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Article

Induced growth of Fe-N_x active sites using carbon templates

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ABSTRACT

Highly active Fe-N_x sites that effectively improve the performance of non-precious metal electrocatalysts for oxygen reduction reactions (ORRs) are desirable. Herein, we propose a strategy for introducing a carbon template into a melamine/Fe-salt mixture to inductively generate highly active Fe-N_x sites for ORR. Using ⁵⁷Fe Mössbauer spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction, we studied the structural composition of the Fe and N co-doped carbon catalysts. Interestingly, the results showed that this system not only converted inactive Fe and Fe-carbides into active Fe-N_x and other Fe-nitrides, but also improved their intrinsic activities.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are one of the most promising candidates for clean electricity generation technologies; they have attracted increasing attention because of the limited supply of fossil fuel resources and environmental pollution caused by traditional energy production methods [1]. The catalytic species at the PEFC cathode typically includes Pt, which has a low natural abundance resulting in a significant restriction of the ability to meet global market demand; thus, non-precious metal catalyst alternatives are highly desired. To date, Fe-N_x doped carbons (Fe-N/C) are considered to be the most promising potential alternatives to Pt and its alloys as ORR catalysts at the cathodes of PEFCs [1–7].

Therefore, Fe-N/C catalysts with superior catalytic activities are being actively pursued through a variety of strategies; these include: (1) adjusting the type and amount of Fe compound [8–11] and N source [11–13]; (2) altering the synthetic conditions, *e.g.*, tuning the temperature [9,10,14] and pressure [15] of pyrolysis methods as well as investigating non-pyrolyzing routes such as axial ligand tethering [16], covalent grafting [17], and ball-milling [18]; (3) forming nanostructures, such as core-shell nanoparticles [18], ordered mesoporous carbons [19], arrays [20], thin graphene sheets [14,21,22], and amorphous carbon spheres [23]; (4) building composites including binary materials, such as graphene/carbon nanotubes [9], graphene/carbon black [24,25], graphene nanoribbons/carbon nanotubes [26], and carbon nanoparticles/carbon nanofibers

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[27], and ternary hybrids, such as carbon nanospheres/carbon nanotubes/graphene sheets [10]; (5) introducing post-processing, such as acid-washing [14,19–21], pore-forming [28], and reheating [28,29]; and (6) designing different typical Fe phases [29–31] to regulate the generation of Fe-nitrides, Fe-carbides, and Fe-nanoparticles. All these efforts are aimed at enhancing the ORR catalytic activities of the compounds.

Concurrently, significant progress has been made in identifying the detailed compositions of the Fe-based species through spectroscopic studies. A growing body of work suggests that the mode of Fe- N_x coordination plays a key role in promoting the electrocatalytic performance for ORR [7–36]. Moreover, it should be noted that Fe and Fe carbides have recently been identified as possible active species [37–42]. For example, adjacent Fe-carbides particles can boost the ORR activity of Fe- N_x sites [41,42], and Fe nanoparticles encapsulated in CNTs can modify the electronic structure of the carbon atoms [31], thereby indirectly participating in electrocatalysis. However, the extent of the role of Fe remains controversial, although it is clear that their ORR activity is inferior to that of the Fe- N_x sites [29–31]. Further, in-depth studies focused on the Fe- N_x species have revealed that Fe- N_4 , and/or other Fe-nitrides, may be the primary contributors to the electrocatalytic performance of Fe-N/C catalysts. This information provides direction for the development of highly active ORR electrocatalysts. However, there is yet to be a rational strategy for the preferential induction of dense growth of highly active Fe- N_x sites.

In this work, we suggest the following effective solution for inducing the formation of Fe- N_x active sites: Introducing a carbon template into the precursor mixture containing melamine and Fe salts results in preferential generation of active Fe- N_x sites rather than inactive Fe and Fe-carbide compounds. This was confirmed through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Mössbauer spectroscopy characterization. This method enhances the intrinsic ORR activities of the active species.

