Significant advantages of sulfur-doped graphene in neutral media as electrocatalyst for oxygen reduction comparing with Pt/C

Xinxin Shi¹,²,³,⁴, Jiaona Zhang¹,²,³ and Tinglin Huang¹,²,³

¹ School of Environmental and Municipal Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, China;
² Key Laboratory of Northwest Resource, Environment and Ecology, MOE, Xi’an University of Architecture and Technology, Xi’an, 710055, China;
³ Shaanxi Key Laboratory of Environmental Engineering, Xi’an University of Architecture and Technology, Xi’an, 710055, PR China.
⁴ shixinxin@xuat.edu.cn

Abstract. Sulfur-doped graphene (SDG) has been found to be an efficient electrocatalyst for oxygen reduction reaction. However, previous studies on the catalytic activity of SDG have been mainly confined to O₂-saturated alkaline media which is a typical alkaline fuel cell environment. Air-cathode microbial fuel cells (ACMFCs), as a novel energy conversion and wastewater treatment technology, use the oxygen from air as cathodic reactant in neutral media with low concentration of O₂. Thus, it is meaningful to explore the catalytic performance of SDG in such ACMFC environment. The result showed that in ACMFC environment, the peak current density of SDG in CV test was surprisingly 4.5 times higher than that of Pt/C, indicating a much stronger catalytic activity of SDG. Moreover, SDG exhibited a stronger tolerance against the crossover of glucose (a typical anodic fuel in ACMFC) and better stability than Pt/C in neutral media.

1. Introduction

Microbial fuel cell (MFC), which can extract energy from organic matter by utilizing microorganisms as a catalyst at the anode, has been widely recognized as a promising technology for energy-efficient wastewater treatment or even for green energy generation[1-2]. Air-cathode microbial fuel cells (ACMFCs), as one kind of MFCs using oxygen (O₂) as electrons acceptor, have attracted a lot of attentions due to the zero-cost and the relative high redox potential of O₂ coming from air. However, without efficient catalyst, the oxygen reduction reaction (ORR) would be sluggish and the performance of an ACMFC would be quite poor, which has largely hindered the scale-up and commercialization of ACMFCs. Pt/C has been a commonly used, effective catalyst for ORR at the cathode of ACMFCs. However, it suffers from the disadvantages of high cost, poor long-term stability under the operating conditions, and poor tolerance against fuel crossover. The development of non-precious metal or metal-free electrocatalyst has aroused extensive research interests, and several kinds of alternatives of Pt/C have been synthesized including tetramethoxyphenylporphyrin (TMPP)[3], iron-chelated ethylenediaminetetraacetic acid[4], manganese oxide[5] and heteroatom (N, B, S, or P)-doped carbon materials[6]. Recently, the novel sulfur-doped graphene showed several interesting results as an effective heteroatom-doped carbon-based catalyst. Yang et al.[7] synthesized SDG with a
higher electrocatalytic activity for ORR than Pt/C in alkaline media by using benzyl disulphide as sulfur source annealing with graphene oxide (GO) in argon. Later, different synthesized methods were proposed such as annealing graphene oxide in gases containing S element (H2S[8], CS2[9], and SO2[9]), balling graphite and sulfur (S0)[10], magnesiothermic reduction of CO2 and Na2SO4[11]. All of these SDGs exhibited competitive or even better catalytic activities compared to commercial Pt/C. Attempts have been made to explore the catalytic mechanism. Jeon et al.[10] and Zhang et al.[12] studied the electronic structure of SDG using functional theory (DFT) methods and calculated the statistical distributions of the spin and charge densities with Mulliken methods. The results showed that the covalently bonded sulfur (-C-S-S-C-) or oxidized sulfur (O=S=O) at the zigzag and armchair edges of graphene enhanced both positive charges and spin densities on the adjacent carbon atoms. And those carbon atoms with high positive charges and spin densities could serve as active sites, thus promoting catalytic activity.

