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^{57}Fe-Mössbauer spectroscopy and electrochemical activities of graphitic layer encapsulated iron electrocatalysts for the oxygen reduction reaction

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ABSTRACT

Graphitic layer encapsulated iron based nanoparticles (G@FeNPs) have recently been disclosed as an interesting type of highly active electrocatalysts for the oxygen reduction reaction (ORR). However, the complex composition of the metal-containing components and their contributions in catalysis remain unclear. As a representative catalyst of the unique encapsulated structure, a series of G@FeNPs catalysts were prepared by a high-pressure pyrolytic process with uniform and essentially identical morphologies but varied compositions. The catalysts exhibited a high onset potential of 0.85 V at 0.1 mA cm^{-2} in acidic media. By ^{57}Fe-Mössbauer spectroscopy the iron containing components were identified including α-Fe, γ-Fe, γ-Fe_2O_3, and Fe_3C as well as a minor doublet component due to Fe^{3+} in high spin and/or Fe^{2+} in low spin state. The ORR activities are evaluated in terms of the mass specific kinetic current density found to be positively correlated with the Fe_3C content in the range of study, indicating involvement of the encapsulated nanoparticles in the ORR catalysis. The recognition of the Fe compositions and active sites provides new insights to the confined Fe-based ORR electrocatalysts and therefore options for further development of non-precious metal materials.

1. Introduction

A core subject of the proton exchange membrane fuel cell (PEMFC) has been the development of alternative cathodic electrocatalysts for the oxygen reduction reaction (ORR) to replace the currently used platinum-based catalysts. The past decades have witnessed the remarkable progress on non-precious metal catalysts (NPMCs), since the pioneering work of Co phthalocyanine was introduced by Jasinski [1]. An interesting type of materials is transition metal-based NPMCs in the form of metal-nitrogen-carbon composites (M-N-C) typically synthesized by pyrolysis [2–9]. The precursors have largely been expanded from the early macrocycle molecules such as phthalocyanines and porphyrins to a wide variety of small molecules containing nitrogen, carbon and transition metals. Breakthroughs have been achieved, for example, by the polyaniline-derived Fe-N-C with improved durability due to the low H_2O_2 yield [4], and microporous carbon supported Fe-N-C resulting from an optimized two-step pyrolysis process with high catalytic activity [2]. Exploration of active sites has suggested that the key active motifs are the Fe^{2+} atoms coordinated with four nitrogen atoms embedded in the in-plane carbon ($Fe^{2+}N_4/C$) [10,11]. This type of NPMCs exhibits high ORR activity while the stability remains the currently focused issue.

High temperature pyrolysis of iron containing precursors, in fact, involves formation of carbon around iron nanoparticles, since the amorphous carbon dissolves in the iron phase and then assembles into graphitic carbon by atomic diffusion to the surface [12]. It is therefore natural that the pyrolytic catalysts often contain some encapsulated metallic nanoparticles [13]. Several research groups have attempted to synthesize NPMCs of the encapsulated structures. Deng et al. first demonstrated that pod-like iron nanoparticles confined in carbon nanotubes (CNTs) exhibited significant ORR activity and particularly for the stability [14]. Other metal containing components such as inorganic Fe_3O_4 [15], Fe_3C [16,17] and Fe/Fe_3C [18] have also been reported in the carbon-encapsulated structures. Recently, a novel approach of high-pressure pyrolysis by Hu et al. allowed for preparation of a typical catalyst of iron-containing nanoparticles in the graphitic layer encapsulated structure [19]. Characteristics of the materials include uniform iron containing nanoparticles, in a mass content range of over 10%, encapsulated in CNTs [20] or/and graphene layers [21]. The encapsulating carbon layers are likely due to the high pyrolytic pressure, curved into hollow microspheres.

For the encapsulated NPMCs, the catalytic contribution of those

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encapsulated metal containing phases is currently still much debated. On one hand, the interaction of the FeN_x/C sites with encapsulated metal containing particles was emphasized [22], which is believed to boost the ORR activity. On the other hand, removal of the inorganic metal species from the Fe-N-C catalyst was found to enhance the ORR activity [23]. Very recently, a novel approach by Cl_2 etching and H_2-restoring provides encouraging results for understanding the active site [24]. The authors prepared encapsulated Fe-based catalysts that contain FeN_x/C and confined Fe species. By using Cl_2 etching, both FeN_x/C and confined Fe species were converted into $FeCl_3$ and the ORR activity was lost. Further, this treated sample underwent H_2 reduction. Due to N-containing species removed in Cl_2 etching, the $FeCl_3$ can only be converted into Fe species, which excludes the existence of FeN_x/C. The recovery of ORR activity after H_2 reduction demonstrates the active sites of encapsulated Fe species. This encouraging result indicates the active contribution of the inner Fe phases. Further identification of the Fe phases and correlations of the iron components with the electrochemical activity should be very informative.

In our previous work, a series of graphitic layer encapsulated iron nanoparticles (G@FeNPs) catalysts were, by varying temperature and duration of the high-pressure pyrolysis, prepared with essentially identical morphologies but different compositions [25]. The present paper is devoted to a ^{57}Fe-Mössbauer spectroscopy study on various Fe components of the wrapped metal-containing phases. The identified metal components include α-Fe, γ-Fe, γ-Fe_2O_3, Fe_3C as well as a minor component due to (super)paramagnetic Fe^{3+} (high spin) and/or paramagnetic Fe^{2+} (low spin). In terms of the kinetic current density, the ORR activity of the materials was evaluated. The variation of the ORR activity was found to positively correlate with the content of Fe_3C. This experimental evidence relating to encapsulated Fe_3C to the ORR activity brings new insights to the current understanding of the active sites and opens avenues to further development of high performance non-precious metal catalysts.