2. Experimental

2.1. Preparation and characterization of the catalysts

In brief, the carbon catalysts are synthesized via heat-treatment of the precursor mixtures. To generate the binary FeN carbon nanotube/carbon nanosphere (CNT/CS) catalyst, we first dispersed 4 g of melamine and 20 mg of $FeSO_4 \cdot 7H_2O$ into 50 mL of deionized water with vigorous ultrasonication. After addition of the CS template (typically 50 mg), the Fe salts and melamine molecules preferentially absorb onto the surface of the CS agglomerations. After thoroughly blending the precursor mixture, it was dried in a rotary evaporator at 60 °C and then heated at 900 °C for 1 h in a tube furnace under ultrapure argon. Using suitable analogous procedures, FeN-CNT and N-CS were also obtained.

The ^{57}Fe Mössbauer spectra were recorded at room temperature using an MS 500 instrument (Oxford Instruments, U.K.), and the data were fitted using Recl software. XPS

measurements were performed on a Kratos Ltd. XSAM-800 spectrometer with Mg K_{α} radiation, and the data were fitted via Gaussian/Lorentzian fitting using XPSPEAK41 software. XRD patterns of the catalysts were obtained using an XRD-6000 X-ray diffractometer (Shimadzu) with a Cu K_{α} radiation source operating at 40 kV and 30 mA. Scanning electron microscopy (SEM) images were obtained using a field-emission S-4800 microscope (HITACHI). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F microscope. N_2 adsorption isotherms of the catalysts were recorded using an ASAP2020 surface area and porosity analyzer (Micromeritics, USA).

2.2. Electrochemical measurements

Electrochemical experiments were performed using a CHI 440 electrochemical workstation and rotator in a standard three-electrode cell using a Pt foil counter electrode. The ORR tests were performed in O_2 -saturated electrolytes at a potential scan rate of 5 mV/s, and CV curves were scanned in Ar -saturated electrolytes at a potential scan rate of 100 mV/s. The catalyst loadings were 0.6 and 0.1 mg/cm² for the prepared catalysts and 20 wt% Pt/C, respectively. To calibrate the reference electrodes to the reversible hydrogen electrode (RHE) scale, the RHE zero potential was estimated from the value at which the current crosses zero by measuring the polarization curves of the hydrogen electrode reactions on the Pt/C-loaded electrode in electrolytes saturated with H_2 . The calibration values were $E(RHE) = E(\text{reference}) + xV$, where x equals 0.915 and 0.32 in alkaline and acid solutions, respectively.

A rotating ring-disk electrode (RRDE) was used as the working electrode. The electron transfer numbers (n) and peroxide yields were calculated based on the following equations:

$$n = 4I_D / (I_D + I_R/N) \quad (1)$$

$$HO_2^- (\%) = 200I_R / (N \times I_D + I_R), \quad (2)$$

where I_D and I_R represent the disk and ring currents, respectively, and N is the current collection efficiency of the Pt ring (0.25 in our system).

2.3. Calculation of the specific activity, mass activity, and turnover frequency

The specific activities (SAs), mass activities (MAs), and turnover frequencies (TOFs) of the catalysts were calculated using the following equations:

$$SA (A/C) = j_k / ECSA \quad (3)$$

$$MA (A/g) = j_k / m_{\text{catalyst}} \quad (4)$$

$TOF (A/\text{site}) = MA / [(C_{Fe,XPS} \times A_{Fe-N_x, \text{Mössbauer}}) \times NA / M_{\text{carbon}}]$ (5) respectively, where j_k , $ECSA$, m_{catalyst} , $C_{Fe,XPS}$, $A_{Fe-N_x, \text{Mössbauer}}$, and NA represent the kinetic current density, electrochemical surface area, catalyst loading, Fe atomic percent in the catalyst (determined by XPS), area percent of Fe- N_x species (determined from the Mössbauer spectra), Avogadro's constant (6.02×10^{23}), and atomic weight of carbon (12.01 amu).

3. Results and discussion

Preparation of the Fe-N_x doped carbon catalysts begins with thermal annealing of the melamine in the presence of Fe salts. In a typical procedure, as is schematically illustrated in Scheme 1, melamine was mixed with the Fe salts and Vulcan XC-72 CSs to form a homogeneous mixture. Through the adsorption interactions, the Fe salts and N-rich melamine effectively disperse on the surface of the CS template, thus facilitating uniform nucleation and growth of the carbon nanotubes and Fe-N_x species via pyrogenation. Concurrently, the nitrogen species (*e.g.*, NH₃) formed during decomposition of the melamine precursor attacks the CS agglomerations to produce N (and Fe-N_x) doping.

