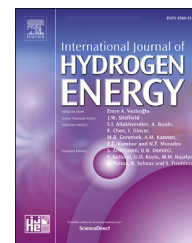




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Metallic iron doped vitamin B12/C as efficient nonprecious metal catalysts for oxygen reduction reaction

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ABSTRACT

The development of efficient nonprecious metal catalysts for oxygen reduction reaction (ORR) is crucial but challenging. Herein, one simple and effective strategy is developed to synthesize bimetallic nitrogen-doped carbon catalysts by pyrolyzing Fe-doped Vitamin B12 (VB12) supported carbon black (Fe-VB12/C). A typical Fe₂₀-VB12/C catalyst with a nominal iron content of 20 wt% pyrolyzed at 700 °C exhibits remarkably ORR activity in alkaline medium (half-wave potential of 0.88 V, 10 mV positive than that of commercial Pt/C), high selectivity (electron transfer number > 3.93), excellent stability (only 6 mV negative shift of half-wave potential after 5000 potential cycles) and good methanol-tolerance. The superior ORR activity of the composite is mainly attributed to the improved mesoporous structure and co-existence of abundant Fe-N_x and Co-N_x active sites. Meanwhile, the metallic Fe are necessary for the improved ORR activity by means of the interaction of metallic Fe with neighboring active sites.

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Introduction

Fuel cells are considered as one of most promising energy conversion technologies owing to their high energy efficiency and eco-friendly [1–3]. However, due to the high cost of platinum-based catalyst and the sluggish kinetics of oxygen reduction reaction (ORR), developing nonprecious metal catalysts (NPMCs) with excellent ORR performance is crucial to the commercialization of fuel cells but challenging [4–6]. Among various NPMCs, transition metal-nitrogen-carbon (denoted as M-N-C; M = Fe, Co or their alloys) complexes or

composites are the most promising candidates for ORR [7–20], because of their low price, high activity, durability and excellent methanol-tolerance.

Since Jasinski reported the electrocatalytic activity of Co-phthalocyanine in 1964 [21], there has at least two significant breakthroughs for preparing M-N-C catalysts in the thermal treatment (e.g. 600–1000 °C) and the introduction of cheap nitrogen sources [7,22–25]. Recently, more intensive researches have been devoted to develop high activity M-N-C catalysts by heat-treating a mixture of carbon materials, nitrogen-containing precursor and transition metal salts. For example, Wan et al. [26] developed a Fe-N-C catalyst with

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outstanding ORR activity through a pyrolysis a mixture of glucose coated carbon nanotubes, FeCl_3 and melamine. Lin et al. [27] prepared a FeCoN /graphene catalyst at a pyrolysis temperature of 750°C , which demonstrated as a cathode material for the ORR in a fuel cell with a maximum power density output of 130 mW cm^{-2} at 0.25 V . Although the intrinsic nature of active sites in M-N-C catalysts is still uncertain to date, it is commonly accepted that there are at least two fundamentally different active sites in terms of metal-free C-N_x site (such as pyridinic and quaternary N) [28,29] and M-N_x site (Fe-N_x or Co-N_x , such as FeN_{2+2} , FeN_2 , and FeN_4 or CoN_4) [14,15,30–32]. Furthermore, many recent studies have elucidated that metallic M particles or M_3C moieties ($\text{M} = \text{Fe}, \text{Co}$ or their alloy) played an important role in improving the ORR activity directly as catalytic activity species [33,34] and/or by the interaction of the metal dopants with the neighboring sites [26,35].

To obtain a promising M-N-C catalyst, one possible effective strategy is to develop the low cost metal macrocycle materials with M-N_x center, of which cyanocobalamin (Vitamin B12, VB12) with a porphyrin-like structure is one good candidate. Since Zagal et al. have reported the electrochemical performance of VB12 adsorbed on a graphite electrode [36,37], many researchers [38–41] successively investigated the VB12-based Co-N-C complex as efficient electrocatalyst for ORR. However, the electrochemical performance of these catalysts still need to be further improved. Some researchers have reported that the Fe-N-C catalyst shows higher ORR activity than Co-N-C catalyst under same conditions, although the latter is much stable in acid/alkaline medium [27,31,32,42,43]. In addition, it has been reported that Fe catalyzes the ORR mainly through a 4-electron direct pathway and has a much higher turnover frequency for H_2O_2 disproportionation reduction than Co does [27,44,45].

