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Tungsten carbide synthesized by low-temperature combustion as gas diffusion electrode catalyst

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ABSTRACT

Tungsten carbide powder, which is used as the catalyst for a gas diffusion electrode, has been prepared by low-temperature combustion synthesis for the first time. The average particle size of the prepared tungsten carbide is 200 nm, determined by X-ray diffraction and field-emission scanning electron microscopy. The effects of the carbon/tungsten (C/W) molar ratio on the formation of tungsten carbide and carbon content on the complete carbonization temperature are discussed. The optimal synthesis temperature is 1100 °C, and the optimal C/W molar ratio is 19/3. The electrocatalytic properties of tungsten carbide for the oxygen reduction reaction are evaluated through the use of polarization curves and electrochemical impedance spectroscopy in neutral and alkaline electrolytes. The current density of the tungsten carbide-based gas diffusion electrode is as high as 350 mA cm⁻² at 0.4 V versus Hg/HgO. It is demonstrated that the tungsten carbide catalyst exhibits excellent electrocatalytic performance, comparable with that of Pt.

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Introduction

In order to improve the adverse effects of fossil fuels burning on the environment, and reduce dependence on fossil fuels, development of pure electric and fuel cell vehicles has become a much sought after goal around the world. The metal–air battery is an ideal replacement for traditional batteries, and has attracted attention due to the relative abundance of its

source materials, simple structure, high specific power and energy density. However, until now, due to the lack of highly efficient low-cost electrode catalysts for the oxygen reduction cathode, metal–air batteries have been only used in small-scale special applications, such as pagers and hearing aids, indicating that the development of a more effective, metal–air battery catalyst could have much wider application.

Oxygen reduction cathodes for the metal–air battery are usually gas diffusion electrodes, and the choice of catalyst for

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the gas diffusion electrode is largely responsible for the battery performance. At present, the catalysts for the gas diffusion electrode mainly include: (1) noble metals, such as Pt [1], Ag [2], Pt–Au [3], Pd₄₉Pt₄₇Co₄ [4], Pt–Co [5], and Pt–Ru–Co [6]; (2) metal oxides, such as Co₃O₄ [7], MnOOH [8], and MnO₂ [9]; (3) mixed metal oxides, such as Ni_xCo_{3-x}O₄ [10], La_{0.6}Ca_{0.4}CoO₃ [11], La_{0.1}Ca_{0.9}MnO₃ [11], LaNiO₃ [11], LaNi_{0.8}Co_{0.2}O₃ [12], and Mn_xCo_{3-x}O₄ [13]; (4) macrocyclic compounds, such as cobalt tetramethoxy phenylporphyrin (CoTMPP) [14], cobalt phthalocyanine (CoPc) [15], and iron phthalocyanine (FePc) [16]. Among these catalysts, platinum is the most suitable electrocatalyst for the oxygen reduction reaction (ORR) due to its high electrocatalytic activity and chemical stability. However, there are several obstacles to utilizing Pt catalysts in most practical applications, including high cost and easily susceptible to poisoning by carbon monoxide [17]. Improving the properties of oxygen reduction cathode materials and seeking inexpensive and efficient catalysts has become a major focal point in the field of metal–air battery research.