The morphology of the resultant FeN-CNT/CS catalyst is shown in Fig. 1(a) and (b). As is evident from the SEM results (Fig. 1(a)), the nanotubes, which were uniformly ~30–40 nm diametral, were interspersed among the CS agglomerations, resulting in a picture reminiscent of earthworms loosening the soil. This structure should produce a porous carbon, which is necessary for good dispersion of the Fe-N_x species and the activity of the catalytic reaction. Furthermore, the TEM results (Fig. 1(b)) show that the bamboo-like nanotubes possess the characteristic peapod-like structures of the bean-like Fe-based nanoparticles embedded within them. Additionally, the dark area on the surface of the CS in Fig. 1(b) is the nucleation zone for the Fe-based nanoparticles, which could correspond to the headwaters or roots of the carbon nanotubes. However, removal of the CS template resulted in an accumulation of the different types of nanotubes, *i.e.*, thick/thin, long/short, and traditional/bamboo-like nanotubes, as is evident from the SEM picture in Fig. 1(c). Many studies have reported on the synthetic methods and possible growth mechanisms of carbon nanotubes [43–45]. The primary growth models that have been proposed include tip-growth and base-growth mechanisms. The variety of types of nanotubes in FeN-CNT suggests that both growth models occur; this is very similar to the results reported by Wu *et al.* [44]. The irregular morphology might be also ascribed to the presence of a variety of Fe-based nanoparticle catalysts. Introduction of the CS template results in uniform adsorption of Fe salts and N-rich melamine on its surface, which leads to uniform nucleation of Fe-based nanoparticles. Accordingly, uniform growth of nanotubes occurred in FeN-CNT/CS. Although the growth mechanism is not completely clear, it is evident that the presence of N causes the formation of bamboo-type morphologies [45].

Only mixing melamine with CS in the absence of Fe salts, N-doping occurred but the topography of N-CS kept the same as CS (Fig. 1(d)). From these results, it is evident that there is an

Scheme 1. Synthetic scheme for the preparation of FeN-CNT/CS and FeN-CNT Fe-N_x doped catalysts.

effective synergy between the nanotubes and CS in FeN-CNT/CS, suggesting that the CS template is important for the formation of Fe-N_x active sites and promotion of ORR performance.

The ORR activities of the catalysts were evaluated using rotating-disk electrode (RDE) and RRDE measurements in alkaline media. As shown in Fig. 2(a), FeN-CNT/CS, which has a half-wave potential of 0.78 V, clearly demonstrates a higher ORR activity than FeN-CNT and N-CS. Although the onset potentials of FeN-CNT and FeN-CNT/CS are similar, FeN-CNT delivered a lower current density in the fuel cell operating range (~0.6–0.8 V), which confirms the importance of the CS template in improving the ORR activity. Accordingly, we investigated the effects of CS addition on the structure and activity of catalysts: Slightly adjusting the CS ratio in the precursor did not significantly affect the morphology nor electrochemical activity of the formed binary composites. However, reducing the amount of CS reduces the yield, while adding excess CS template generates N-CS (or even CS) with an aggregated morphology and dramatically decreased the ORR activity.

For the ORR, a four-electron pathway, which occurs at Pt-based catalysts, is desirable. From Fig. 2(b), we determined that the Koutecky-Levich (K-L) plots of the two catalysts had very similar slopes, indicating that FeN-CNT/CS also favors a four-electron pathway. Furthermore, the disk and ring currents of FeN-CNT/CS were obtained using RRDE measurements (Fig. 2(c)). From these values, we calculated an electron transfer number of ~4 (*i.e.*, >3.98) and a very low H₂O₂ yield (<1%) over the entire potential region (Fig. 2(d)); these results indicate a high selectivity for the four-electron reduction of oxygen. In addition, FeN-CNT/CS showed superior durability than commercial Pt/C, as evidenced by the chronoamperometric curves at the potential of 0.7 V (*vs.* RHE) shown in Fig. 2(e). Moreover, the methanol tolerance of FeN-CNT/CS was investigated in a 0.1 mol/L KOH solution containing methanol. From the results shown in Fig. 2(f), it is evident that the ORR polarization curves at the FeN-CNT/CS electrode were almost equivalent in the presence and absence of methanol. This differs significantly

Fig. 1. SEM (a) and TEM (b) images of FeN-CNT/CS; SEM image of FeN-CNT (c); TEM image of N-CS (d).

