Nitrogen-doped carbon layer coated CeNiO$_X$ as electrocatalyst for oxygen reduction reaction

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ABSTRACT

It is highly desirable but challenging to develop and construct a high activity, good stability and cost-effective catalyst system applied for oxygen reduction reaction (ORR). In this study, a series of CeNiO$_x$@CN-n catalysts (carbonized polypyrrole coated CeNiO$_x$) is prepared by an in-situ polymerization method. The effects of bimetal component and nitrogen-doped carbon layer thickness in a "nitrogen-doped carbon layer-oxide composite" system are explored for ORR. It shows that the atomic ratio of Ce: Ni = 1:1 is the optimal ratio, and the ratio of polypyrrole: oxide = 1: 1 is the optimal layer thickness. As the best-performing electrocatalyst, CeNiO$_x$@CN-4 follows a 4e$^-$ pathway for ORR. Moreover, it exhibits good electrocatalytic activity and stability. Especially, its ability of anti-methanol poisoning is stronger than that of Pt/C catalyst. Predictably, this "nitrogen-doped carbon layer-oxide composite" system would open up a potential way to design more efficient electrocatalysts.

1. Introduction

Due to expensive prices and limited reserves of noble metals, the study of non-noble metal catalysts becomes a hot spot for oxygen reduction reaction (ORR) in fuel cells, thanks to their low cost, comparable catalytic features and relatively high abundance [1–4]. Currently, because the doping of heteroatom into carbon matrix can enhance activity and conductivity of materials, the nitrogen-doped carbon materials have aroused much attention [5–7]. Especially, by introducing electron-rich nitrogen atoms into the carbon, the π electrons are conjugated to the lone-pair electrons of nitrogen atoms [8,9]. While, there is a disagreement concerning the active sites, there is an agreement on the requirements to prepare nitrogen-doped carbon, namely (i) carbon, (ii) surface nitrogen and (iii) transition metals (Fe, Ni) [10].

Nowadays, the metal oxides are also brought into sharp focus [11–14], and nickel oxide (NiO) is received tremendous interest owing to its high theoretical capacity, low cost and abundant source compared with other oxides [13]. It has been reported that NiO possesses potential applied for ORR [15,16]. Furthermore, with proper composition, its composite exhibits a higher ORR catalytic performance than single NiO [17–19]. Thus, to construct a system through combining advantages of oxide composite and nitrogen-doped carbon has profound significance for ORR.

Presently, Ce has received remarkable attention as a promoter for improving the catalytic performance, due to its anti-corrosion ability, oxygen vacancy defects and high oxygen-storage capacity [20]. Meanwhile, among the nitrogen-doped carbon materials, polypyrrole (PPy) is a popular material because of its stability and simple operability [21]. However, up to now, combining nitrogen-doped carbon with oxide composite into one system is rarely reported. In this work, a "nitrogen-doped carbon layer-oxide composite" system was constructed based on the excellent properties of NiO, Ce and the feasibility of PPy, and a series of CeNiO$_x$@CN-n catalysts were obtained. What's more, the effects of the oxide compositions and the coated thickness of the carbonized PPy layer for ORR were also investigated.

2. Experimental section

2.1. Fabrication of different oxide composite

The CeNiO$_x$ was prepared by hydrothermal and heat treatment

methods. In detail, $Ce(NO)_3 \cdot 6H_2O$ (1.7 g) and $Ni(NO_3)_2 \cdot 6H_2O$ (1.2 g) were added into a round bottom flask, and then H_2O (60.0 mL) was added. After dissolved completely, $C_{19}H_{42}BrN$ (1.5 g) was added and ultrasonic treated for 30 min. When the solution became a translucent state, $CO(NH_2)_2$ (1.2 g) was added into the flask and stirred for 30 min. Subsequently, the solution was transferred to a hydrothermal reactor and reacted at 160 °C for 24 h. At room temperature, the solid was washed with a large amount of ultra-pure water, anhydrous ethanol and acetone successively. Then, the solid was dried in an oven (50 °C). Finally, the dried material was calcined at 300 °C for 3 h in a muffle furnace to obtain $CeNiO_x$ composite. The other two samples, Ce_2NiO_x and $CeNi_2O_x$ were prepared by the same methods.

2.2. Synthesis of CeNiO_x@CN-n with different layer thickness

The carbonized PPy layer was wrapped on the oxide surface by an in-situ polymerization method. Taking the fabrication of CeNiO$_x$@CN-4 catalyst as an example: Firstly, the above-obtained $CeNiO_x$ (0.5 g) was added into H_2O (250.0 mL). After ultrasonic dispersion, $C_{18}H_{29}NaO_3S$ (2.8 g) was added into above solution and stirred for 30 min. Afterwards, C_4H_5N (1.4 mL) and 0.4 M $Na_2S_2O_8$ (35.0 mL) were slowly added in turn. Secondly, the above solution was located in an ice bath (0–2 °C) and stirred for 12 h. Then, the solid was cleaned with ultra-pure water and anhydrous ethanol. Thirdly, the resultant was dried in an oven (50 °C, 12 h) to obtain CeNiO$_x$@PPy-4. And the obtained CeNiO$_x$@PPy-4 was calcinated at 500 °C and 800 °C for 3 h under N_2 protection, respectively. Ultimately, the target catalyst (CeNiO$_x$@CN-4) was obtained. Other different layer thickness catalysts were prepared according to the same procedure, namely Ce$_2$NiO$_x$@CN-n, CeNiO$_x$@CN-n and CeNi$_2$O$_x$@CN-n (where n is the molar ratio of carbonized PPy, n = 1, 2, 3, 4, 5 and 6).

