Feature Article

Iron functionalization on graphene nanoflakes using thermal plasma for catalyst applications

U. Legrand*, J.-L. Meunier, D. Berk

Plasma Processing Laboratory (PPL), McGill University, Chemical Engineering, Montréal, Québec, Canada

ABSTRACT

Graphene nanoflakes (GNFs), a stack of 5–20 layers of graphene sheets, are generated here using methane decomposition in a thermal plasma followed by homogeneous nucleation of the 2-dimensional structures in the gas stream. The GNFs are functionalized with nitrogen and iron to improve their electrocatalytic activity. The iron functionalization step is carried out as a post-processing step within the same thermal plasma reactor used to grow the nanoparticles. Two different iron precursors are tested in the reactor, iron powder and iron (II) acetate solution. The iron source carried by a nitrogen flow is injected in the argon plasma, and parameters such as the plasma power, pressure, and the exposure time during functional-ization are optimized for enhanced catalyst activity. Structure and composition of the resulting catalysts are characterized, and their electrocatalytic performances in terms of onset potential, half wave potential and current density show an increase compared to the non-functionalized GNFs. This study proves the ability to entirely produce a pure and highly crystalline graphene-based non-noble metal catalyst using a thermal plasma single batch process with simple precursors such as methane and nitrogen gas, and an iron powder or iron acetate solution.

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1. Introduction

Fuel cells, and more particularly alkaline fuel cells (AFCs) form promising energy conversion devices already found in diverse applications, such as transport and portable electronic devices [1]. Based on the oxidation of hydrogen with oxygen or other oxidizing agents, they present the advantage of releasing water vapour as a product without any pollutants. One key component in AFCs is the catalyst that enables the hydrogen oxidation, and more particularly the oxygen reduction to occur at the low temperature of the device, typically 80 °C. Platinum still outperforms any other catalyst material, the drawbacks being price and availability [2]. Generally the oxygen reduction reaction (ORR) is the limiting factor in AFCs, and requires most of the overall catalyst loading. Decreasing the price of the catalyst is thus one of the major issues that needs to be addressed to allow AFCs to reach larger markets. This can be achieved by reducing the amount of platinum used or by replacing the platinum with a cost effective non-noble metal catalyst (NNMC) [3–8], which is resistant to corrosion.

The present research on NNMCs is mainly based on the enhancement of the electrocatalytic activity of nitrogen functionalized carbon-based matrices by the addition of iron. Iron atoms can first form catalytic sites when linked by four to six atoms of nitrogen to the carbon support; such active sites were studied by Jasinski more specifically for the activity of iron and cobalt phthalocyanine towards the ORR [9], while Kramm et al. evaluated and proposed possible active configurations of the Fe/N/C sites [10]. Unfortunately, it is very difficult to identify with certainty the presence of such sites in catalysts material. Iron can also be found in the form of iron oxide nanoparticles, which also catalyses the ORR [11]. Whether atomically dispersed catalytic sites or iron oxide nanoparticles are the active elements in the catalysts, the carbon-based matrix has to be resistant to corrosion and electrically conductive. Graphene materials provide good conductivity as well as resistance to corrosion from their relatively small defect concentrations, and so form excellent structures to support nitrogen-iron based functionalities and/or iron oxide nanoparticles [12–14].

Highly crystalline graphene has been shown to be the best candidate for the ORR because of its resistance to both acidic and basic environments, and its high electrical conductivity [15]. A common method to produce graphene is by the reduction of graphene oxide obtained by the exfoliation of graphite, resulting in a graphene containing a large number of defects in its crystalline structure [16].

Preparation of the graphene structure as a catalyst support material using for example the method developed by Proietti et al. [17] also generates additional defects in the structure, defeating the purpose of getting a highly crystalline graphene.

The present work intends to introduce a new and original method for the synthesis of a complete non-noble metal catalyst using a high temperature thermal plasma reactor. Introduction of iron to nitrogen functionalized graphene nanoflakes (N-GNFs) for producing active ORR catalysts has been demonstrated by Pascone et al. using a wet-chemical method as a post-production step [18]. One objective of the present paper is to take advantage of the high reactivity of the plasma environment in the GNFs synthesis phase and produce a ready-made iron catalyst in a single batch process. The reactor is first used to grow the graphene structure through homogeneous nucleation from the gas phase, as proposed by Pristavita et al. [19,20] in the production of the GNFs. It has been shown that nitrogen can be added to GNFs within the thermal plasma system resulting in low (∼2 at% using the GNF nucleation stage) and high (∼25 at% using the downstream afterglow plasma) functionalization levels [21]. Up to 70% of the overall nitrogen was found to be attached through pyridinic or pyrrolic sites on graphene in a similar way to the phthalocyanine structure [21]. The GNFs maintained a good crystalline structure after the different functionalization steps with both low and high contents of nitrogen.

