



# Electrochemical Oxidation of Sulfur Dioxide on Nitrogen-Doped Graphite in Acidic Media



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## ARTICLE INFO

### Article history:

Received 2 December 2014

Received in revised form 28 February 2015

Accepted 25 April 2015

Available online 28 April 2015

### Keywords:

Electrochemical oxidation

Sulfur dioxide

Nitrogen-doped graphite

Electrocatalyst

Rotating disk electrode

## ABSTRACT

This work reports on the electrochemical oxidation of sulfur dioxide on nitrogen-doped graphite (NG) in acidic media. The NG samples were prepared via one-step pyrolysis of the mixtures of sugar and urea at 700–1000 °C in argon atmosphere. Mechanism analysis indicated that the electrochemical oxidation reaction of sulfur dioxide on NG was irreversible and diffusion controlled. Moreover, the influence of pyrolysis temperature on the electrocatalytic activity of NG was also investigated. The electrochemical measurement and physical characterization results revealed that elevating the pyrolysis temperature could enhance the electrocatalytic activity of NG, which might ascribe to the improved surface area, graphitization degree and electrical conductivity.

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## 1. Introduction

The electrochemical oxidation of sulfur dioxide has been concerned over last few decades for its potential applications involved in flue gas desulfurization [1–3], water splitting for hydrogen production [4–8], electrochemical sensing of sulfur oxides [9,10], and electrochemical filter for proton-exchange membrane fuel cells [11]. Although the reaction is thermodynamically favorable, it does not occur at a significant rate by itself because of the sluggish kinetics [12]. Therefore, advanced electrocatalyst which can improve the reaction rate with low overpotential is necessary.

Noble metals, such as Pt and Au, have been extensively studied and identified as effective electrocatalysts [13–18]. However, the high cost hinders their large-scale applications. Metal macrocycles complexes also have electrocatalytic activity for sulfur dioxide electrochemical oxidation [2,19,20]. Nikolov et al. [2] demonstrated that sulfur dioxide can be electrooxidized on cobalt phthalocyanine modified active carbon electrodes in the presence of air without external current. Bolade and Tebello [19] considered that metallophthalocyanines complexes (CoPcs FePcs and MnPcs) were

active catalysts for sulphite electrochemical oxidation due to the metal based redox processes. But metal macrocycles complexes are usually complicatedly to fabricate so that they are not suitable for large-scale application. Another kind of catalysts for sulfur dioxide electrochemical oxidation is carbon material, while they are regarded as poor catalysts due to the high overpotentials [21–23]. Dribinskii [21] considered that sulfur dioxide was oxidized on graphite with adsorbed hydroxyl species at potentials above 1.24 V. Hunger and Lopicque [22] produced an exhaustive study of the oxidation of S(IV) oxyanions on natural and impregnated graphite in neutral and alkaline media. They found the oxidation of S(IV) relating to the surface oxidable intermediates. Quijada and Vázquez [23] studied sulfur dioxide oxidation on glassy carbon electrodes and found the oxidation started at 1.0 V while a wave centered at 1.4–1.5 V.

In recent years, nitrogen-doped carbon materials have been widely used in the field of electrochemical energy storage and conversion [24–26]. Researchers have demonstrated that electrochemical properties of carbon materials can be significantly enhanced by introducing electron-rich nitrogen atoms into the structure [27,28]. However, there has been few reports about nitrogen-doped carbon materials used as electrocatalysts for sulfur dioxide electrochemical oxidation.

In this work, we fabricated nitrogen-doped graphite (NG) via one-step pyrolysis of sugar and urea used as carbon and nitrogen

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sources. The obtained NG samples were investigated as electrocatalysts for sulfur dioxide electrochemical oxidation in acidic media as many other researchers did. In order to make a comparative evaluation, commercial 50% Pt/C and XC-72 were served as references. The mechanism about electrochemical oxidation of sulfur dioxide on NG samples were also proposed.

## 2. Experimental

### 2.1. Preparation of NG

The NG samples were synthesized following a procedure in the literature [26]. Sugar and urea were used as carbon and nitrogen precursors. Firstly, 100 mg sugar and 6 g urea were dispersed uniformly in 6 mL ultrapure water by agitating vigorously for 30 min. Then the mixtures were dried on the heating stage at 60 °C for 12 h. Finally, the dry mixtures were heat-treated at various temperatures ranging from 700 to 1000 °C for 1 h under argon flow and then cooled down to room temperature naturally. These samples were denoted as NG700, NG800, NG900 and NG1000. The number represents the temperature of heat treatment.

