international journal of hydrogen energy XXX (2018) I-6



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#### **Short Communication**

# Poison tolerance of non-precious catalyst towards oxygen reduction reaction

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#### ARTICLE INFO

Article history: Received 9 December 2017 Received in revised form 9 March 2018 Accepted 20 March 2018 Available online xxx

Keywords: Microbial fuel cell Poison tolerance Oxygen reduction reaction Sulfion Ammonium

#### ABSTRACT

Oxygen reduction reaction (ORR) plays an important role in microbial fuel cell (MFC) performance. But the poison ions in wastewater may have a considerable effect on the activity of ORR catalysts. In this paper, we herein investigated the effect of typical  $NH_4^+$  and  $S^{2-}$  ions on the activity of different ORR catalysts, such as biomass derived carbon (bamboo charcoal (BC)), nitrogen doped graphene (N-G), iron/nitrogen co-doped graphene (Fe/N-G) and Pt/C catalysts. The results showed that the ORR catalytic activity was decreased in the presence of both  $NH_4^+$  and  $S^{2-}$  ions. In detail, the  $NH_4^+$  ion only had a slight and similar effect on the catalysts. However, the effect of  $S^{2-}$  on catalyst activity was much more negative, compared to that of  $NH_4^+$ . Notably, the BC, N-G and Fe/N-G catalysts exhibited a higher poison tolerance than Pt/C, indicating that BC, N-G and Fe/N-G catalysts could serve as poison tolerance ORR catalysts in both of  $NH_4^+$  and  $S^{2-}$  condition.

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#### Introduction

Oxygen reduction reaction (ORR) was crucial for energy conversion and storage in bioelectrochemical systems such as microbial fuel cells (MFCs), the majority of MFCs use oxygen as the cathode electron acceptor. ORR in cathode is mainly limited by high overpotential and slow reaction kinetics [17]. To address this issue, many efforts have been devoted to develop a highly active catalyst towards four-electron ORR. To date the benchmarks catalyst for ORR cathode is usually platinum (Pt), though its high cost has induced a dense research for alternative catalysts. A further weakness of Pt as ORR catalyst is its low poison tolerance in practical operation. Researches have demonstrated that the performance of the fuel cell would drop if the Pt catalysts exposed to parts per million of common poison species e.g. sulfur dioxide, hydrogen sulphide, nitrous oxides, aromatic hydrocarbons etc. [9,16].

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A group of alternatives such as carbonaceous or metalbased catalysts have so far been the most widely utilized catalysts for ORR. The carbonaceous catalysts exhibit interesting properties that make them feasible for practical

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Please cite this article in press as: Yang W, et al., Poison tolerance of non-precious catalyst towards oxygen reduction reaction, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.03.135

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https://doi.org/10.1016/j.ijhydene.2018.03.135

applications. The most notable characteristics of these catalysts for improving ORR process are undoubtedly their high surface area, high electrical conductivity, low cost and durability in operation, which are beneficial for real commercialization. Carbonaceous materials such as activated carbon, carbon nanotubes, graphene and other carbonaceous materials have been widely reported as cathode catalysts [19]. Transition metal-based catalysts represent another avenue of exploration followed by the MFC field. Generally, transition metals are earth-abundant, inexpensive and considerable catalytic activity. These catalysts, such as manganese oxides, cobalt oxides and iron oxides, have been shown to be remarkably insensitive against CO, methanol, chloride etc., making them serve as interesting alternatives to Pt [21,22].

Recently, many researches have shown that the specific operation conditions in MFCs could cause further strong limitations on the ORR. Generally, Pt catalyst can achieve a higher catalytic activity than that of carbonaceous catalyst in phosphate buffer solution (PBS), but its performance would be severely deteriorated and only exhibited a comparable or even lower performance compared to carbonaceous catalyst under MFC relevant condition [15]. It was reported that various pollutants or ions are naturally and commonly present in wastewater, several of these were mainly related to  $S^{2-}$ , NH<sub>4</sub><sup>+</sup> etc., which were well known to negatively cause the severe performance loss of proton exchange membrane (PEM) fuel cell [10]. Work by Halseid et al. also showed that the presence of ammonium significantly decreases the ORR activity of polycrystalline Pt catalyst [3]. This was probably due to the reason that the poison species (such as  $S^{2-}$  and  $NH_4^+$ ) absorbed on the surface of catalyst would cover the active sites or compete the active sites with oxygen, resulting in a decrease of the available catalytic active sites and catalytic activity in a relatively short time [14]. Notably, the previous studies have shown that the ammonium is one of the most important inorganic compounds in wastewater or agricultural wastes, especially in urine contained wastewater [4,6]. On the other hand, it is also known from the literature that sulfaterich wastewaters are commonly from animal husbandry, mining, food processing, pharmaceutical industry, pulp and paper wastewater etc., the sulfide (such as hydrogen sulphide) can be produced as reduzate by the complex biological reduction process in bioelectrochemical systems [7,12,23]. And, dissolved sulfide and hydrogen sulfide are also commonly found in petrochemical processing wastewater [20]. Since the sulfide and ammonium have been reported as poison species for Pt catalysts, the poison tolerance of ORR catalysts is a crucial design metric in the practical wastewater treatment.