The inspiring achievements on SDG provide a strong motive to introduce SDG into the ACMFCs as a high efficient catalyst for ORR at the cathode. However, such researches has not been reported so far. Moreover, previous studies on the catalytic activity of SDG has been mainly confined to O2-saturated alkaline media which is a typical alkaline fuel cell (AFC) environment or a commonly used testing environment for catalyst activity. The working environment of catalysts in a ACMFC is different from such environment (hereinafter referred to as AFC-like environment) that is featured in the following respects: (a) The electrolyte in ACMFCs is neutral (50mM phosphate buffer solution, PBS) to ensure the activity of bacteria at anode[13], in contrast with the alkaline electrolyte of the AFC-like environment[14]; (b) Comparing to the O2-saturated activity test environment, the cathodes of ACMFCs work at normal atmospheric pressure without aeration, i.e., in a condition of low O2 concentration[15]; (c) To decrease the internal resistance, the anode and the cathode are usually assembled in the same chamber of an ACMFC, which means that the anodic substrate connects with the surface of cathode directly and will cause serious fuel crossover if the catalyst (for example, Pt/C) at the cathode has poor catalytic selectivity for ORR[16].

Keeping mind of these key differences, the potential of SDG as a new ORR catalyst to replace Pt/C will be studied in this exploratory work, regarding the catalytic activity, selectivity and stability of SDG in ACMFCs environment (i.e., the condition of neutral electrolyte and low O2 concentration).

2. Materials and methods

2.1. Synthesis of SDG

As in the work by Yang et al.[7], SDG was prepared as follows: the commercial graphene oxide (Xianfeng inc., China) and benzyl disulfide (Sinopharm Chemical Reagent Co., Ltd, China) were first added into ethanol with the mass ratio of 1:1 and then ultrasonically dispersed for about 8 hours. The resulting suspension was spread onto an evaporating dish and dried at 40°C. The dried powders were annealed at 1100°C for 3 hours and then cooled to room temperature in a quartz tube furnace with a whole-process protection of argon atmosphere.

2.2. Electrode preparation

The working electrodes were prepared by SDG or Pt/C ink onto a pre-polished glassy carbon electrode, with detailed progress as follows: glassy carbon electrode (4mm diameter, Hengsheng inc., China) was first polished by a 0.5μm alumina slurry (Hengsheng Inc., China) and then ultrasonically rinsed in deionized water, ethanol, acetone and nitric acid in sequence (each for 2min). The catalyst ink was prepared by adding a 2mg SDG or Pt/C into the 250ul Nafion solution (0.2%) and ultrasonically treated for 30min. Finally, a 15ul well-dispersed catalyst ink was dropped using a pipette onto the pre-polished glassy carbon disk electrode, and then the ink was dried at room temperature.
2.3. Electrochemical measurement
The electrochemical tests were carried out using potentiostat (Princeton 2273, USA) with a typical
three-electrode cell. The working electrodes were prepared as above mentioned, and a platinum wire
was used as the counter-electrode and an Ag/AgCl (3M KCl filled) electrode as the reference electrode.
All experiments were conducted at room temperature. A 100mM KOH (pH=14) and a 50mM PBS
(pH=7) solution were used respectively as the alkaline and neutral electrolyte. The high-O$_2$ (dissolved
oxygen concentration was about 40mg/L ) and no-O$_2$ electrolytes were obtained by aeration of high
pure O$_2$ and Ar gas respectively for about 30min prior to measurements, and the low-O$_2$ electrolyte
obtained at natural no-aeration condition that consistent with the practical ACMFC environment
dissolved oxygen concentration is about 5–6mg/L). The cyclic voltammogram (CV) tests were
performed at the scan rate of 10mV/s and all potentials in this work were versus that of Ag/AgCl
electrode. Chronoamperometric responses was measured at -0.3V in an O$_2$-saturated 50mM PBS.