### 2.2. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three-electrode cell on an electrochemical workstation (CHI 630D) with a rotating disk electrode system at room temperature. A sample of nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> was used as background electrolyte. The working electrolyte was prepared by dissolving 0.005 M anhydrous Na<sub>2</sub>SO<sub>3</sub> in nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. Platinum foil and saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. Working electrode was prepared as follows. Well-dispersed catalyst ink was made by mixing 2 mg catalyst (NG, commercial

50% Pt/C, and XC-72 respectively) with 50 μL Nafion (Du Pont Corp., 5 wt.%) and 1 mL isopropanol. Then the prepared catalyst ink of 10 μL was dropped on a glassy carbon electrode (GCE, 4 mm in diameter) and dried in air at room temperature. All potentials in this paper are referred to standard hydrogen electrode (SHE).

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques on a rotating disk electrode (RDE) were used to evaluate the sulfur dioxide electrochemical oxidation activity of the prepared NG catalysts. In cyclic voltammetry measurements, the background capacitive currents were recorded by scanning the working electrode between 0 and 1.4 V at a scan rate of 50 mV s<sup>-1</sup> in background electrolyte. Then cyclic voltammograms were measured in the working electrolyte at series of scan rates. For linear sweep voltammetry tests, the working electrode was scanned from 0.5 to 1.4 V at a scan rate of 5 mV s<sup>-1</sup> in the background electrolyte and working electrolyte. The electrode rotation speed was 1600 rpm. The sulfur dioxide oxidation current was corrected by the background current. Especially, the surface of the catalysts was clean by scanning the working electrode between 0 and 1.4 V at a scan rate of 100 mV s<sup>-1</sup> for 6 cycles of cyclic voltammetry in the background electrolyte before recording.

### 2.3. Physical characterizations

The morphology was characterized by transmission electron microscopy (TEM, JEOL JEM-2000EX). The surface area was measured with nitrogen absorption/desorption conducted at 77 K and calculated with BET method (BET, Micromeritics ASAP 2010). The crystalline structures were characterized by X-ray diffraction (XRD, Rigaku D/max-2500PC). Raman spectra were collected on a Raman spectrometer (Jobin Yvon LabRAM HR800) using 532 nm laser. Chemical compositions were analyzed with X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi).

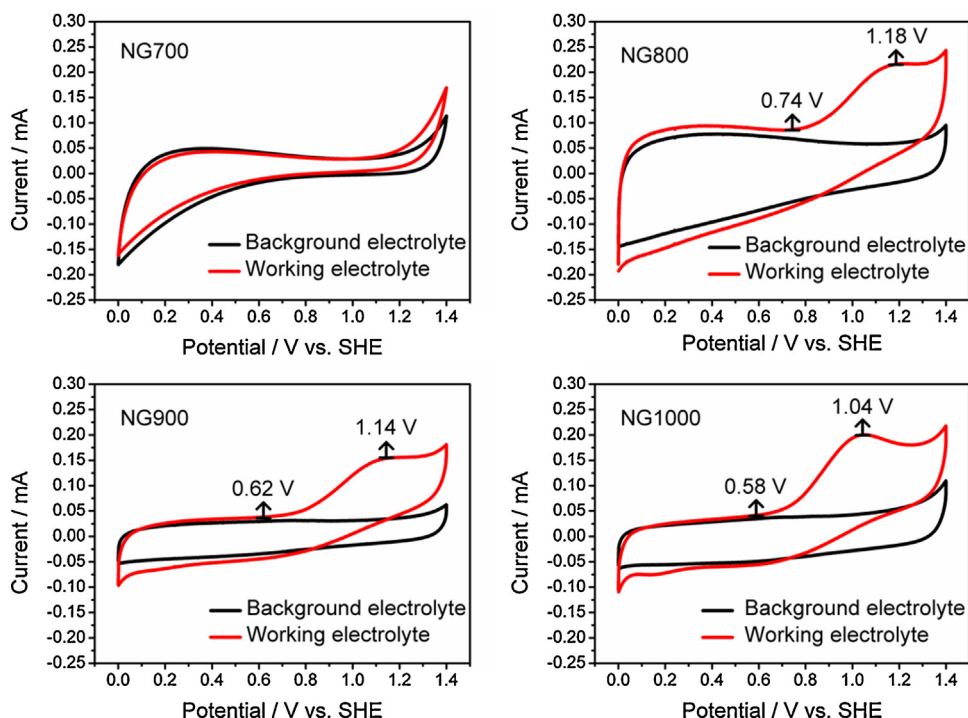


Fig. 1. CV curves of NG700, NG800, NG900 and NG1000 in background and working electrolyte at a scan rate of 50 mV s<sup>-1</sup>.

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