



A bimetallic carbide Fe₂MoC promoted Pd electrocatalyst with performance superior to Pt/C towards the oxygen reduction reaction in acidic media



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ABSTRACT

Novel and stable bimetallic carbide (Fe₂MoC) anchored on graphitized carbon (GC) has been synthesized by an ion-exchange method. The Pd supported on GC-Fe₂MoC electrocatalyst (Pd/GC-Fe₂MoC) shows superior activity and stability to commercial Pt/C for oxygen reduction reaction (ORR) in acidic media. The XPS spectra reveal that the excellent performance of Pd/GC-Fe₂MoC should be due to the excellent electron-donating (synergistic effect) of Fe₂MoC to Pd, which not only facilitates the reduction of O₂ but also increases the linkage strength between Pd and Fe₂MoC. The Koutecky-Levich plots indicate 4-electron transfer for the Pd/GC-Fe₂MoC catalyzed ORR.

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1. Introduction

Transition metal carbides are effective to promote the noble metal based electrocatalysts because of their synergistic effect on noble metals. The synergistic effect is caused by the electron transfer between the carbides and noble metals [1–4], which well facilitates not only the oxidation of fuels and CO-like poisons [5–9], but also the reduction of oxygen (ORR) [10–15]. Therefore, with the combination of carbides and noble metals, great improvements in electrocatalytic activity in both anode and cathode have been obtained. However, the ORR performance still remains low in present due to slow kinetics [16,17], which needs large amount of Pt metal to improve the cathode current, leading to higher cost.

Palladium (Pd) has been proposed as a potential candidate for cathode electrocatalysts, due to their inherent catalytic activity and low cost compared with Pt. Pd-based electrocatalysts have good ORR performance in alkaline media [18–20]. However, the activity of Pd-based electrocatalysts towards ORR in acidic media is still lower than that of the Pt-based electrocatalysts [21–25]. Recently, bimetallic carbides (Co₆Mo₆C₂ [26] and Co₃W₃C [27]) have shown

to be highly active and stable for promoting Pt- or Pd-based electrocatalysts towards ORR in acidic media, which are imagined to boom the study of bimetallic carbides.

Herein, we report novel bimetallic carbide composite (GC-Fe₂MoC), which comprises Fe₂MoC and graphitized carbon (GC, as matrix). The GC-Fe₂MoC promoted Pd electrocatalyst (Pd/GC-Fe₂MoC) exhibited higher activity and stability compared with commercial Pt/C towards ORR in acidic media. It has been realized that is due to the electron-donating effect (synergistic effect) and the inherent stability of Fe₂MoC.

2. Experimental

2.1. Preparation of GC-Fe₂MoC and GC-MoC composites

Typically, polyacrylic weak-base anion exchange resin (D314, 10g, Shanghai Hualing Resin CO., Ltd, China) was firstly impregnated with 100 ml 0.014 mol L⁻¹ ammonium molybdate ((NH₄)₆Mo₇O₂₄, A.R., Chemical Reagent Factory of Hefei University of Technology, China) for 6 h, then, the solid was separated and impregnated with 100 ml 0.200 mol L⁻¹ potassium ferrocyanide (K₄[Fe(CN)₆], A.R., Guangzhou Chemical Reagent Co., China) for 4 h. The resulting solid product was separated and dried at 80 °C overnight. Then, the product was heated at 1300 °C for 1 h in N₂

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atmosphere. After cooled down to room temperature, the sample was grinded into powder by ball mill to get the GC-Fe₂MoC composite.

For comparison, the GC-MoC (MoC on graphitized carbon) was prepared. The preparation procedure is similar to that of GC-Fe₂MoC without the adding of K₄[Fe(CN)₆].

2.2. Preparation of electrocatalysts

Pd supported on GC-Fe₂MoC was prepared. Typically, GC-Fe₂MoC (50 mg) was added into a mixture of 55.56 mg Palladium chloride (PdCl₂, A. R., Sinopharm Chemical Reagent Co., Ltd) and 20 ml glycol (A.R., Tianjin Fuyu Fine Chemicals Co., Ltd, China) in ultrasonic bath for 30 min to form a uniform ink. The pH of the mixture was adjusted to 10 by 1 mol L⁻¹ NaOH/glycol solution. The sample was then put into a microwave oven (900 W) for heating at a 15 s on and 10 s off procedure for 10 times [28]. Afterwards, the mixture was washed with deionized water and dried in vacuum at 60 °C for 8 h to get the Pd/GC-Fe₂MoC electrocatalyst. The Pd content in the electrocatalyst was 40 wt% stoichiometrically. The actual Pd contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP, IRIS(HR), USA).

For comparison, Pd/GC-MoC and Pd/C electrocatalysts with equivalent content of Pd were also synthesized.

2.3. Preparation of electrodes

For electrode preparation, Pd/GC-Fe₂MoC (or Pd/GC-MoC, Pd/C and GC-Fe₂MoC, 5 mg) or commercial Pt/C (4 mg, 47.6 wt %Pt, TTK, Japan) were dispersed in 1.95 ml ethanol and 0.05 ml 5 wt% Nafion suspension (DuPont, USA) under ultrasonic agitation to form the electrocatalyst ink. The electrocatalyst ink (0.005 ml) was deposited on the surface of a glass carbon rotating disk electrode (0.25 cm²) and dried at room temperature. The total Pd or Pt loadings were all 0.02 mg cm⁻². The actual Pd or Pt content was determined by Inductively Coupled Plasma-atomic Emission Spectrometry (ICP, IRIS(HR), USA) method.