Fig. 2. (a) Polarization curves for the ORR activities of FeN-CNT/CS, FeN-CNT, and N-CS. (b) K-L plots of FeN-CNT/CS at different potentials relative to Pt/C at 0.8 V. (c) RRDE experiments and (d) electron transfer number and H₂O₂ yield of the FeN-CNT/CS catalyst. (e) Chronoamperometry and (f) ORR polarization curves of FeN-CNT/CS in the absence and presence of 0.1 mol/L methanol relative to Pt/C. All measurements were performed at an electrode rotation speed of 1600 r/min in oxygen-saturated 0.1 mol/L KOH.

from the results for the Pt/C electrode, which showed a dramatic decrease in ORR activity after the addition of methanol. The merits of avoiding the “crossover” issue make this catalyst very promising for direct methanol fuel cell applications.

N₂ adsorption/desorption isotherms and the Barrett-Joyner-Halenda (BJH) pore-size distribution (Fig. S1) are key to elucidating the structures of the formed nanocarbons. The pore sizes of the samples containing nanotubes (*i.e.*, FeN-CNT/CS and FeN-CNT) are in the range of ~0–100 nm; in comparison, the pore sizes of N-CS are in the range of ~50–1000 nm. Therefore, the Brunauer-Emmett-Teller (BET) surface areas (BSAs) and total pore volumes (TPVs) of FeN-CNT/CS and FeN-CNT can be attributed to the mesoscale pores. Table 1 shows that the BSA and TPV values of FeN-CNT/CS are 177 m²/g and 0.41 cm³/g, respectively, which facilitate the dispersion of the Fe-N_x species. Both the single materials provided lower BSA and TPV values: 68 m²/g and 0.21 cm³/g, respectively, for FeN-CNT and 160 m²/g and 0.36 cm³/g, respectively, for N-CS. From these results, it is reasonable to propose that there is an effective synergy between the nanotubes and CS in FeN-CNT/CS that does not occur in the absence of either component. This supports that the CS tem-

plate promotes both the formation of Fe-N_x active sites and ORR performance.

For non-precious metal electrocatalysts, it is well-known that the types of Fe-N_x species and doping density play a crucial role in enhancing the ORR activity. In the following sections, we will discuss, in detail, the inductive effect of the CS template on the growth of Fe-N_x active sites using XRD, XPS, and ⁵⁷Fe Mössbauer spectroscopy to analyze the elemental and structural compositions of the prepared catalysts. As shown in Fig. 3, the XRD patterns can be used to compare the compositions of the three catalysts. Clearly, the C(002) characteristic peak of FeN-CNT/CS combines with those of FeN-CNT and N-CS, which indicates successful *in situ* growth of nanotubes on the CS template, as seen in Fig. 1(b). Additionally, it is evident that the conspicuous metallic Fe and Fe-carbides are present in FeN-CNT. Given that the type of Fe-N_x species formed, especially non-crystalline Fe-N₄, is not evident in the XRD pattern, it is likely that it is the dominant Fe-N_x species in FeN-CNT/CS. Thus, adding the CS template to the melamine/Fe-salt mixture promoted Fe-N_x coordination.

Furthermore, XPS characterizations were performed to analyze the bonding configurations of N and Fe. From the high

Table 1

The BSA and TPV values determined from the N₂ adsorption-desorption isotherms, and the N and Fe speciation results from XPS analysis for the three different nanocarbons.

Sample	S _{BET} (m ² /g)	Total pore volume (cm ³ /g)	N (at%)				Fe (at%)	
			Pyridinic N	Pyrrolic N	Quaternary N	“N–O”	Fe ⁰	Fe ^{2+/3+}
FeN-CNT/CS	177	0.41	0.59	0.25	0.12	0.14	0.097	0.296
FeN-CNT	68	0.21	1.79	1.29	0.96	0.44	0.660	0.780
N-CS	160	0.36	0.37	0.18	0.06	0.08	/	/

Fig. 3. XRD patterns of FeN-CNT/CS, FeN-CNT, and N-CS.

