



Low cost iodine intercalated graphene for fuel cells electrodes



Adriana Marinoiu^{a,*}, Mircea Raceanu^{a,b}, Elena Carcadea^a, Mihai Varlam^a, Ioan Stefanescu^a

^a RD Institute for Cryogenics and Isotopic Technologies- ICIT, 4 Uzinei St., Rm Valcea, Romania

^b University Politehnica of Bucharest, 313 Splaiul Independentei, Bucharest, Romania

ARTICLE INFO

Article history:

Received 30 October 2016

Received in revised form 26 January 2017

Accepted 27 January 2017

Available online 31 January 2017

Keywords:

Iodine doped graphene

Catalyst

Fuel cell

ABSTRACT

On the theoretical predictions, we report the synthesis of iodine intercalated graphene for proton exchange membrane fuel cells (PEMFCs) applications. The structure and morphology of the samples were characterized by X-ray photoelectron spectroscopy (XPS) analysis, specific surface area by BET method, Raman investigations. The presence of elemental iodine in the form of triiodide and pentaoidide was validated, suggesting that iodine was trapped between graphene layers, leading to interactions with C atoms. The electrochemical performances of iodinated graphenes were tested and compared with a typical PEMFC configuration, containing different Pt/C loading (0.4 and 0.2 mg cm⁻²). If iodinated graphene is included as microporous layer, the electrochemical performances of the fuel cell are higher in terms of power density than the typical fuel cell. Iodine-doped graphenes have been successfully obtained by simple and cost effective synthetic strategy and demonstrated new insights for designing of a high performance metal-free ORR catalyst by a scalable technique.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) technology is under a rapid development in a wide variety of application fields such as vehicular power supply, distributed power plant, portable power sources and so on as clean and efficient power sources. For a successful PEMFC commercialization, the highly active and cost-effective electrodes (anode and cathode) are required. Up to date, platinum and platinum-based composites have been considered as the most efficient catalysts, based on its electrochemical performance [1–3]. However, the platinum's drawbacks, besides its high cost, CO poisoning effect, have been its lack of stability once it becomes active inside a fuel cell. Moreover, one of the bottlenecks for a large scale applications of FC is the sluggish oxygen reduction reaction (ORR) at the cathode side. In this context, it is essential to identify non-precious metals or metal-free electrocatalysts possessing a high catalytic activity and long time steadiness operation, in order to reduce or replace Pt as ORR electrocatalysts in FC [4–7].

Although numerous scientific efforts have been directed towards the development of non-precious metal electrocatalysts, their limited results regarding the electro-catalytic activity, cycle stability and environmental hazard, constrained their practical

application in FC [8–11]. Subsequently, considerable research efforts have been dedicated to developing of carbon-supported electrocatalysts, effective in upgrading the performance PEMFCs and reducing the use of precious metals. Thereby, considerable research efforts have been dedicated in order to develop durable catalyst support materials, such as carbon nanotubes, carbon molecular sieves and graphitic mesoporous carbon, due to their unique electric and micro- and macrostructure properties.

Since the single-layer graphene was discovered, this research area has attracted great interest because it may lead to a new way to improve the electrocatalytic activity in fuel cells [12–15]. Nowadays, a durable electrocatalyst based on graphene nanoplatelets as support, which exhibits 2–3 times durability of commercial Pt/C is the subject of many studies [16–18].

In particular, graphene's high electrical conductivity and large surface area make it an interesting material for energy storage or conversion [19]. A key issue is to develop advanced techniques in order to produce low cost and efficient graphene materials, by combining structural functions with superior electronic properties, having in mind the environmentally context. However, the exfoliation of graphite into graphene oxide is more interesting due to their low cost synthesis, high yield and easy processibility compare to graphene [20].

Lately, doped carbon based materials using different heteroatoms such as boron, nitrogen, sulphur, phosphorus, halogen and their mixture have attracted a particularly attention as

* Corresponding author.

E-mail address: adriana.marinoiu@icsi.ro (A. Marinoiu).

metal-free ORR electrocatalyst [21–24]. The difference in electronegativity between heteroatom dopants and carbon atom in covalently doped graphitic carbon frameworks could polarize adjacent carbon atoms. Moreover quantum mechanics calculations demonstrated that the electron accepting/donating ability of the heteroatom dopants created net positive/negative charges on adjacent carbon atoms in graphitic lattice and therefore facilitates the ORR process [25–29]. Furthermore, the physical–chemical properties of iodine doped graphene, such as chemical state, thermal stability and work function conditions have not been intensively investigated even though they are critical parameters for successful realization of graphene based electrodes in industrial application.

Our recently results regards the successful preparation of graphene and graphene nanocomposites, by a simple route and their use as electrodes for FC [30]. The conclusions that emerge from present study, come from the applying of the recently adopted protocol for synthesis of graphene materials and subsequent electrodes manufacturing for FC, supported by testing and validation.

The work entails the developing and testing a new concept of electrodes for FC, emerging from up-to-date design of catalysts on the basis of non-noble metal materials synthesized using different precursors and synthetic parameters/strategies. The composition/morphology–ORR activity correlation provides us a better understanding of the nature of the active sites in different materials. We hypothesize that the ORR activity could be improved due to electrocatalytic efficiency of iodine doping, facilitated by forming charge transfer complexes of I_3^- and I_5^- , which enhance the doping capability and graphene work function. The direct measurement of the doping efficiency is achieved by several up-to-date methods providing the adequate and complete informations regarding the composition but also the insights on the chemical nature of the dopant.