2.4. Electrochemical characterization

The electrochemical measurements were performed on a PAR-STAT 2273 instrument in a three-electrode cell in an O₂-saturated 0.1 mol L⁻¹ HClO₄ solution scanned between 0.03 to 1.1 V at a scan rate of 5 mV s⁻¹, at 25 °C controlled by a water-bath thermostat. A Pt foil (1.0 cm²) and a reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively.

All chemicals were of analytical grade and used as received.

2.5. Physical characterization

The morphologies of the synthesized materials were characterized by transmission electron microscopy (TEM, JOEP JEM-2010, JEOL Ltd.) operating at 200 kV. The graphitization degrees were determined with Laser Micro-Raman Spectrometer (Renishaw inVia, Renishaw plc). The structures of the samples were determined on an X-ray diffractometer (XRD, D/Max-III A, Rigaku Co., Japan, CuK1, λ = 1.54056 Å radiation) and an X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250, Thermo-VG Scientific).

3. Results and discussion

Fig. 1 shows the XRD patterns of the GC-Fe₂MoC and GC-MoC composites. The patterns of GC-Fe₂MoC and GC-MoC composites match the characteristics of Fe₂MoC (PDF#17-0911) and MoC (PDF#65-0280) respectively by comparing JCPDS cards. Besides, the diffraction peaks at 2θ around 26.0° correspond to C (002) facet of

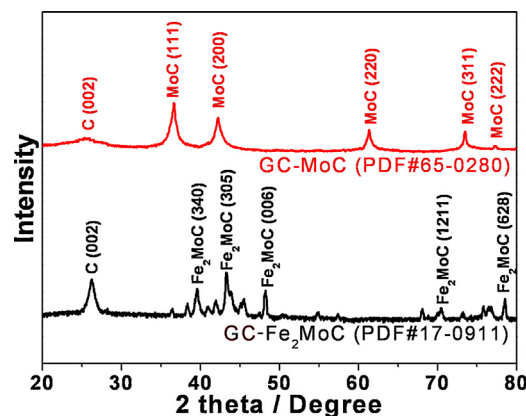


Fig. 1. XRD patterns of GC-Fe₂MoC and GC-MoC composites.

graphite. But it is apparent that GC-Fe₂MoC has more graphitization degree than GC-MoC. Literatures reported that Fe compound as graphitization catalyst leads to graphitization of organics by a complex process involving the dissolution of carbon atoms into catalyst followed by the precipitation of graphitized carbon [29–31]. Above results proved that the addition of Fe compound lead to high graphitization degree of the GC-Fe₂MoC. Meanwhile, the Fe compound also acts as a reagent leading to the formation of Fe₂MoC.

Fig. 2 shows the Raman spectra of GC-Fe₂MoC and GC-MoC composites. The G peaks at 1598 cm⁻¹ for GC-MoC and at 1580 cm⁻¹ for GC-Fe₂MoC correspond to a splitting of the E_{2g} stretching mode of graphite and reflects the structural intensity of the sp²-hybridized carbon atom [32,33]. The positive shift on GC-MoC compared to that on GC-Fe₂MoC means the inferior graphite orientation of the former than that of the latter. The D peak at 1350 cm⁻¹ is attributed to the vibrations of carbon atoms with dangling bonds in disordered graphite planes and the defects incorporated into pentagon and heptagon graphite-like structures. The ratios of the G-line to D-line were used to determine the degree of the graphitization. The I_G/I_D values for GC-Fe₂MoC and GC-MoC were 2.46 and 1.21, respectively. These results confirm that the Fe compound favors the graphitization of D314 resin, leading to higher graphitization degree of GC-Fe₂MoC.

Fig. 3a is the TEM image of the GC-Fe₂MoC. The particles with the diameter ranged from 5 to 15 nm are uniformly dispersed. From the HRTEM image (Fig. 3b), the lattices of the Fe₂MoC (305) and graphite (002) can be clearly seen. Fig. 3c is the TEM image of Pd/GC-Fe₂MoC, the particles with the diameter of no more than 5 nm and with the diameter around 10 nm should be

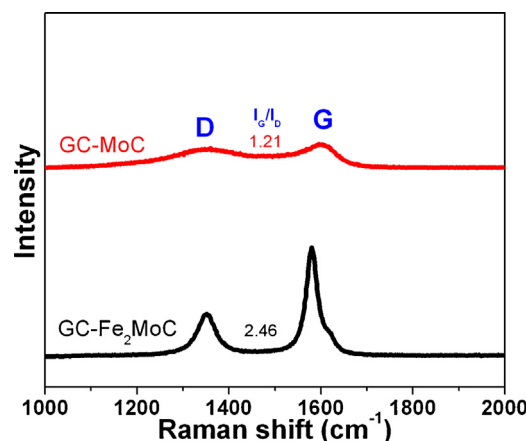


Fig. 2. Raman spectra of GC-Fe₂MoC and GC-MoC composites.

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