Tungsten carbide (WC) is a promising catalytic material for the gas diffusion electrode, since its catalytic behavior resembles platinum [18], but its stability [19–21], anti-toxic and oxidation resistance are much higher than those of platinum [22]. Mustain et al. [23] studying the stability of Pt/WO₃ in acid media found the sequential electrochemical oxidation of WC to WO_x and WO₃ at E > 0.8 V followed by the formation and dissolution of H_xWO₃. The proposed degradation mechanism for WC and WO₃ demonstrated that as long as the support surface is exposed to the acidic electrolyte, neither represents a long-term stable support material for Pt electrocatalysts. The formed nonconductive WO₃ could isolate Pt particles by coating on their surface, leading to electrochemically inaccessible Pt particles. But the presence of Pt on WC surface can stabilize WC and further inhibit WC oxidation, which is consistent with the results reported in the literature [24,25]. Furthermore, Mark et al. [26] compared the stability of the most commonly used carbides in electrochemical applications: tungsten carbides (WC and W₂C) and molybdenum carbide (MO₂C) in electrolytic solutions by varying pH values, where WC exhibits the largest region of stability at a relatively lower pH value. It has been reported that tungsten carbide exhibits high catalytic activity in electro-catalysis [27], and is a promising material for hydrogen evolution reactions and hydrogen oxidation reactions in electro-catalysis [28]. Pt nanoparticles supported by WC substrate show remarkable catalytic activity for ORR [29], has anti-poisoning properties for carbon monoxide in methanol electro-oxidation, and exhibits improved methanol oxidation performance [30]. Additionally, tungsten carbide particles as a counter-electrode for dye-sensitized solar cells have been shown to improve catalytic activity for iodide reduction [31,32], and when combined with titania in nanocomposites, has shown synergistic effects for electrocatalysts [33]. The infiltrated WC–YSZ (yttrium stabilized zirconia), as a potential anode for direct methane-fueled solid oxide fuel cells (SOFCs), performed stably with no catastrophic degradation at 800–900 °C [34]. However, catalytic activity of WC is lower than Pt.

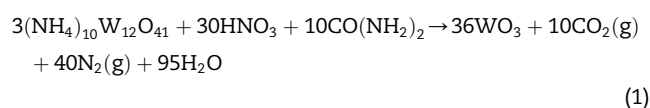
It was confirmed that the preparation method and processing conditions play a critical role in the electrochemical behavior and chemical stability of tungsten carbide [35,36].

Until now, WC powder has been prepared by many methods, such as chemical precipitation [37], mechanical alloying [38,39], sonochemical synthesis [40], microwave synthesis [41–43], a temperature-programmed method [44,45], and hydrothermal methods [46]. However, some of these preparation methods have deficiencies. For example, it is easy to introduce the impurities by chemical precipitation method. Mechanical alloying requires high temperatures and consumes large amounts of energy, the distribution of the WC particle size is not uniform by the method. Due to a consequence of the temperature dependence of dielectric and heating frequency, the preparation process of WC is not easy to control by Microwave heating method. Polymeric carbon will be formed on the surface of WC in the temperature-programmed method, which can affect the surface activity. So far, preparation of tungsten carbide catalyst by the low-temperature combustion synthesis has not been reported. Low-temperature combustion synthesis (LCS) is based on the exothermic redox reaction between the oxidizer and the appropriate fuel, which could induce spontaneous redox reaction at much lower temperatures than the actual phase formation temperature. The products fabricated by the LCS method could have smaller grains with homogeneous size, since all reactants are mixed in solution at the molecular level, leading to a faster reaction rate. Currently, the LCS method is widely used to synthesize ultrafine ceramic powders of complex oxide compositions and luminescent materials [47–49]. Its widespread use in this area is due to the fairly simple equipment needs, short reaction times and high energy efficiency. In this study, tungsten carbide powder was synthesized by means of the LCS method, and processing conditions, such as temperature and carbon source contents, were varied in order to determine the optimal conditions for synthesizing WC with superior electrocatalytic properties. Finally, the catalytic activity of synthesized WC for the ORR was investigated through the use of polarization curves and electrochemical impedance spectroscopy (EIS).

Experimental details

WC catalyst preparation

Ammonium tungstate ((NH₄)₁₀W₁₂O₄₁, analytical grade), urea (CO(NH₂)₂, analytical grade), nitric acid (HNO₃, 65 wt.%), and glucose (C₆H₁₂O₆·H₂O, analytical grade) were used as raw materials in the synthesis. In this system, ammonium tungstate was used as the tungsten source, nitric acid as an oxidant, urea as fuel, and glucose as the carbon source. The low-temperature combustion synthesis process is a redox reaction, thus combustion products are generally oxides, CO₂, N₂, and H₂O. The combustion reaction can be described as follows:



(NH₄)₁₀W₁₂O₄₁, CO(NH₂)₂, and HNO₃ were weighed according to the 3:30:10 molar ratio in Eq. (1). The amount of

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