We are also going to consider to use in our research several approaches regarding the electrode manufacturing: spraying on membrane, spraying on gas diffusion layer. Thereafter, the role of the support morphology and surface area for the best performing catalyst composition is going to be explored. For comparison, diagnostic experiments with nanostructured electrocatalytic systems utilizing noble metals Pt, at possibly the lowest loadings permitting their high practical utility. In this respect, importance of the carbon support will also be addressed. Because the informations related to the electrochemical science and technology of ORR is not yet well explained, any achievements in the basic science of electrocatalytic systems providing good ORR performances could be primary importance.

2. Experimental

2.1. Catalysts preparation

The general synthesis of prepared doped graphenes included the following steps: pre-oxidation, oxidation, exfoliation, reduction, separation of elemental iodine for the GrI1 and GrI2 preparation, respectively the electrophilic substitution by reduction and separation of elemental iodine for the GrI3 and GrI4 samples obtaining. Different methods were used for preparation of iodine doped graphene materials, namely: (a) the nucleophilic substitution of graphene oxide (GrO) by reduction with HI via a non-catalyzed reaction (GrI1); (b) the nucleophilic substitution of GrO by reduction with HI, catalyzed by AlI_3 (GrI2); and (c) the electrophilic substitution of commercial graphene (GrI3 and GrI4). The raw materials were graphite for GrI1 and GrI2 and respectively commercial graphene for GrI3 and GrI4.

2.1.1. Synthesis of GrI1 – uncatalyzed HI reduction

2.1.1.1. Pre-oxidation step. A detailed description of the synthesis process of graphene oxide (GO) has been reported elsewhere [12,14]. In a typical synthesis, the graphite powder was mixed with conc. H_2SO_4 (35 ml), 4 g P_2O_5 and 4 g $K_2S_2O_8$ at 80 °C, under stirring. The washed solid was separated by decantation, redispersed in distilled water and separated by decantation followed by filtration on a G3 glass filter funnel and washing on the filter. The obtained GO product is dried to constant weight in air at 60 °C and crushed.

2.1.1.2. Oxidation step. In this step, the GO is mixed with 300 ml H_2SO_4 95 wt.% and 35 g P_2O_5 (strong exothermic effect). Then 30 g of $KMnO_4$ was slowly added into the flask while maintaining vigorous stirring and the temperature was kept below 10 °C. The mixture was stirred at 45 °C until it became pasty brownish, and it was then diluted using de-ionized (DI) water. 30 ml H_2O_2 (30 wt.%) solution was slowly poured into the mixture, after which the color of the mixture changed to bright yellow. The mixture was centrifuged, and then the pellet was resuspended and washed with a 1:10 HCl aqueous solution in order to remove residual metal ions. The resulting precipitate was washed repeatedly with DI water until a neutral pH was observed. The GO used in the synthesis was obtained by drying the precipitate in a vacuum.

2.1.1.3. Exfoliation step. The GO solution obtained in step 2 is homogenized by stirring for 1 h using an IKA Ultraturrax T 25, then it is ultrasonic pulsed for 4 h at 110 W/40 kHz and max. 40 °C with an ultrasound bath ELMA T 490DH model. About 2500 ml solution graphene oxide (GrO) 3.4 g l^{-1} is obtained.

2.1.1.4. Reduction step. For reducing the GrO to graphene and to dope it with iodine, in a 2 liter 4-neck flask a 1147 ml GrO dosing solution (equivalent to 3.9 g GrO) was introduced. This flask was placed in a glycerol thermostatic bath and equipped with mechanical stirring, thermometer, reflux condenser and addition funnel. Approx. 145 g HI 55 wt.% (equivalent to 80 g HI) is added in 3 h at 80–85 °C. The reaction time is established at 24 h at this temperature. The reaction mass was cooled and separated by centrifugation, which is the only applicable separation method. The separated solid was washed three times by redispersion in 1500 ml water and decanting/centrifugation. Although the third wash test for SO_4^{2-} is negative, the solution is still acidic pH (approx. 3.0) and the test for X^- is positive due to the HI presence. The separated solid (31.77 g) is brought to constant weight at 50 °C in a vacuum desiccator placed in an oven (approx. 7 h) 2.74 g solid is obtained. After grinding to a powdery form, a black product is obtained having the following chemical composition.

2.1.1.5. Separation of elemental iodine. The elemental iodine is separated by repeated extraction with acetone. Therefore, 1.75 g solid product obtained in previous stage is placed in a cartridge paper and is extracted in a Soxhlet extractor with acetone until extract is colorless. After drying to constant weight (loss mass is approx. 31%) at 50 °C are obtained 1.21 g solid encoded GrI1.

2.1.2. Synthesis of GrI2 – catalyzed HI reduction by AlI_3

2.1.2.1. Pre-oxidation step. 35 ml H_2SO_4 , 95 wt.%, 4 g P_2O_5 and 4 g $K_2S_2O_8$ were introduced in a glass reactor of 250 ml volume, thermostated by soaking in glycerol and equipped with mechanical stirrer and a reflux condenser cooled with air and equipped with silica gel drying tube at room temperature. The mixture was stirred for 30 min, and then the PMM7 graphite was added. The reaction mass was brought to 80 °C, then was stirred for approx. 4 h at 80–85 °C and slowly cooled under stirring at room temperature. The obtained dark blue reaction mass is dispersed under stirring

متن کامل مقاله

دریافت فوری ←

ISIArticles

مرجع مقالات تخصصی ایران

- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان دانلود رایگان ۲ صفحه اول هر مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات