of 1600 rpm. (b) current-time chronoamperometric response of CN₁ and CN₂ at 1.955 V_{RHE}

The OER activities of CN₁ and CN₂ were evaluated in the N₂-saturated 0.1 M KOH aqueous solution, and the results are shown in Fig. 6a. The control sample (CN₂) shows a relatively poor OER activity, and the current density at 1.9 V_{RHE} is only 0.5 mA cm⁻². While an obvious current density of 3.5 mA cm⁻² that comparable with the commercial Pt/C (60%) is observed at 1.9 V_{RHE} for CN₁, suggesting a significantly improved OER activity. The OER catalytic activity may derive from the pyridinic N, which is reported to function as active site for OER.[35] The OER performance on CN₁ is expected to be improved significantly by careful optimizations of the structures of the PIL.

The OER stability for CN₁ and CN₂ was examined using chronoamperometry at 1.955 V_{RHE} in the N₂-saturated 0.1 M KOH aqueous solution at a rotate rate of 1600 rpm. The results are presented in Fig. 6b. The current for CN₁ maintained around 67% of the initial value after the 3600s-stability test. This value is higher than that of CN₂, which was found to be 60%.

Conclusion

A new precursor based on the NO₃⁻ functionalized polymerizable ionic liquid is developed for synthesizing heteroatom-doped and curved carbon nanosheets in one-step. Our method relies on the synergistic effects of the negligible vapor pressure and polymerizable property of the ionic liquid. Additionally, the NO₃⁻ anions used as counterions to the hydrolyzed ionic liquids decompose and release gases to enable the formation of the curved sheet structure during the pyrolysis process. Due to the N-doping effects and three-dimensional crosslinkable porous structure, the as-prepared sample provides an onset potential of 0.92 V_{RHE} for ORR in 0.1 M KOH solutions. The sample also shows profound CH₃OH tolerance and a catalytic activity toward OER. Our strategy that utilizes the

functionalized polymerizable ionic liquids as the precursors therefore provides a fast and efficient route for the one-step production of nitrogen-doped and curved carbon nanosheets with dual electrocatalytic activities for ORR and OER. The results imply the promising potentiality for functionalized polymerizable ionic liquids as precursors for metal-free non-precious metal catalysts toward ORR and OER.

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