International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Nitrogen-doped Bimetallic Carbon Nanosheets as Efficient Electrocatalysts for Oxygen Reduction Reaction

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Received: 22 March 2021 / Accepted: 3 May 2021 / Published: 31 May 2021

The research and development of high activity, low cost and high stability non-noble metal oxygen reduction electrocatalyst is very important to promote the commercial development of fuel cell. In this paper, cheap sucrose and urea is used as the raw materials to preparation a multi-pore nitrogen-doped carbon nanosheet coated ferro and cobalt binary metal nanoparticle composite (GNCN-FeCo) by simple pyrolysis. The GNCN-FeCo showed better oxygen reduction reaction (ORR) catalytic activity than commercial Pt/C in alkaline media, benefit from multi-pore structure and FeCo-N_x active center. GNCN-FeCo has the same onset potential as Pt/C and much better half-wave potential (positive about 70 mV compared to commercial Pt/C), and the reaction process is a 4-electron transfer process ($n\approx4$); Moreover, its onest potential is quiet close to that of Pt/C catalyst in acidic medium, and its half-wave potential is only negative about 20 mV in comparison with Pt/C. Meanwhile, GNCN-FeCo displays excellent methanol resistance in 0.5 M H₂SO₄ and 0.1 M KOH. These results indicate that GNCN-FeCo may have the potential to replace the Pt/C catalyst as an efficient ORR catalyst.

Keywords: Nitrogen doped carbon nanosheets, Non-precious metals, Oxygen reduction catalyst, Fuel cell, Electrochemistry

1. INTRODUCTION

The fuel cell is an equipment that converts chemical energy into electrical energy without going through the Carnot cycle. Electrocatalyst may be a key component in fuel cells and metal-air batteries [1, 2]. Nevertheless, the inherently sluggish dynamics of the oxygen reduction reaction (ORR) require tall loads of Pt catalyst at the cathode. The high cost, rare supply, CO poisoning, and poor durability of Pt continue to impede the widespread application of fuel cell technology[3-5]. Over the past years, intense investigations have been devoted to explore low-cost and efficient ORR

electrocatalyst based on platinum alloy/carbon, Pt-Me/C (Me =Co, Fe, Ni, Cu etc.)[6] and non-precious metals[7, 8].

Until now most non-noble-metal electrocatalysts used for ORR were concentrated on [9-12]: (1) Transition metal macromolecules; (2) Chevrel phase transition metal sulfides; (3) transition metal oxides; (4) transition metal carbon-nitrogen composite materials. Some progress has been made in preparing Fe (or Co) N/C composite materials to catalyze ORR[13-15]. Biddinger reported that acetonitrile pyrolyzed more than 2 wt% Fe, Co, Ni to prepare nitrogen-containing carbon nanofiber catalysts, without methanol poisoning in the ORR process[16], and Nitrogen-doped ordered porous carbon (C-N_x) is synthesized by polyacrylonitrile (PAN) [17]. The C-N_x catalyst presents a high onset potential and high current density for ORR. Lei etal prepared a ordered and high ORR activity Fe-N-C catalyst through a self-assembly route assisted by hydrogen bonds[18]. Xiaogang Fu et al. preparation series of FeCo-Nx catalysts with graphene as a carbon support and polyaniline (PANI) as the nitrogen source, and the alloy of Fe and Co as metal precursors. FeCo-N-rGO catalysts show excellent ORR catalytic activity in in fuel cells and metal-air batteries. In alkaline solution, its half-wave potential is 46 mV more positive than that of Pt/C catalyst, and negative 119 mV in acid solution. Moreover, the catalyst also shows good stability and methanol tolerance, but the preparation process is more complicated[19].