So far, alternative MFC ORR catalysts were usually studied exclusively from the performance point of view, the poison tolerance rarely being explicitly addressed in MFC relevant conditions. In this paper, we mainly aim to evaluate the effect of typical  $NH_4^+$  and  $S^{2-}$  ions on the ORR activity of the biomass derived carbon (bamboo charcoal (BC)), nitrogen doped graphene (N-G), iron/nitrogen co-doped graphene (Fe/N-G) and Pt/C catalysts. The effect of the poison species on half-wave potential, limiting oxygen reduction current densities and stability is discussed in pH neutral condition.

#### Material and methods

#### Preparation of catalysts

Graphene oxide was prepared via a modified Hummer's method [18]. Iron phthalocyanine (FePc) used for synthesis was from Shanghai Titan technology co. LTD (China). The nitrogen doped graphene (N-G) was prepared by heat treating graphene oxide at 700 °C within a quartz tube for 3 h under NH<sub>3</sub> atmosphere. Iron/nitrogen co-doped graphene (Fe/N-G) was prepared from a mixture of FePc and graphene oxide via pyrolysis at 700 °C as previously described [22]. The Pt/C catalyst (20 wt.%, Alfa Aesar Chemical Co., LTD, China) was used as purchased. The bamboo charcoal (BC) as a biomass derived carbon was prepared as previously described [17].

#### **Electrode** preparation

Prior to use, the glassy carbon (GC, BAS.inc., Japan) electrode was first polished with 0.05  $\mu$ m Al<sub>2</sub>O<sub>3</sub> powders, followed by rinsing with deionized water. The catalyst ink was prepared by dispersing 2 mg of the catalyst samples (BC, N-G, Fe/N-G, Pt/C) in a mixture containing 1.9 mL of isopropyl alcohol and 0.1 mL of Nafion solution (5 wt.%, Shanghai Hesen, China), followed by stirring and ultrasonic treatment for 15 min respectively. Then the electrode was prepared by dropping the catalyst ink (10  $\mu$ L) onto the top of the GC electrode and drying at room temperature.

#### Electrochemical tests

The electrochemical tests were performed using an electrochemical workstation (ParSTAT MC, Princeton, USA). A three compartment electrochemical glass cell was used for the aqueous electrochemical tests, in which a Pt wire served as the counter electrode and an Ag/AgCl (saturated with KCl) electrode served as the reference electrode, the prepared GC electrode was used as working electrode. The rotating disk electrode (RDE) tests were conducted using a RRDE-3A Rotating Ring Disk Electrode (ALS Co., Ltd, Japan). The experiments were performed in nitrogen-sparged growth medium and oxygen-sparged solution, respectively. To obtain a current response that only contains faradic current, the current obtained under nitrogen-sparging was subtracted from that obtained under oxygen-sparging. For the linear sweep voltammetry (LSV) tests, the potential of the working electrode was scanned from 0.4 to -0.6 V vs. Ag/AgCl at 10 mV s<sup>-1</sup> and at 2500 rpm. The effect of NH<sub>4</sub><sup>+</sup> and S<sup>2-</sup> on the ORR performance was studied in a concentration range from 1 to 50 mM and from 1 to 4 mM, respectively. The concentration ranges mainly came from relevant previous researches [9,11,14], reflecting the practical conditions in MFCs as far as possible. The nature of the used poison species may be different from those in actual bioelectrochemical systems in some degree.

The potentials reported in this study were the values vs. the Ag/AgCl electrode, unless otherwise noted. All

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