3. Results

3.1. Electrocatalytic activity of SDG in ACMFC environment
The ORR catalyst are commonly used in alkaline fuel cells (AFCs), proton exchange membrane fuel
cells (PEMFC) and direct methanol fuel cells (DMFCs), etc., in which the ORR occurred in an
alkaline media with sufficient O$_2$. And the catalytic activity for ORR catalyst is usually tested in O$_2$-
saturated 100mM KOH solution\[7, 9, 10\]. In such environment, the SDG synthesized in this work
showed catalytic activity for ORR close to Pt/C, evidenced in Figure 1 by the comparable peak current
densities of the two catalysts. The lower peak potential of SDG than Pt/C could be arising from its
lower surface area which was indicated by the much thinner CV profile for SDG than that for Pt/C.

In order to assessed the performance of SDG in ACMFC environment, i.e. neutral media with low
O$_2$ concentration, the CV tests were performed in a 50 mM unaerated PBS (pH=7.0, O$_2$ concentration
is consistent with that of normal influent of ACMFCs, i.e., 5–6mg/L). The peak current density of
SDG was surprisingly 4.5 times higher than that of Pt/C, thus indicating a much stronger catalytic
activity of SDG (Figure 2).

![Figure 1. CV curves for SDG and Pt/C in high-O$_2$ KOH solution (100mM).](image1)

![Figure 2. CV curves for SDG and Pt/C in low-O$_2$ PBS (50mM).](image2)

Since the changes of working conditions, i.e., the combined changes in oxygen concentration and
alkalinity from AFC-like environment to ACMFC environment, greatly deteriorates the performance
of Pt/C while causing nearly no damages on SDG, it would be interesting to further investigate which
of these two changes dominate the damage of Pt/C. As shown in Figure 3, either of these changes
dramatically decreased (up to 85% in both cases) the catalytic activity of Pt/C, while showing
ignorable adverse influence on SDG. It should be pointed out that no obvious peaks were observed in
O₂-free electrolyte (either alkaline or neutral) for both Pt/C and SDG, and this ensured the feasibility of using peaks of CV curves to characterize the catalytic activity for ORR.

Moreover, it is interesting to make a comparison between the SDG in this work with other S doped carbon catalysts in recent efforts. The SDG showed outstanding catalytic activity in terms of the peak potential and peak current density in CV test. The peak current density of SDG is higher than many other reports. However, there is few study about electrocatalytic activity of S doped carbon catalysts in neutral condition.

![Figure 3. The individual effect of oxygen concentration (a, b) and alkalinity (c, d) on the electrocatalytic activities of Pt/C and SDG.](image)

3.2. Electrocatalytic selectivity of SDG in ACMFC environment

By introducing glucose (a common anodic substrate in ACMFCs) into the neutral electrolyte, the catalytic selectivity of SDG in ACMFCs was investigated and the compared with that of Pt/C with the aid of chronoamperometric responses (i-t). As shown in Figure 4, the addition of glucose reversed the current density of Pt/C from reductive current (negative) to oxidative current (positive), indicating the very poor tolerance of Pt/C to the crossover in the ACMFC environment. However, SDG exhibited a better tolerance to the crossover of glucose, evidenced by the remained current density as high as 60% without current inverse.

Pt/C serves as both reduction and oxidation catalyst at the same time, resulting in the undesired oxidation of fuels by the oxygen at the cathode instead of the anode (i.e., fuels crossover). Such crossover effect would not only waste the fuel but also decrease the energy generation[16]. To reduce the internal resistance, generally there is no membranes in an ACMFC, i.e., the anode and the cathode are in the same chamber separated by the electrolyte, meaning that the anodic substrate could get to the surface of cathodic catalyst freely. Consequently, the performances of ACMFCs are greatly suffered from the crossover of anodic fuels. The good tolerance to the fuel crossover made SDG as a more favored ORR catalyst in ACMFCs than Pt/C. Further examination on other anodic substrates and
microbial metabolites in the electrolyte of ACMFCs, such as acetate, formate and lactate, is beyond the scope this study and will be conducted in future.

3.3. Electrocatalytic stability of SDG in ACMFC environment

![Figure 4](image4.png) **Figure 4.** Chronoamperometric responses of SDG and Pt/C electrodes upon the addition of 1 M glucose at 5000s in ACMFC environment.

