



The Effect of Annealing Temperature on Nickel on Reduced Graphene Oxide Catalysts on Urea Electrooxidation



Dean E. Glass, Vicente Galvan, G.K. Surya Prakash*

Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, 837 Bloom Walk, Los Angeles, CA, 90089, United States

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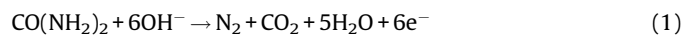
ABSTRACT

The annealing temperature effects on nickel on reduced graphene oxide (Ni/rGO) catalysts for urea electrooxidation were investigated. Nickel chloride was directly reduced in an aqueous solution of graphene oxide (GO) followed by annealing under argon at 300, 400, 500, 600, and 700 °C, respectively. X-ray Diffraction (XRD) patterns revealed an increase in the crystallite size of the nickel nanoparticles while the Raman spectra displayed an increase in the graphitic disorder of the reduced graphene oxide at higher annealing temperatures due to the removal of oxygen functional groups. The Ni/rGO catalysts annealed at higher temperatures displayed oxidized nickel surface characteristics from the Ni 2p X-ray Photoelectron Spectra (XPS) due to the oxidation of the nickel from the oxygen functional groups in the graphitic lattice. In the half-cell testing, the onset potential of urea electrooxidation decreased while the urea electrooxidation currents decreased as the annealing temperature was increased. The nickel catalyst annealed at 700 °C displayed a 31% decrease in peak power density while the catalyst annealed at 300 °C displayed a 13% increase compared with the unannealed Ni/rGO catalyst in the micro direct urea/hydrogen peroxide fuel cells tests.

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1. Introduction

With the continuing increase in energy consumption worldwide, novel methods of generating and storing energy are necessary to keep up with the increasing demand. One particular energy generation method is from fuel cells utilizing liquid-based reactants such as formic acid [1,2], methanol [3–5], and hydrazine [6]. Compared to fuel cells that employ gas-based reactants, liquid-based fuel cells can efficiently store and transport reactants with minimal changes required to the existing infrastructure [7]. Another type of fuel that has recently attracted attention for use in liquid-based fuel cells is urea, which is soluble in aqueous medium. Urea can be electrochemically oxidized in the alkaline media based on the following equation [8]:



Urea is most commonly found in human and animal waste at around 2 wt% [9], and is currently being manufactured in large quantities from ammonia as a fertilizer. Its high energy density (16.9 MJ L⁻¹) and relatively high hydrogen content (10.1% weight)

[9,10], make it an enticing candidate as both a potential hydrogen carrier source and fuel.

Numerous studies have shown that nickel is the prime metal electrocatalyst for urea oxidation. Many different morphologies of nickel have been synthesized in order to gauge and optimize the urea oxidation activity including nickel oxides [11,12], hydroxides [13,14], nanoparticles [10,15], and foam [16]. One of the ways to enhance the activity of metal catalysts such as nickel is by employing a catalyst support. The support is often employed to effectively disperse the catalyst nanoparticles as well as to add synergistic effects on the electronic structure of the catalyst. Some of the catalyst supports that are currently being explored are carbon nanotubes [17,18], carbon blacks [19], and metal supports [20]. One of the most widely studied supports in the past decade has been graphene. Graphene has attracted significant attention due to its promising characteristics such as high surface area [21], charge carrier mobility [22], capacitance [23], and functionalization ability [24]. Due to this, graphene can be implemented in a wide variety of applications such as batteries [25,26], capacitors [27,28], and sensors [29,30].

The Direct Urea Fuel Cell (DUFC) has attracted much attention as a potential new type of fuel cell based on the electrooxidation of urea in the alkaline conditions. One of the advantages of the DUFC is the ability to employ non-noble metal catalysts such as nickel and manganese for the oxidation and reduction reactions, respectively.

* Corresponding author.

E-mail address: gprakash@usc.edu (G.K. S. Prakash).

This differs from some of the other liquid-based proton exchange membrane (PEM) fuel cells such as Direct Methanol Fuel Cells (DMFCs) which require platinum- and ruthenium-based catalysts [3,31], and Direct Formic Acid Fuel Cells (DFAFCs) which require palladium-based catalysts [32] for the reaction at the anode. The alkaline environment in which DUFCs are also run in do not require the use of platinum for the oxygen reduction reaction (ORR) at the cathode [33]. However, anion exchange membranes (AEMs) are not as optimized and commercially manufactured as the present proton exchange membranes (PEMs). More recently, membraneless micro fuel cells have been studied to eliminate the use of a membrane [34]. Paper-based fuel cells have recently emerged as a more cost effective alternative to traditional membrane electrode assembly (MEA)-based fuel cells for testing catalysts [35]. The intrinsic properties of paper/porosity and capillary action remove the need for external pumps and membranes. Moreover, the use of paper allows for facile manipulation of cell design. Another advantage is the use of small volumes of fuel, thus allowing for urine to be a more practical source of urea. This can further be implemented for urea sensors in urine testing. A more recent form of the DUFC is the direct urea/hydrogen peroxide fuel cell [36–38]. The hydrogen peroxide is reduced at the cathode compartment from the following equation [38]:



This type of fuel cell has just recently started to be studied for the urea electrooxidation performance and displays much promise.