The present study mainly focusses on testing and optimizing a second *in situ* post-synthesis step, namely the addition of iron to the N-GNFs structures within the same plasma reactor. The optimal conditions used for GNFs growth and nitrogen functionalization steps are maintained as defined in previous work [20]. Two sources of iron are tested here following the growth and the nitrogen functionalization of GNFs, these being (a) iron powder and (b) iron (II) acetate solution, both using nitrogen as a carrier gas. Experimental tests are performed under different operating conditions within the reactor in order to achieve both nitrogen and iron functionalization on the GNFs (N/Fe-GNFs) within a single overall batch process made without opening the reactor. The resulting materials are then characterized for the structure of the graphitic material, the atomic composition of the sample surface, and the activity in the ORR.

2. Experimental methods

2.1. Catalyst generation

The generation of GNFs following Pristavita et al.'s procedure [20] uses methane as a carbon source that is decomposed within an argon thermal plasma. The argon thermal plasma is generated by an inductively coupled plasma (TP-ICP) torch, with a power of 20 kW delivered to the torch while the pressure within the reactor is 55.3 kPa. GNFs are formed as small nuclei through homogeneous nucleation. Modelling studies provide indications that GNFs essentially grow laterally in a sheet-like geometry within a very narrow nucleation and growth temperature window of 3700–4900 K in the plasma decay zone [22]. The nanoparticles are deposited on the walls and at the end plate downstream of the reactor, these deposits being further functionalized in the plasma recombination zone. The experimental reactor is axisymmetric with respect to the flow pattern, including the exit flow that extends radially from the downstream endplate. This provides a very good match with the modelled 2-D geometry, and an experimental flow pattern having a true stagnation point flow geometry with no recirculation loops throughout the reactor [22]. A small amount of nitrogen is added during the growth, leading to nitrogen content up to 2 at% on the surface of the GNFs.

As indicated above, iron is added in two different forms by switching off the methane gas feeding and introducing the iron source without opening the reactor. The main tested parameters during the functionalization step are the type of iron source (powder or iron acetate solution), the pressure within the reactor, the power delivered to the ICP torch, and the exposure time to the iron vapour.

The first iron source is a mixture of two iron powders fed to the reactor using a PFV100-VM-NO powder feeder from Tekna. A mixture is used because large iron particles with a size range between 10 and 300 μm are easy to feed continuously but difficult to vaporize while small iron particles between 1 and 10 μm are easy to vaporize but difficult to feed; mixing the powders takes advantage of both aspects, i.e. a continuous feeding and a good rate of vaporization. The optimized amount of small particles is 30 wt% (weight percent) of the total weight of iron powder injected within the reactor. A flow of 1 slpm of nitrogen has been chosen in order to carry the flow rate of 10 mg/min of iron particles from the powder feeder to the reactor and help the implementation of iron atoms on the GNFs surface. The iron particles are injected in the plasma zone, 9 cm downstream of the ICP torch nozzle using a side port on top of the reactor. This type of injection overcomes difficulties of particle transport within the injecting probe of the ICP torch.

The second source of iron is a ferrous acetate solution at a concentration of 1 mg/mL. The introduction of 10 mL of this solution is made using a 20 mL stainless steel syringe from Chemyx, using a Nexus 3000 pump, delivering the solution at a flow rate of 1 mL/min. The liquid is carried to the reactor using a flow rate of 1 slpm of nitrogen. In contrast to the iron particles, the ferrous acetate solution is fed through the injection probe of the ICP torch in the core of the plasma. It is expected that the difference in location of the iron source injection has a minor influence on the resulting vaporization, both streams being effectively injected within a relatively large volume having a temperature field range of 6500–7500 K occurring downstream of the torch nozzle [16]. In contrast, the physical state of the precursors in the form of a liquid solution or solid particles is dominant in controlling the quantity of iron vapour generated in the stream. Because of practical injection considerations generating different iron mass feeds, the amounts of iron vapour generated from the two sources are different. Also, it is expected that the level of iron functionalization is going to differ from one iron source to the other.

Two specific conditions for the power delivered to the ICP torch as well as the pressure within the reactor are chosen, namely 20 kW/55.3 kPa (8 psia) and 25 kW/13.8 kPa (2 psia). These were established through the theoretical modelling of the temperature and flow fields in the reactor showing that these two pairs of values presented similar temperature distribution profiles with the core of the plasma jet in the ICP torch reaching 10,000 K, and the walls of the reactor being cooled at 300 K [22]. The main difference between the two power/pressure conditions is in the velocity profiles. The maximum calculated velocity of the plasma, 160 m/s in the 13.8 kPa case, is four times greater than that in the 55.3 kPa case [23]. It is expected that the difference in the velocities and consequently in the residence time of the excited species in the plasma recombination zone would influence the iron functionalization of the GNFs. Also, the exposure time of the GNFs to the iron vapour is expected to be a key factor in the iron functionalization step. A short exposure time would lead to an insufficient amount of catalytic sites generated while a long exposure time could overload the samples with iron when considering the limited amount of the nitrogen-based host sites. The overall tested conditions are summarized in Table 1.

2.2. Physical characterization

The structure of the N/Fe-GNFs was studied using Scanning Electron Microscopy (SEM) on a FEI Inspect F-50 FE-SEM and Transmission Electron Microscopy (TEM) on a FEI Tecnai G2 F20 200 kV