2. Experimental section

2.1. G@FeNPs preparation

The G@FeNPs catalysts were synthesized by a high-pressure pyrolysis approach. The autoclave reactor was made of modified stainless steel Swagelok® valve parts with a quartz cup (3.3 mL). A mixture of cyanamide and ferrocene in a mass ratio of 9:1 was first well mixed and transferred to the quartz cup in the autoclave in an oxygen-free glove box. The autoclave was then tightly closed and placed into the furnace, which was pre-heated to the desired temperature and held for a certain period. The pressure inside the reactor was estimated to be around 500–600 bar by assuming formation of small gaseous molecules of the precursors during the pyrolysis, which was approximately agreement with estimation by the water vapour test [25].

Two series of catalysts were synthesized with varied pyrolytic temperatures and durations. The first series of catalysts were pyrolyzed at temperatures of 600, 700 and 800 °C for 35 min and the second were prepared at a fixed temperature of 700 °C for varied durations from 15 to 240 min. The samples are named after the pyrolytic temperature (in °C) and duration (in min), for example, sample 700–75 was pyrolyzed at 700 °C for 75 min.

Transmission electron microscopy (TEM) was performed on Tecnai-T20-G2 at 200KV. X-Ray diffraction was performed on a Philips PW1700 diffract-meter using a Cu Kα (λ = 1.5405 Å) radiation source.

^{57}Fe Mössbauer spectra were measured at both room temperature (295 K) and low temperature (18 K) using a ^{57}Co source embedded in a rhodium matrix and a constant accelerator spectrometer. The isomer shifts were given relative to that of α-Fe at room temperature. The samples for Mössbauer spectroscopy were prepared by pressing ca. 100 mg of the sample powder in to pill-shapes 15 mm in diameter and 2 mm thick.

2.2. Electrochemical measurements

Electrochemical tests were carried out in a standard three-electrode cell, a 5.0 mm glassy carbon disk and a carbon rod were used as the working electrode and counter electrode, respectively. The reference electrode was a saturated calomel electrode (SCE). The potential was converted into a reversible hydrogen electrode (RHE) afterwards. All the electrochemical experiments were performed on a Versa STAT3 (Princeton Applied Research) and 760C Bipotentiostat (CH Instruments) in N_2 or O_2-saturated $HClO_4$ solution. The commercial Johnson Matthey 20% Pt/C was chosen as the reference catalyst. A catalyst ink was prepared by dispersing 10 mg of catalyst into a mixed solution of 514 μL ethanol and 80 μL of 5% Nafion. The ink was applied on the glassy carbon rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) followed by drying in air. The catalyst loading of the Pt/C catalysts for both RDE and RRDE was 0.25 mg cm^{-2} while that of the G@FeNP catalysts was 0.65 mg cm^{-2}. The kinetic current density ($j_{K,}$ $mAcm^{-2}$) was derived from the RDE measurements using the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} \tag{1}$$

where j and j_L are the measured current and diffusion limiting current density, respectively. The mass kinetic current density is further normalized to the total catalyst mass (J_K, A g^{-1}), which is the same (0.65 mg cm^{-2}) for all samples. For the RRDE measurements, the disk electrode was scanned at a rate of 10 mV s^{-1}, and the ring potential was held constant at 1.2 V vs. RHE. The H_2O_2% and transferred electron number per oxygen molecule (n) were calculated by the followed equations:

$$H_2O_2\% = 200\frac{I_r/N}{I_d + I_r/N} \tag{2}$$

$$n = 4\frac{I_d}{I_d + I_r/N} \tag{3}$$

where I_d is the disk current and I_r the ring current, and N is the current collection efficiency of the Pt ring, which was determined to be 0.37.

3. Results

3.1. Encapsulated structure

General characterization of the two series of G@FeNPs catalysts with varied pyrolysis temperature and duration was reported previously [25]. A brief highlight is given here, which provides a basis for the present study focusing on the encapsulated iron components and active sites by ^{57}Fe-Mössbauer spectroscopy.

TEM characterization reveals that pyrolysis of ferrocene and cyanamide at 600 °C involves polymerization of the cyanamide, leading to formation of melamine-rich microspheres with ferrocene dispersed evenly in the spheres (Fig. 1). The pyrolytic temperature has a significant impact on the morphology of the catalysts. At 600 °C, microspheres around 500–700 nm in diameters were formed (Fig. 1a). At 700 °C, the microspheres maintain their morphologies but become porous as the precursors start to gradually decompose. Metal or metal carbide from decomposition of ferrocene catalyze the carbon deposition, leading to formation of uniformly distributed iron-containing nanoparticles encapsulated by the carbon layers (Fig. 1c). When the temperature was further increased to 800 °C, the microspheres were found to be less regular in shape (Fig. 1h). When the temperature is fixed at 700 °C, a pyrolytic duration of 15–35 min does not seem to be sufficient to achieve complete decomposition of the precursors. After pyrolysis for longer than 35 min, the microspheric morphology of the