Various types of urea fuel cells hold much promise for various energy devices and sensor applications. In previous studies, nickel salts were reduced onto graphene oxide in a variety of ways, which led to increased urea oxidation activity [15,39]. However, there is much optimization that is required for nickel-based catalysts in both the metal structure as well as the support. One of the various catalyst treatment types is annealing that can influence metal catalyst and support structure morphology. This can affect the oxidation properties of the catalyst. In this study, we examine the effects of annealing temperature on the catalytic performance of nickel on reduced graphene oxide catalysts for urea oxidation activity and incorporate for the first time an inexpensive paper-based a micro direct urea/hydrogen peroxide fuel cell to assess the overall urea electrooxidation activity.

2. Experimental

2.1. Catalyst Preparation

Graphene oxide (GO) was synthesized via the modified Hummer's method [40]. Briefly, 2.0 g of graphite powder (325 mesh, 99.8%, Alfa Aesar) was added to 50 mL anhydrous sulfuric acid (Macron) and stirred for one hour. 5.0 g of potassium permanganate (Macron) was then added and the solution was stirred in the ice bath for two hours followed by heating in an oil bath at 40 °C for another hour. Then, 100 mL of Millipore water (Direct-Q UV, 18.2 MΩ) and 15 mL of 30% hydrogen peroxide (Macron) was added to terminate the reaction. The GO was vacuum filtered and washed three times with a 10% HCl solution and then five times with Millipore water before being dried in an oven at 80 °C.

The nickel on reduced graphene oxide (Ni/rGO) catalysts were synthesized via an aqueous-based reduction method. Briefly, 0.75 g of the previously synthesized GO was dissolved into 200 mL Millipore water and vigorously stirred and sonicated for one hour. Then, 3.0374 g of NiCl₂·6H₂O was dissolved into 100 mL Millipore water and added to the GO solution in order to obtain a 50%-wt nickel catalyst loading. 30 mL of hydrazine hydrate solution (24-

26%, Sigma-Aldrich) was added dropwise to the solution and the pH was adjusted to 10 by adding a 3.0 M aqueous sodium hydroxide solution. The solution was then heated to 80 °C in an oil bath for one hour and then centrifuged and washed with Millipore water until the supernatant reached a pH of 7. The Ni/rGO catalysts were then annealed at 300, 400, 500, 600, and 700 °C, respectively under argon for five hours (the catalysts will be referenced as Ni/rGO- followed by the annealing temperature for the remainder of the paper). An unsupported nickel catalyst was also synthesized in the same manner with an aqueous-based reduction from the NiCl₂·6H₂O salts.

2.2. Catalyst Characterization

For all of the characterization methods, pristine catalyst samples were used. Powder X-Ray Diffraction (XRD) measurements were performed on a Rigaku X-Ray diffractometer using a Cu-Kα (0.154056 nm) radiation source with a scan rate of 6° min⁻¹ from a 2θ value of 10° to 90°. X-Ray Photoelectron Spectroscopy (XPS) measurements were taken on a Kratos Axis Ultra with a Monochromatic Aluminum X-Ray radiation source. Raman measurements were performed on a Horiba XploRA ONE Raman microscope with a 532 nm wavelength laser excitation. Scanning Electron Microscopy (SEM) images were taken on a JEOL JSM-7001F electron microscope with an acceleration voltage of 15 kV. Transmission Electron Microscopy (TEM) images were taken on a JEOL JEM 2100F with an acceleration voltage of 200 kV.

2.3. Electrochemical Measurements

A standard rotating disk electrode (RDE) setup was used for the half-cell tests. The measurements were taken on a Solartron SI 1287 Potentiostat and analyzed using Corware Software. Catalyst ink solutions were prepared by adding 5 mg of catalyst to a 1 mL solution consisting of 10% isopropyl alcohol, 90% Millipore water, and 10 mg of 5% Nafion[®] solution (Ion Power). The solution was sonicated and 20 μL was pipetted onto a glassy carbon electrode (Pine Instruments, 0.195 cm² active surface area) yielding a nickel loading of around 0.1 mg cm⁻². The electrode was dried and placed in a three cell testing system with the RDE as the working electrode, a platinum wire as the counter electrode, and a mercury oxide (MMO, 4.24 M KOH filling solution) reference electrode. The cell was purged with ultra-pure argon (99.999%) for 15 min before electrochemical testing

2.4. Micro Direct Urea/Hydrogen Peroxide Fuel Cell Assembly and Testing

The micro fuel cell was fabricated by cutting strips of filter paper (Whatman) in the "Y" shape as shown in Fig. S4. Catalyst ink solutions were formulated with a 1:9:1 composition of catalyst: Millipore water: anionomer solution (Tokuyama anionomer, AS-4, 5% weight in 1-propanol). Two filter paper strips were aligned and the catalyst ink was sonicated and painted on both sides of the anode side of the electrode with an active surface area of 0.125 cm². Colloidal graphite was used as the cathode catalyst and prepared with the same catalyst ink composition and surface area as aforementioned. Strips of stainless steel mesh were wrapped around the catalysts ink and the micro fuel cell briefly pressed to ensure efficient connectivity between the catalyst ink and the potentiostat wires.

The micro fuel cells were tested by immersing the anode compartment into a solution of 6.0 M KOH and 0.33 M urea and the cathode compartment into a 30% hydrogen peroxide solution (Millipore). The polarization curves were taken on a Solartron

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