resolution XPS spectra of N 1s and Fe 2p shown in Fig. 4, the N 1s spectra can be deconvoluted into pyridinic-N (~398.3 eV), pyrrolic-N (~400.2 eV), quaternary-N (~401.4 eV), and “N-O” (~403.1 eV) and the Fe 2p spectra can be fitted with zero-valent iron (Fe^0) and oxidation iron ($\text{Fe}^{2+/3+}$). It is worth mentioning that the pyridinic-N peak in XPS may also include contributions from Fe-N_x because of their negligible bonding energy difference [46]. As summarized in Table 1, the total surface N contents of FeN-CNT/CS, FeN-CNT, and N-CS were

1.1, 4.5, and 0.7 at%, respectively. Although the N content of FeN-CNT is more than four times that of FeN-CNT/CS, the ORR activity of FeN-CNT is inferior. Moreover, the N content of N-CS is similar to that of FeN-CNT/CS but it has the lowest ORR performance. Regardless, introducing Fe resulted in an immediate increase in the ORR activity even at low Fe contents of 0.39 and 1.44 at% for FeN-CNT/CS and FeN-CNT, respectively. These results confirm that the formed Fe-N_x species are highly active for ORR, which keeps consistency with that of the previous reports [7–36]. Interestingly, the addition of the CS template affects the oxidation state of Fe: The proportion of Fe^0 in FeN-CNT/CS (0.097 at%) is significantly lower than that in FeN-CNT (~0.66 at%). That is, the CS template induces the formation of oxidized $\text{Fe}^{2+/3+}$, which can further couple with N to form the various Fe-N_x species.

To identify the compositions of the Fe-N_x species, ^{57}Fe Mössbauer spectra were obtained. As can be clearly seen in Fig. 5, the Mössbauer spectra feature singlet, doublet, and sextet signals; the assignments are given in Table 2. Generally, singlets indicate superparamagnetic Fe and Sextet1 corresponds to $\alpha\text{-Fe}$. Together, these signals comprise ~70% of the Fe in FeN-CNT but only ~25% in FeN-CNT/CS. Additionally, the Fe-carbides in FeN-CNT, as represented by Sextet3, are not evident in FeN-CNT/CS. Surprisingly, the proportion of the total Fe-N_x species (Fe-N_4 and other Fe-nitrides) represented by the

Fig. 4. N 1s XPS spectra of FeN-CNT/CS (a), FeN-CNT (b), and N-CS (c); (d) Fe 2p XPS spectra of FeN-CNT/CS and FeN-CNT.

Fig. 5. ^{57}Fe Mössbauer spectra of FeN-CNT/CS (a) and FeN-CNT (b).

Table 2

Mössbauer parameters for the fitted lines and their assignments of FeN-CNT/CS and FeN-CNT.

Sample		δ_{iso}	E_Q	H_0	Real area A (%)	Assignment	Ref.
FeN-CNT/CS	Singlet	-0.09	0.00	0.00	15.8	Superparamagnetic	[9,14,29,42]
	Doublet1	1.01	1.57	0.00	23.6	Fe-N ₄	[9,14,42]
	Doublet2	-0.76	2.14	0.00	2.3	Fe-N ₄	[9,14,42]
	Sextet1	-0.004	0.03	32.61	8.7	α -Fe	[9,42]
	Sextet2	0.17	3.99	15.53	49.64	Fe-nitrides	[9,14,29]
FeN-CNT	Singlet	-0.08	0.00	0.00	23.2	Superparamagnetic	[9,14,29,42]
	Doublet1	0.39	0.94	0.00	1.8	Fe-N ₄	[9,14,42]
	Doublet2	1.05	1.71	0.00	8.3	Fe-N ₄	[9,14,42]
	Sextet1	0.002	0.01	32.40	46.2	α -Fe	[9,42]
	Sextet2	0.36		24.20	5.7	Fe-nitrides	[9,14,29]
	Sextet3	0.24	0.10	20.20	14.8	Fe-carbides	[9,14,42]

two doublets and Sextet2 is much higher in FeN-CNT/CS (~75%) than in FeN-CNT (~15%). All the results suggest that the addition of the CS template to the melamine/Fe-salt mixture greatly reduces the content of metallic Fe and Fe-carbides by inducing the growth of Fe-N_x species including Fe-N₄ and other Fe-nitrides. Finally, in FeN-CNT/CS, the ORR active Fe-N_x sites are dominant.