In this paper, the sugar and urea is used as carbon and nitrogen precursor, ferric and cobalt nitrate is used as a metal precursor, and nitrogen-doped carbon nanosheet encased ferric and cobalt nanoparticles catalyst(GNCN-FeCo) is prepared by simple pyrolysis the mixture. Due to the synergistic effect of useful pore structure and Me-N_x group[20], GNCN-FeCo catalyst showed high catalytic activity for oxygen reduction reaction. In the alkaline solution, the half-wave potential is about 70 mV more negative than Pt/C catalyst; in the acidic solution, its oneset potential is close to Pt/C, and its half-wave potential is only about 20 mV more negative than Pt/C. Moreover, GNCN-FeCo also shows excellent ability to be immune to methanol crossover and remarkable stability in O_2 -saturated 0.1-M KOH compared with Pt/C. However, the cost of GNCN-FeCo catalyst is much lower than that of Pt/C. One potential utilize can be imagined as an ORR electrocatalyst for fuel cells.

2. EXPERIMENT

2.1 Chemicals

Sucrose was purchased from Honglu Co. Ltd (Tianjing). Ferric nitrate nonahydrate and cobalt nitrate hexahydrate were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). Potassium hydroxide was purchased from Xilong Chemical Co. Ltd (Sichuan). Urea was purchased from Kemiou Chemical Reagent Co. Ltd (Tianjin). Pt/C (20 wt%) was purchased from Alfa Aesar Chemical Co. Ltd (Shanghai). Nafion solution (5 wt%) was purchased from Dupont Company(Shanghai).

2.2 Material synthesis

To prepare the sample GNCN-FeCo, the specific steps are as follows: first, 0.03 g $Fe(NO_3)_3 \cdot 9H_2O$, 0.02 g $Co(NO_3)_2 \cdot 6H_2O$, 0.1 g sucrose and 6 g urea were dissolved in 30 mL deionized water and stirred continuously for 1 h, and then dried at 80 °C to obtain the solid mixture. The solids were ground into a uniform fine powder in a mortar and placed in a crucible. Subsequently, the power was heat-treated in an argon atmosphere in a tubular furnace from room temperature to 550 °C and held at 550 °C for 1 h. After that, the sample was heated to 850 °C (with the heating rate of 3.5 °C min⁻¹) and kept at 850 °C for 2 h. Finally, the pyrolyzed sample was naturally cooled in an argon atmosphere. The obtained sample is labeled as GNCN-FeCo. In contrast, the samples prepared under the same conditions were labeled as GNCN (without Fe(NO₃)₃•9H₂O and Co(NO₃)₂•6H₂O),GNCN-Fe(without Co(NO₃)₂•6H₂O), and GNCN-Co(without Fe(NO₃)₃•9H₂O), respectively.

In a typical synthesis of GNCN-FeCo, sucrose (0.1g), urea (6g), Fe(NO₃)₃ • 9H₂O (0.03g) and Co(NO₃)₂ • 6H₂O (0.02g) were mixed uniformly under stirring for 1 h, then, dried at 80 °C. Next, the solid was treated in an argon atmosphere through a two-step pyrolysis procedure. During the low-temperature pyrolysis (~550 °C), urea can be decomposed and converted into lamellar g-C₃N₄, which was used as a template for the late synthesis of nano-lamellar carbon materials[22, 23]. At the high-temperature pyrolysis (~850 °C), sucroses can crystallize on the g-C₃N₄ template and form the nanosheet[24]. Meanwhile, the g-C₃N₄ template would be decomposed[25]. The decomposition of urea and g-C3N4 can release a large number of nitrogen-containing compounds, such as NH₃, C₂N²⁺, C₃N²⁺, and C₃N³⁺[25-29], which serve as a nitrogen source, and introduce nitrogen dopants into the network structure of carbon nanosheets. During the process, ferric salt and cobalt salt undergo oxidation reactions and are wrapped by N-doped carbon nanosheets to form stable substances, which may improve the conductivity and stability of catalysts.

2.3 Characterization of the samples

The morphology and details of sample were characterized by transmission electron microscopy (TEM, Tecnai-G2-TF20). TEM image (Fig. 1g) exhibited the obtained GNCN with sheet-like morphology, which was inherited from g-C₃N₄ template[30]. When Fe(NO₃)₃·9H₂O and Co(NO₃)₂·6H₂O was introduced into precursor, the resultant GNCN-FeCo remained the sheet-like morphology. Meanwhile, nanoparticles with an average diameter of 10 nm were uniformly embedded in the carbon layer (Fig. 1b). As shown in energy dispersive X-ray (EDX) spectroscopy, C, O, N, Fe and Co were detected, which corroborated N, Fe and Co elements have been successfully doped in the carbon layers (Fig. 1c). According to calculation, the molar ratio between Fe and Co was 1:1.



Figure 1. (a) The TEM image of the GNCN, (b)The TEM image of the GNCN-FeCo, (c) The EDX of the GNCN-FeCo

N₂ adsorption-desorption isotherm curves were conducted at 77 K (Micromeritics ASAP 2020), where Brunauer-Emmett-Teller (BET) method was used to determine the specific surface areas and Barrett-Joyner-Halenda (BJH) models was used to calculated, average pore sizes and pore volume.

The specific surface area and pore structures of catalysts were evaluated by N_2 absorptiondesorption isotherms and pore size distribution curves. As revealed in Fig. 2a and c, both the GNCN and the GNCN-FeCo showed type II isotherm, associated with hierarchical pore structure. However, the GNCN-FeCo possessed a higher BET specific surface area of 337.28 m² g⁻¹ than that of the GNCN (254.03m² g⁻¹, Table 1).

Table 1. BET surface area pore structural parameters of the GNCN and the GNCN-FeCo

Sample	BET surface area	Pore volume	Average pore size
	(m^2/g)	(cm^{3}/g)	(nm)
GNCN	254.03	1.59	23.93
GNCN-FeCo	337.28	0.72	11.09



Figure 2. (a) Nitrogen adsorption/desorption isotherm of the GNCN; (b) Pore size-distribution of the GNCN; (c) Nitrogen adsorption/desorption isotherm of the GNCN-FeCo; (d) Pore size distribution of the GNCN-FeCo.

The reason was analyzed by the pore diameter distribution calulated by BJH method (Fig. 2b and d). The pore diameter distribution curve revealed that both the GNCN and GNCN-FeCo had a wide pore diameter distribution with mesoporous and macropore structures. Howerver, the GNCN-FeCo appeared a smaller pore volume and average pore size due to the FeCo nanoparticles implanted in carbon network. The inserted nanoparticle may partly increase the particular surface area of the GNCN-FeCo.

X-ray photoelectron spectroscopy (XPS) data were obtained on a VG Scientific ESCALAB250Xi photoelectron spectrometer. The surface electronic state and chemical property was investigated by X-ray photoelectron spectroscopy(XPS). XPS of the GNCN-FeCo showed the obvious C, N, O, Fe and Co signals (Fig. 3a). The high-resolution spectrum of C1s appeared an asymmetric peak residing at 284.6 eV[23], indicating that the formation of the sp²-hybridized carbon with a graphitic-like structure (Fig. 3b). This graphitic-like structure would be beneficial for improving electron conductivity, and enhance the utilization of active site. The high-resolution spectrum of N 1s can be deconstruct into five peaks: pyridinic N at 398.3 eV, nitrile N at 399.5 eV, pyrrolic N at 401.3 eV and oxidized N at ~403.0 eV[23, 31], where most of nitrogen existed as pyridinic N (Fig. 3c). Pyridinic N locating at the internal defect of graphene is generally believed to easily, capture a metal element, and then form metal-pyridinic N Structure like porphyrin (Fig. 4). Next, Co and Fe elements were also analyzed by high-resolution XPS. For Co 2p spectrum, the peak at around 778.3 eV was ascribed to Co⁰ $2p_{3/2}$, while the peak at around 780.4-783.0 eV[32] was corresponded to Co²⁺ $2p_{3/2}$

(Fig. 3c). In the Fe 2p spectrum, the binding energies at around 706.9 eV,708.0 eV and 711.0 eV were assigned as Fe⁰ 2p_{3/2}, Fe²⁺ 2p_{3/2} and Fe³⁺ 2p_{3/2}[33], respectively (Fig. 3d). Interestingly, most of metal existed as oxidized state, such as Co²⁺, Fe²⁺ and Fe³⁺ (Fig. 3c and d). Additionally, it has been confirmed that GNCN-FeCo catalysts contain a higher content of nitrogen, especially, pyridinic N (Fig. 3b and Table 2). Then, we speculate the presence of Fe/Co-N species anchored on three-dimensional hierarchically porous carbon because the valence state of metal elements in Fe/Co-N species was between the (II) to (III) state.



Figure 3. (a) XPS full spectrum of the GNCN-FeCo catalyst; High-resolution C 1s spectra (b), N 1s spectra (c), Fe 2p spectra (d) and Co 2p spectra (e) of the GNCN-FeCo catalyst.



Table 2. Surface composition of the GNCN and the GNCN-FeCo

Figure 4. Schematic diagram of possible defects in graphene

2.4 Electrochemical test

The electrochemical tests were carried out on an electrochemical workstation (μ Autolab III) with a rotating disk electrode (RDE) system in a three-electrode cell at room temperature. A platinum (Pt) wire and a saturated silver chloride electrode(Ag/AgCl) were used as counter and reference electrode, respectively. All the measured potentials were converted to the reversible hydrogen electrode (RHE) reference scale based on[21]: $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197 V$.

The Catalyst ink were prepared as follows: 4 mg of the catalyst or commercial 20 wt% Pt/C catalyst in a 1.0-mL blend of water, ethanol, and Nafion with a volume proportion of 75:21:4. The blend was sonicated for 3 h to make a homogeneous ink and kept in a fixed vial.

Working electrode (glass carbon rotating disk electrode of 3 mm in diameter) was prepared as follows: the glassy-carbon electrode was firstly polished by 0.5 μ m and 0.3 μ m alumina powder, in sequence. Afterwards, the working electrode was rinsed with ethanol and ultra-pure water, and then dried in the 60 °C oven for 20 min. Finally, glassy carbon electrode coated with 5 μ L suspension were placed in an oven at 60 °C and dried for 30 min.

The catalyst loading on the RDE is 0.283 mg cm⁻².A 0.1 M KOH or 0.5 M H₂SO₄ solution was used as the electrolyte. Electrolyte was immersed with bubbling O₂ at least 30 min before each experiment, in order to guarantee O₂ saturated during the recording. Cycles voltammetry (CV) was collected with a sweep rate of 50 mV s⁻¹ from 0.1 to 1.2 V (vs. RHE) in 0.1 M KOH and 0.5 M H₂SO₄ solution, respectively. Linear scanning voltammogram (LSV) scanning from 0.1 to 1.2 V (vs. RHE) was recorded with a sweep rate of 5 mV s⁻¹ and a rotatain rate from 400 to 2400 rpm. The stability and methanol tolerance measurement were conducted by chronoamperometry technique at the bias

potential of 0.66 V(vs. RHE) in O₂-saturated 0.1 M KOH electrolyte (0.50 V vs. RHE in O₂-saturated 0.5 M H₂SO₄ electrolyte) with a rotation rate of 1600 rpm.

The apparent electrons transfer number (n) can be determined according to K-L equation[21]:

$$\frac{1}{J} = \frac{1}{J_l} + \frac{1}{J_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k}$$

Where J and J_k represent the measured current desity and kinetic current densities, respectively, ω represents the electrode rotation speed, and B could be determined from the slope of K-L plots based on the Levich equation[2, 21]:

 $B=0.62nFC_0(D_0)^{2/3}v^{-1/6}$

Where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant, C_0 is the solubility of O_2 in solution, D_0 is diffusivity of O_2 , and v is the kinematic viscosity of solution.

