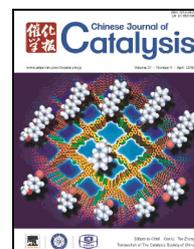


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Article

A Fe-N-C catalyst with highly dispersed iron in carbon for oxygen reduction reaction and its application in direct methanol fuel cells

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ABSTRACT

Exploring non-precious metal catalysts for the oxygen reduction reaction (ORR) is essential for fuel cells and metal–air batteries. Herein, we report a Fe-N-C catalyst possessing a high specific surface area (1501 m²/g) and uniformly dispersed iron within a carbon matrix prepared *via* a two-step pyrolysis process. The Fe-N-C catalyst exhibits excellent ORR activity in 0.1 mol/L NaOH electrolyte (onset potential, $E_o = 1.08$ V and half wave potential, $E_{1/2} = 0.88$ V vs. reversible hydrogen electrode) and 0.1 mol/L HClO₄ electrolyte ($E_o = 0.85$ V and $E_{1/2} = 0.75$ V vs. reversible hydrogen electrode). The direct methanol fuel cells employing Fe-N-C as the cathodic catalyst displayed promising performance with a maximum power density of 33 mW/cm² in alkaline media and 47 mW/cm² in acidic media. The detailed investigation on the composition–structure–performance relationship by X-ray diffraction, X-ray photoelectron spectroscopy and Mössbauer spectroscopy suggests that Fe-N₄, together with graphitic-N and pyridinic-N are the active ORR components. The promising direct methanol fuel cell performance displayed by the Fe-N-C catalyst is related to the intrinsic high catalytic activity, and critically for this application, to the high methanol tolerance.

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1. Introduction

The oxygen reduction reaction (ORR) is the cathodic reaction of energy sources such as fuel cells and metal–air batteries. The slow kinetics of the ORR hinders the performance of such energy-related technologies. Presently, Pt and its alloys set the benchmark for ORR, being the most active catalysts, however, the limited reserves and the high cost of Pt limits commercialization of the above power sources. The pursuit of highly efficient and low-cost electrocatalysts to replace current expensive

Pt catalysts for ORR applications has attracted a wealth of scientific interest for several decades [1–6].

Since cobalt phthalocyanine was observed to catalyze the ORR in 1964 [2], significant effort has been devoted to the synthesis of non-precious metal catalysts [3,7]. In particular, iron-based catalysts, synthesized by the pyrolysis of precursors composed of nitrogen, carbon and iron, have attracted extensive attention owing to their promising ORR activity. Previous studies have shown that the ORR activity of iron-based catalysts strongly depends on the synthesis procedure and the

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precursor nature, which may influence the chemical states of iron and nitrogen heteroatoms and also the textural structure of the catalysts [8].

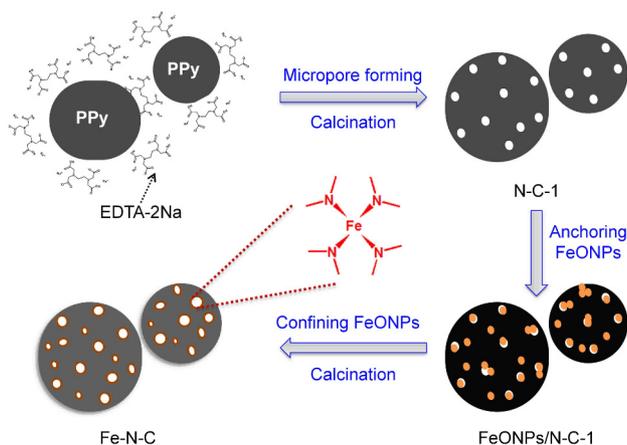
Conventional one-pot pyrolysis processes typically generate a low abundance of active sites, as when thermally activated Fe atoms are prone to agglomerate into large particles at high temperatures. To disperse iron uniformly in the host, various strategies, including ball-milling [3], wet-impregnation and ion exchange [9] have been extensively adopted. Recently, a spatial confinement strategy was proposed to synthesize various materials, including ultrafine metals and alloys where growth was restricted within two or three dimensional confined environments. The principal function is to confine the diffusion of atoms or the growth of particles to a limited space, thus producing unique characteristics in morphology, composition and/or microstructure [10,11].