The SA can be used to elucidate the differences in electrocatalyst activities. We estimated the electrochemical surface area (ECSA) from the CV curves (Fig. S2(a)) in acid media; the results were 10.8, 18.2, and 4.8 C/g for FeN-CNT/CS, FeN-CNT, and N-CS, respectively, as shown in Table S1. FeN-CNT/CS shows a lower ECSA than FeN-CNT, although FeN-CNT/CS has a higher BSA (177 m²/g) than FeN-CNT (68 m²/g) (Table 1). These results suggest that the high N-doping of 4.48 at% in FeN-CNT is due to its high ECSA. Furthermore, we calculated the kinetic current density (j_k) from the polarization curves acquired in acid (Fig. S2(b)) and alkaline (Fig. 2(a)) solutions. By normalizing the j_k , which represents the electrochemical activity, with the ECSA, we obtained SA values for FeN-CNT/CS, FeN-CNT, and N-CS (Table S1) of 0.448, 0.313, and 0.19 A/C, respectively, at 0.7 V (vs. RHE) in the acid media and 1.562, 0.639, and 0.152 A/C, respectively, at 0.75 V (vs. RHE) in the alkaline media. FeN-CNT/CS shows the highest SA, suggesting that the growth of Fe-N_x species that is induced by the CS tem-

plate plays a vital role in enhancing its catalytic activity.

Next, we calculated the MAs of the catalysts by normalizing the j_k at 0.75 V (vs. RHE) with the catalyst mass in the alkaline media. As shown in Fig. 6(a), FeN-CNT/CS has the highest MA even though FeN-CNT contains the most N, while that of N-CS is negligible; this indicates that the ORR activity is primarily derived from the highly active Fe-N_x sites. By combining the MA with the Mössbauer spectra and XPS results, the TOFs were calculated to determine the intrinsic activity per active site [42]. Although we propose that the doublets in Mössbauer spectra represent the ORR active sites, TOFs were calculated assuming both the doublets (D1+D2) and all the possible Fe-N_x species (D1+D2+S2) were active sites. The results were 33.04×10^{-20} and 11.03×10^{-20} A/site for FeN-CNT/CS and 15.93×10^{-20} and 10.18×10^{-20} A/site for FeN-CNT, as displayed in Fig. 6(b). Both methods of calculation revealed that the TOF of FeN-CNT/CS is higher than that of FeN-CNT, implying that the CS template significantly promotes the activities of the Fe-N_x sites. The results show that the introduction of the CS template into the melamine/Fe-salt mixture not only promotes the conversion of the inactive Fe and Fe-carbide sites into active Fe-N_x sites but also essentially enhances the catalytic activities of the Fe-N_x sites.

4. Conclusions

Fig. 6. (a) The mass activities of FeN-CNT/CS, FeN-CNT, and N-CS. (b) The calculated TOFs for FeN-CNT/CS and FeN-CNT per possible active site at 0.75 V (vs. RHE) in alkaline media.

In summary, we confirmed the effectiveness of introducing a carbon template into the melamine/Fe-salt mixture to preferentially create catalytically active Fe-N_x sites for ORR. Characterization of the compounds provides evidence that the template facilitates the uniform nucleation of Fe-N_x species and the growth of nanotubes on the skin of carbons. The introduction of the carbon template significantly suppresses the formation of inactive Fe-based particles (*i.e.*, metallic Fe and Fe-carbides) and changes the coupling of Fe and N to induce the growth of ORR-active Fe-N_x species including Fe-N₄ and other Fe-nitrides. In addition, their intrinsic activities were significantly enhanced. We believe that this work provides an important strategy for promoting the dense-doping of highly active Fe-N_x sites.

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Graphical Abstract

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Induced growth of Fe-N_x active sites using carbon templates

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Introduction of a carbon nanosphere template (CS) into a melamine/Fe-salt mixture resulted in the *in situ* growth of uniform nanotubes on the skin of the CS. Using this method, we successfully constructed binary FeN-CNT/CS in which the formation of highly dense Fe-N_x active sites is promoted instead of Fe and Fe-carbides in FeN-CNT. Importantly, the intrinsic ORR activities of the Fe-N_x sites were also improved.