3. RESULTS AND DISCUSSION

3.1 Electrocatalytic performance for oxygen reduction reaction

The ORR electrocatalytic of the sample and the 20 wt% Pt/C was tested for a rotating disk electrode (RDE) in O₂-saturated 0.1 M KOH arrangement employing a three-electrode framework. All the experimental results were calibrated with regard to reversible hydrogen electrode (RHE). The cyclic voltammetry (CV) and linear scanning voltammogram (LSV) study of GNCN-X and Pt/C was conducted in both Ar- and O₂-saturated electrolytes. The LSV of 20 wt% Pt/C in O₂-saturated 0.1 M KOH and 0.5 H₂SO₄ is shown in Fig. S1 and S2. As shown in Fig. 5a, the sample of GNCN showed little ORR catalytic activity, while GNCN-Fe, GNCN-Co displayed well-defined cathodic ORR peaks in O₂-saturated 0.1 M KOH from LSV curves . But the onset potential of the GNCN-FeCo is more positive than other catalysts, and the limiting current density is higher than that of the samples GNCN-Fe and GNCN-Co. The half wave potential of GNCN-FeCo is 0.86 V vs. RHE, which higher than that of other three sample.

As exhibited in Fig. 5b, GNCN-FeCo had the similar onest potential compared with the commercial Pt/C, but a higher half-wave potential, which positively 70 mV compared to the commercial Pt/C. The excellent electrocatalytic activity of the GNCN-FeCo for ORR can be also revealed from CV cycles (Fig. 5c). A well-defined cathodic oxygen reduction peak is observed at 0.8~1.0 V vs. RHE in O₂-saturated 0.1 M KOH electrolyte. In addition, the LSV at the rotation speeds varied from 400 to 2400 rpm were tested(Fig. 5d). The limiting current density increases with the increase of the rotation speed.

The dynamic data catalytic reaction can be calculated by the K-L equation based on the LSV curve. The K-L curves shown in Fig. 5-6e have good linear correlation at different potentials, and the K-L curves are approximately straight lines with almost the same slope at different potentials, which indicates that the oxygen reduction reaction on GNCN-FeCo catalyst is a first-order kinetic process. The electron transfer number n can be calculated from the slope of the K-L curve (Fig. 5d and e). The electron transfer number of GNCN-FeCo is 3.2 at 0.71 V vs. RHE , which is smaller than that

of the commercial Pt/C (4.0). It suggests that the GNCN-FeCo exhibits a mainly direct 4e⁻ ORR process with the part formation of a certain amount of intermediate peroxide. The critical improvements of ORR performance on the GNCN-FeCo can be considered to the synergistic impact on Fe, Co, N-doped carbon and FeCo-Nx catalytic active center.



Figure 5. (a) LSV curves of non-noble metal catalysts in O₂-saturated 0.1 M KOH at 1600 rpm; (b) LSV curves of the GNCN and the GNCN-FeCo compared to the commercial Pt/C in O₂-saturated 0.1 M KOH at 1600 rpm; (c) Cyclic voltammetry curves of GNCN-FeCo electrodes tested in Ar and O₂ saturated 0.1 M KOH, respectively, at a scan rate of 50 mV s⁻¹; (d) LSV curves with various rotation rates of the GNCN-FeCo electrode; (e) K-L plots of the GNCN-FeCo electrode at 0.71V vs. RHE.

The development of novel oxygen reduction catalysts with excellent electrochemical performance and low cost in acidic environments is highly desired. To investigate the reliability of the



GNCN-FeCo catalyst in acidic solution, the ORR electrochemical performance of the sample was tested in 0.5 M H₂SO₄.