![Figure 5](image5.png) **Figure 5.** Chronoamperometric responses of SDG and Pt/C electrodes in ACMFC environment.

![Figure 6](image6.png) **Figure 6.** XRD patterns of GO and SDG (a), XPS survey spectrum (b), high resolution XPS spectra of C1s (c) and S2p (d), and typical TEM image of SDG.

The stability, especially important for practical application of ACMFCs, was measured for SDG as a ORR catalyst using chronoamperometric method and also compared with that of Pt/C. It can be seen in Figure 5 that the current for SDG exhibited very slow attenuation, with the high relative current up to 99% persisted for more than 20000s. In contrast, the Pt/C electrode exhibited an apparent decrease, with a current loss of approximately 20% observed after 20000s. These results demonstrated that SDG has a better durability than Pt/C in ACMFC environment.
3.4. Micro characterization
As shown in Figure 6a, x-ray diffraction (XRD) powder pattern of SDG is very different from GO (peak at 10.5°) and demonstrates a prominent [002] peak at 26.5° and the other minor [100] peak at 43.3°, which is very similar to graphite powders[10]. The calculated d-spacing of [002] crystal plane is about 0.35 nm, slightly larger than the interlayer spacing in graphite (0.335 nm), implying the formation of high-quality graphene structures in SDG [11]. X-ray photoelectron spectroscopy (XPS) survey scans (Figure 6b) of SDG imply that the S atoms were indeed doped into the graphene with the contents of 1.1 at.%. And high-resolution XPS spectrum of the S2p exhibit two C-S peaks at 163.6 and 164.8 eV, respectively (Figure 6c). Corresponding to the S2p spectrum, the C1s spectrum consists of a C=O/C-S peak at 284.8 eV along with graphitic C-C (284.2 eV) and O=C-OH (288.7 eV) peaks (Figure 6d)[10]. In addition, Figure 6e showed a typical TEM image of SDG and transparent sheets with wrinkled and folded features are easily observed. The morphology is similar to that reported for reduced graphene oxide [17] and the partially crinkled nature may originate from the defective structures formed during the fabrication of GO and the heteroatom doping processes.

4. Discussion
The different catalytic properties between SDG and Pt/C, we believe, stem from their different underlying catalytic mechanism. For Pt/C, the catalytic activity for ORR is given by the moderate strength of the oxygen-metal bond interaction, which in turn depends on the position of the metal d states relative to the Fermi level[18]. For SDG, the increasing electronic spin density and charge density of graphene arising from the doping of sulfur play the key role in the high ORR activity of SDG[10, 12]. Unfortunately, a clearer explanation is still unknown and worth a great deal of study efforts in future.

Besides the good performances of SDG in ACMFCs, the other important finding in this work is that the ACMFC environment, i.e., low-O2 neutral electrolyte, greatly limits the electrocatalytic activity of Pt/C for ORR. This provide a convincing explanation to the recently reported (but unexplained) effective roll-pressed carbon black electrode in ACMFCs[19], even though carbon black is sluggish for ORR in normal condition. It is the low-O2 neutral electrolyte of ACMFC help the roll-pressed carbon black electrode become comparable to Pt/C electrode by deteriorating the latter.

5. Conclusions
SDG is a more favorable electrocatalyst for oxygen reduction than Pt/C in ACMFC environment because of its some apparent advantages. For example, (a) high catalytic activity. The peak current density of SDG was 4.5 times higher than that of Pt/C. (b) good tolerance to anodic substrates. After adding glucose, Pt/C occurred current inverse but SDG remained current density as high as 60% without current inverse. (c) excellent stability. After 20000s, SDG had the high relative current up to 99%, but Pt/C electrode exhibited a current loss of approximately 20%. The low-O2 neutral electrolyte seriously deteriorate the electrocatalytic activity of Pt/C for ORR in ACMFC environment. In addition, Many efforts should be paid to explore about electrocatalytic activity of S doped carbon catalysts in neutral condition.

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