2.3. Characterization

Transmission electron microscopy (TEM) experiment was undertaken on FEI TECNAI G^2 TF20 microscope (America). TEM sample was dispersed in ethanol and directly added dropwise onto carbon support films before characterization. X-ray diffraction (XRD) pattern was performed on a Rigaku D/Max-2400 diffractometer (Japan) employing Cu K_α ($\lambda = 0.1541$ nm) radiation source. Scanning electron microscopy (SEM) with elemental mapping and energy dispersive X-ray spectroscopy (EDX) results were collected on a Carl Zeiss Ultra Plus (Germany) field emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) (Thi-5702 America) was a monochromatic Al K_α X-ray source ($h\nu = 29.35$ eV).

Fourier transform infrared spectroscopy (FTIR) was measured in transmittance mode on a Fourier transform infrared spectrometer (Spectrum One, America). Thermo Gravimetric/Differential Thermal Analysis (TG/DTA) was performed using a thermo gravimetric/differential thermal synchronizer (STA449C, Netzsch) to study the thermal decomposition kinetics of the catalyst. Test temperature: 30–800 °C; sweep speed: 10 °C min^{-1}; atmosphere: N_2.

2.4. Electrochemical measurement

Electrochemical experiments were evaluated on a PGSTAT128N Autolab electrochemical workstation (Netherlands) in a standard three-electrode cell. Ag/AgCl and carbon rod were employed as reference and counter electrode, respectively. Meanwhile, the working electrode was a modified glassy carbon disk with a diameter of 5 mm. It was prepared as follows: Catalyst (5.0 mg) was dispersed ultrasonically in Nafion/ethanol (1 mL, 0.25% Nafion) solution and sonicated about 30 min to obtain a uniform ink. Then the catalyst ink (8 μL) was transferred to the surface of glassy carbon electrode and dried in the air. And the catalyst loading is 0.2038 mg cm^{-2}. Before each electrochemical test, the solution was purged by bubbling high-purity N_2 or O_2 gas.

3. Results and discussion

3.1. Effect of oxide composite on electrochemical performance

The effect of the composition on the catalyst performance was explored at first. Under the same layer thickness (x = 5), the cyclic voltammetrys (CVs) of the different components were carried out in N_2- and O_2-saturated 0.1 M KOH solution, the resulting CVs are shown in Fig. 1a. It can be seen that, all catalysts appear no obvious characteristic peaks in N_2-saturated solution. Clearly, the corresponding reduction currents appear at about 0 V (vs. Ag/AgCl) in O_2-saturated solution. It indicates that Ce$_2$NiO$_x$@CN-5, CeNiO$_x$@CN-5 and CeNi$_2$O$_x$@CN-5 have an obvious catalytic activity for ORR. Thus, the ORR activity was further measured in O_2-saturated 0.1 M KOH solution (Fig. 1b). Apparently, the onset potential of CeNiO$_x$@CN-5 catalyst is positive than that of Ce$_2$NiO$_x$@CN-5 and CeNi$_2$O$_x$@CN-5. And the half-wave potentials of these catalysts are in the following order: CeNiO$_x$@CN-5 > CeNi$_2$O$_x$@CN-5 > Ce$_2$NiO$_x$@CN-5. Based on the above, in different bimetallic oxides, n (Ce): n (Ni) = 1: 1 is the best component. So the subsequent explorations of other catalysts are based on fixing the oxides as CeNiO$_x$.
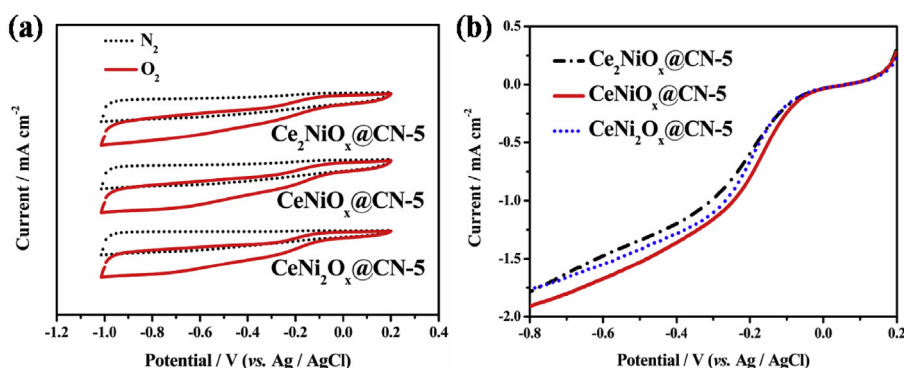

Fig. 1. (a) CVs of Ce$_2$NiO$_x$@CN-5, CeNiO$_x$@CN-5 and CeNi$_2$O$_x$@CN-5 in N_2 and O_2-saturated 0.1 M KOH solution. Scan rate: 50 mV s^{-1}, rotation speed: 1000 rpm; (b) Polarization curves of Ce$_2$NiO$_x$@CN-5, CeNiO$_x$@CN-5 and CeNi$_2$O$_x$@CN-5 in O_2-saturated 0.1 M KOH solution. Scan rate: 5 mV s^{-1}, rotation speed: 1600 rpm.