Figure 6. (a) LSV curves of non-noble metal catalysts in O₂-saturated 0.5 M H₂SO₄ at 1600 rpm; (b) LSV curves of the GNCN and the GNCN-FeCo compared to the commercial Pt/C in O₂-saturated 0.5 M H₂SO₄ at 1600 rpm; (c) Cyclic voltammetry curves of the GNCN-FeCo tested in Ar and O₂ saturated 0.5 M H₂SO₄, respectively, at a scan of 50 Mv s⁻¹; (d) LSV curves with various rotation rates of the GNCN-FeCo electrode; (e) K-L plots of the GNCN-FeCo electrode. (f) K-L plots of the GNCN-FeCo and the commercial Pt/C electrode at 0.45 V vs. RHE.

As shown in Fig. 6a, the GNCN-Co lost ORR electrocatalytic activity in acidic solution, but the GNCN-FeCo catalyst shows the most excellent ORR catalyst property. It can be seen from fig. 6b that the onset potential of the GNCN-FeCo is close to the commercial Pt/C, and the half-wave potential is only 40 mV negative compared with that of commercial Pt/C, representing the excellent ORR

electrocatalytic activity of GNCN-FeCo in 0.5 M H₂SO₄. Moreover, the CV curves shown in Fig. 6c reveal that oxygen reduction peaks appeared for GNCN-FeCo, indicating that the good electrocatalytic activity of GNCN-FeCo in the acidic electrolyte.

Consistently, the limitting current density enhanced with increasing rotation rates in LSV curves, (Fig. 6d). The K-L plots at different electrode potentials show well linearity, n was calculated from the slope of the K-L plots to be 4.0, clearly demonstrating that the GNCN-FeCo catalyze oxygen reduction reaction with an one-step, four-electron response pathway comparable to Pt/C catalyst ranging from 0.25 to 0.45 (vs. RHE) in O₂-saturated 0.5 M H₂SO₄ at 1600 rpm(Fig. 6e,f), follow a first-order kinetic process[34, 35], the oxygen molecules are directly reduced to OH⁻[36].

Catalyst	medium	Onset	Half-wave	Ref.
		potential (V)	potential (V)	
FeCo-NPC		0.97	0.87	[37]
(Fe,Co)/CNT		1.15	0.954	[38]
CuCo@NC		0.96	0.884	[39]
CoOx/BNG		0.95	0.805	[40]
Hollow	Alkaline	0.92	0.834	[41]
Co3O4-x/C	solution			
Co@N–C	0.1 M KOH	0.90	0.82	[42]
CoNi@NCNT/NF		0.97	0.87	[43]
LDH@ZIF-67-		0.94	0.83	[44]
800				
GNCN-FeCo		1.05	0.86	This Work
Co corrole/CNT		0.85	0.78	[45]
Co-NC-1100		0.93	0.80	[46]
Co-N-C@F127		0.93	0.84	[47]
ISAS-Co/HNCS		0.85	0.77	[48]
CoNC	Acidic	0.89	0.785	[49]
SA-Fe-HPC	solution	0.87	0.81	[50]
SA-Fe-N	$0.5 \text{ M H}_2\text{SO}_4$	0.86	0.812	[51]
Fe2-Z8-C		0.85	0.805	[52]
Fe-SAs/NPS-HC		0.84	0.791	[53]
GNCN-FeCo		0.85	0.79	This Work

 Table 3. Comparison of the ORR performance of some non-precious metal catalysts reported in literature

In recent years, lots of non-noble metal electrocatalysts have been developed and designed. The ORR performance of the non-noble metal electrocatalysts was summarized and listed in Table 2.

3.2 The methanol tolerance and electrochemical stability of the GNCN-FeCo

Direct methanol fuel cell has the advantages of safety, reliability and high energy conversion efficiency, which is an important low-temperature proton exchange membrane fuel cell. Nevertheless, methanol crossover may easily poison electrocatalysts, reducing the electrocatalytic activity. we

further test methanol tolerant ability of GNCN-FeCo and Pt/C by adding methanol in the electrolyte via chronoamperometric measurement with a rotation rate of 1600 rpm. After 2.3ml methanol (3M) is injected to the oxygen-saturated 0.1 M KOH (19ml) solution, current density of Pt/C shows a sharp loss of 44.89 % in activity, whereas GNCN-FeCo catalyst retained stable current response(Fig. 7a). When 3M methanol is added to the oxygen-saturated 0.5 M H₂SO₄ solution, GNCN-FeCo kept up more than 90% of their initial ORR performance, while Pt/C held only 80.36%(Fig. 7b). The above results indicate that the GNCN-FeCo exhibits excellent methanol tolerance in both acidic and alkaline media, suggesting that the GNCN-FeCo has a potential application for direct methanol fuel cell.