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碳模板诱导生长Fe-N_x活性位点张世明^{a,b,c}, 张鹤友^b, 张维民^a, 原鲜霞^a, 陈胜利^{b,*}, 马紫峰^{a,c,#}^a上海交通大学化学工程系, 上海电化学能源器件工程技术研究中心, 上海200240^b武汉大学化学与分子科学学院, 湖北省化学电源材料与技术重点实验室,

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摘要: 能源危机和环境恶化是当今社会面临的巨大挑战。燃料电池作为一种高效、清洁的发电装置,受到了社会各界特别是新能源行业的高度关注。尤其是,日本丰田推出Mirai燃料电池汽车量产上市计划,把燃料电池及其关键技术发展推向了一个新的发展纪元。然而,制约燃料电池走向大规模商业化的核心问题依然是其综合性能不具竞争力。其中,氧电极的缓慢动力学以及贵金属Pt的有限资源、高昂成本等是关键所在,因此,亟待实现高性能非贵金属催化剂的突破。

近年来,大量研究表明,Fe-N_x掺杂的碳催化剂具有极大的代Pt潜力,研究者们尝试各种手段进行开发,如:调控Fe化合物及N前驱体的类型与添加量,改变温度、压力等合成条件,采用轴向配位体连接、共价接枝、球磨等非热解路线,构建核壳、有序介孔碳、阵列、类石墨烯薄片、多孔碳等碳纳米结构,制备石墨烯/碳纳米管、石墨烯/碳黑、碳纳米带/碳纳米管、碳纳米颗粒/碳纤维、碳球/碳纳米管/石墨烯等复合材料,进行酸洗、造孔、二次加热等后处理,调控不同类型Fe物种相生成等。此外,EXAFS及Mössbauer等谱学技术已经证实Fe-N_x特别是Fe-N₄为强活性位点。因此,有待提出合理策略以促进非贵金属碳催化剂中Fe-N_x强活性位点的高密度掺杂。

本文提出了一种碳模板诱导Fe-N_x活性位点生长的方法即通过高温热解含有Fe盐的三聚氰胺前驱体混合物,成功制备

了Fe-N_x掺杂的碳催化剂,并结合多种表征技术证实了碳模板对制备碳催化剂结构组成及电化学性能的影响.形貌结果表明,碳模板的引入有利于Fe、N化合物的均匀吸附以至于Fe基纳米颗粒的均一成核,促使竹状碳纳米管在碳模板表面以及中间均一生长;氮气吸脱附及孔径分布曲线显示,引入碳模板形成的复合材料较单一的碳纳米管和碳黑材料具有提高的比表面积和总孔体积,说明复合材料中存在两种单体的有效协同;Mössbauer、XPS及XRD测试数据证实,碳模板可以调控Fe、N两种元素的耦合方式,能够抑制金属Fe和Fe碳化物等非活性Fe物种的生成、诱导Fe-N₄和其它Fe氮化物等强活性Fe-N_x物种的生长.电化学测试数据表明,复合材料具有提升的面积活性和质量活性,且TOF值明显提高,说明碳模板的引入增强了Fe-N_x位点的本征活性;此外,复合材料的氧还原过程为高效的4e⁻途径,且较商业Pt/C催化剂表现出了优异的循环稳定性和甲醇耐受性.

关键词: 氧还原反应; 非贵金属电催化剂; Fe-N_x; 诱导生长; 碳模板

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根据美国科睿唯安 (Clarivate Analytics) 近日公布的2017年度《期刊引证报告》(Journal Citation Reports, JCR), *Chinese Journal of Catalysis* (《催化学报》) 的最新SCI影响因子 (IF) 为 3.525 (2016年为 2.813), 在国内化学类期刊中名列前茅; 在国际化学工程学科137种期刊中排名第26位, 排名居前18.98%, 位居Q1区. 近年, 《催化学报》的学术质量及影响力不断提升, 这是中国化学会催化委员会委员、编委、审稿专家、作者和读者长期不懈努力和共同支持的结果. 衷心感谢各位老师、在期刊宣传、投稿原创性高质量稿件、学术质量把关以及组约优秀稿件、组办高水平专刊等方面所给予的持续和巨大的支持!

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