Herein, we report a simple but effective method to prepare a bimetallic nitrogen-doped carbon electrocatalyst based pyrolyzed Fe-doped VB12 supported carbon black (Fe-VB12/C) at 700°C , which contains M-N_x ($\text{M} = \text{Fe}$ and Co) sites and carbon-encapsulated metallic Fe nanoparticles. The bimetallic catalyst combines the high stability of Co-based catalyst with the excellent catalytic activity of Fe-based catalyst. Thus, the Fe-VB12/C catalyst exhibits remarkably higher ORR activity than the VB12/C and excellent electrochemical stability in alkaline media. Additionally, the microstructure and ORR activities of the Fe-VB12/C catalysts are carefully characterized and compared under different conditions. Our protocol presents a promising candidate to commercial Pt/C in storage devices and energy conversion particular to fuel cells.

Experimental section

Materials

The VB12 and commercial Pt/C (20 wt% Pt) were purchased from Alfa Aesar. The carbon black (Vulcan XC-72) was purified prior to use by solvothermal in 3 M HNO_3 at 120°C for 6 h. Other chemicals were used as received without further modification.

Synthesis of $\text{Fe}_x\text{-VB12/C}$ electrocatalysts

A typical Fe-Co-N-C catalyst with a nominal iron content of 20 wt% was prepared as follows: 302.8 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 50 mg VB12 and 200 mg Vulcan XC-72 were dispersed uniformly in 20 ml de-ionized water ($18.2\text{ M}\Omega$) under constant stirring for overnight at room temperature, then the solution was heated at 80°C to evaporate water. Subsequently, the powder was pyrolyzed to 700°C at a rate of 5°C min^{-1} and then held at 700°C for 2 h in a quartz tube under nitrogen atmosphere. Accordingly, the catalyst was denoted as $\text{Fe}_{20}\text{-VB12/C}$.

To study the effect of Fe loading on the catalytic activities, the catalysts were prepared by changing the nominal iron content from 5 wt% to 25 wt% while keeping the pyrolysis temperature at 700°C . These catalysts were denoted as $\text{Fe}_x\text{-VB12/C}$, in which x represented the wt % Fe in the catalyst precursor.

Synthesis of the control electrocatalysts

For comparison, VB12/C, Fe/C and C were synthesized at 700°C using the exactly same procedure except for no addition of iron source, VB12, and both iron source and VB12, respectively. In addition, the other control experimental was also carried out: the catalyst $\text{Fe}_{20}\text{-VB12/C}$ was etched by refluxing in 20 ml of $2\text{ M H}_2\text{SO}_4$ at 110°C for 8 h to remove the metal nanoparticles, then the suspension was filtered and washed until the filtrate showed a pH value of ~ 7 . Finally, the dried powder was pyrolyzed at 700°C under N_2 -flow for 2 h and was denoted as acid-etched $\text{Fe}_{20}\text{-VB12/C}$ catalyst.

Characterization of electrocatalysts

N_2 adsorption/desorption isotherms were measured with a Quantachrome Autosorb IQ₂-VP instrument. The samples were degassed at 200°C for 6 h under vacuum before the measurement. The surface areas and the pore-size distributions were calculated by using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The morphologies of the catalysts were characterized by JEOL JEM-2000EX transmission electron microscope (TEM) and FEI Tecnai G2 F20 high resolution TEM (HRTEM). Scanning electron microscope (SEM) with a field emission scanning electron microanalyzer (HITACHI S-8010) was carried out with energy dispersed X-ray spectroscopy (EDS). Power X-ray diffraction (XRD) measurements were conducted using a Bruker AXS D8 ADVANCE power X-ray diffractometer with a $\text{Cu K}\alpha$ ($\lambda = 1.5418\text{ \AA}$) radiation source. The surface properties were determined by X-ray photoelectron spectroscopy (XPS) from an ESCALAB 250Xi (Thermo Fisher) attached with an Al $\text{K}\alpha$ X-ray radiation. Thermogravimetric analysis (TGA) was carried out on a TA Q50 instrument under a flow of air with a temperature ramp of $10^\circ\text{C min}^{-1}$.

Electrochemical measurements of electrocatalysts

A rotating ring-disk electrode (RRDE) with a glass carbon disk (4 mm diameter) and a platinum ring (5 mm inner diameter and 7 mm outer diameter) was served as the substrate for the working electrode. Before all electrochemical measurements,

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