Herein, we synthesized a Fe-N-C catalyst *via* a two-step pyrolysis process as illustrated in Scheme 1. The first step generates a nitrogen-doped carbon of high specific surface area (1227 m²/g) by the pyrolysis of polypyrrole (PPy) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na). The second step uses the formed intermediate as a host to anchor iron producing a carbon matrix containing highly dispersed iron. The obtained Fe-N-C catalyst displays superior ORR activity in both alkaline and acid solutions. Furthermore, the methanol tolerance property of the Fe-N-C catalyst is critical in its advantage over the Pt/C catalyst for direct methanol fuel cells (DMFCs) as the Fe-N-C catalyst circumvents problems related to intractable methanol crossover. The DMFCs fabricated employing the Fe-N-C catalyst as the cathode display promising discharging performance.

2. Experimental

2.1. Synthesis of materials

The N-C catalyst was derived from PPy, which was obtained by polymerization of pyrrole. Briefly, 25 g cetyltrimethylammonium bromide (CTAB, C₁₉H₄₂BrN, Tianjin Guangfu Fine Chemical Research Institute) was dispersed in 80 mL ethylene glycol (EG, Tianjin Kemiou Chemical Reagent Co., Ltd.)



Scheme 1. Schematic diagram of the Fe-N-C catalyst synthesis route.

followed by the addition of 6 mL pyrrole monomer (C₄H₅N, Sinopharm Chemical Reagent Co., Ltd.). After stirring for 1 h, 40 mL EG containing 12 g FeCl₃·6H₂O was added dropwise with stirring. The polymerization process continued for 5 h before 200 mL methanol (CH₃OH, Xilong Chemical Co., Ltd.) was added and stirred overnight. The obtained black ink was then filtered, washed with water multiple times and dried in an oven at 80 °C for 8 h to obtain PPy. The obtained PPy was thermally treated under a N₂ atmosphere at 800 °C for 1 h to obtain the black powder, denoted as N-C.

The above PPy was blended with EDTA-2Na (C₁₀H₁₄N₂O₈Na₂·2H₂O, Tianda Chemical Reagent Co., Ltd.) at a mass ratio of 1:2 in deionized water under vigorous stirring for 3 h, followed by evaporating the deionized water at 70 °C before drying at 80 °C. After grinding, the powder was thermally treated at 800 °C for 1 h under a N₂ atmosphere. Thereafter, the sample was sonicated in 1 mol/L HCl for ~2 h, washed with distilled water multiple times and dried in an oven at 80 °C overnight to obtain N-C-1.

FeCl₃ was hydrolyzed in an ethanol solution containing ammonia to obtain an iron oxide colloid (denoted as FeONPs), which was added to N-C-1 followed by thermal treatment to obtain the Fe-N-C sample. Briefly, a 0.2-mmol FeCl₃/ethanol solution and 2 mL 30% NH₃·H₂O was added into 100 mL ethanol in a flask. The mixture was stirred and refluxed at 100 °C for 1 h. Subsequently, 200 mg N-C-1 was added and stirred for 4 h. Thereafter the solvent was evaporated using a rotary evaporator to obtain a black powder, which was then dried in an oven at 80 °C overnight. The obtained sample was pyrolyzed at 900 °C for 1 h under N₂ to obtain a loose and black powder, denoted as Fe-N-C.

N-C-2 was prepared for comparison with the Fe-N-C catalyst to discriminate the role of iron after the second thermal treatment. The N-C-1 was thermally treated in the absence of Fe at 900 °C for 1 h under a N₂ atmosphere.

2.2. Physical characterization

A scanning electron microscope (SEM, JSM-7800F) was used to study particle morphology, and energy-dispersive x-ray spectroscopy (EDX) was recorded on a specific area of the electrocatalyst. A transmission electron microscope (TEM, JEM-2100) was used to study the crystal nature of the electrocatalyst employing an acceleration voltage of 200 kV. The high resolution TEM (HRTEM) micrograph was obtained on a TEM (JEM-2100F) using an acceleration voltage of 200 kV. X-ray diffraction (XRD) studies were performed on a Rigaku X-2000 diffractometer using Cu K_α radiation with a Ni filter. The samples were scanned at a rate of 5°/min. The chemical composition of the four electrocatalysts were characterized by X-ray photoelectron spectroscopy (XPS) measurements (ESCALAB 250Xi) using Al K_α radiation.

Ar isotherms at -186 °C were measured using a Quantachrome Autosorb-iQ instrument. Before analysis, samples were outgassed at 180 °C under vacuum for 4 h. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution was calculated by the non-linear density-functional theory

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