Figure 7. Chronoamperometric responses of the GNCN-FeCo and the commercial Pt/C electrodes and a rotation rate of 1600 rpm in O₂ saturated 0.1 M KOH 0.85 V vs. RHE(a) and (b) 0.5 M H_2SO_4 0.52 V vs. RHE, respectively, after the introduction of 3M methanol (based on electrolyte volume)

The stability is an important evaluation criterion for the ORR catalyst. The stability of different electrocatalysts was summarized and listed in Table 3. the catalyst of this work also exhibited excellent stability in alkaline medium, as appeared in Fig. 8, in O₂-saturated 0.1 M KOH solution, the current density of GNCN-FeCo diminished 3.52% after 43000s of long-term chronoamperometric estimation, compared with 14.06% for Pt/C catalyst. The results show that in alkaline medium, the GNCN-FeCo catalyst has better electrochemical stability than commercial Pt/C.

Table 4. Comparison of the stability of some non-precious metal catalysts reported in literature

Catalyst	Loss (%)	Stability Test	Ref.
		Condition	
Fe/N/C-	12.7%	20 h@0.5V	[54]
DMS(14kD)			
Fe-N-C	28%	20 h@0.3V	[55]
Fe-Nx-C-THT	34.1%	20 h@0.3V	[56]
FeNP-C	63%	24 h@0.4V	[57]
⁵⁷ Fe-N-C (S)	88%	24 h@0.25V	[58]
Fe-NCB	49%	20 h@0.3V	[59]
Fe-N-C	49%	3 h@0.4V	[60]
GNCN-FeCo	3.52%	12 h@1.0V	This Work



Figure 8. Chronoamperometry of GNCN -FeCo and Pt/C electrodes in O₂-saturated 0.1 M KOH at 1.0 V vs. RHE and 1600 rpm.

4. CONCLUSION

In conclusion, a nitrogen-doped carbon nanosheet-encased cobalt and ferric nanoparticles nonnoble GNCN-FeCo cathode catalyst with hierarchically porous structure has been successfully prepared by using Co and Fe as the center atoms, and FeCo-Nx as the catalytic active center. The sample GNCN-FeCo showed superior ORR activity in both alkaline and acidic medium, likely due to the rich pore structure and excellent chemical composition. Furthermore, the GNCN-FeCo showed a satisfied methanol resistance and the stability compared with the commercial Pt/C catalyst . It may have potential application to substitute expensive Pt/C as effective cathode electrocatalyst in fuel cells . This work gives an effective pathway to preparing high-performance non-precious-metal ORR catalysts for fuel-cell.

ACKNOWLEDGEMENTS

The authors are grateful to the National Natural Science Foundation of China (Grant No. 51962019, 21766017), Gansu Province University Fundamental Research Funds (Grant No. 20JR5RA441), National engineering &technology research center funds for Ni-Co new materials(jinchuan group Ltd.).

SUPPORT INFROMATION:



Figure S-1(a) LSV curves with various rotation rates of Pt/C electrode, (b) Koutecky–Levich plots of Pt/C electrode in O₂ saturated 0.1M KOH.



Figure S-2 (a) LSV curves with various rotation rates of Pt/C electrode, (b) Koutecky–Levich plots of Pt/C electrode in O₂-saturated 0.5 M H₂SO₄ electrolyte with a sweep rate of 5 mV s⁻¹.

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