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Full Length Article

Iodine-doped graphene – Catalyst layer in PEM fuel cells

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ABSTRACT

Graphene base materials have received appreciable attention as substrate or nanocomposite with nonmetallic catalysts in alternative energy devices and technologies. The end application of iodine-doped (I-doped) graphene in fuel cells has been recently investigated as innovative nanomaterial for oxygen reduction reaction (ORR). Microscopic and spectroscopic techniques (SEM, FTIR, XRF, XPS) have been combined with structural investigation (BET) and electrochemical techniques for a comprehensive characterization of developed ORR catalysts. Moreover, the durability as ORR electrode have been evaluated in order to assess long-term performance. I-doped graphene was prepared by nucleophilic substitution of graphene oxide (GrO) by reduction with HI. The as-synthesized graphene with incorporation of iodine possesses unique structure revealing high surface area, mesopores and vacancies. The structural characteristics and their synergistic effects could not only improve the ions and electrons transportation but also limits the ohmic resistance. Thus the I-doped graphene exhibited superior electrochemical performances as well as long-term stability, which demonstrate that the I-doped graphene with great potential to be an efficient electrode material.

1. Introduction

Low temperature proton exchange membrane fuel cells (PEMFCs) are continuing to attract considerable interest as one of the most promising power sources for stationary and portable electronic devices. However, in spite of demonstrated indisputable relevant advantages such as renewable source with very low emissions, low operating temperature, high energy efficiency and modularity, there still are important problems to be considered for a complete successful commercialization [1–3]. In particular, the electrocatalyst, whether it's anode or cathode, essentially defines the FC cost effectiveness, performance and durability. Thus the catalyst has earned a full reputation as extremely important component. Platinum nanoparticles supported on carbon black still remain the commercial electrocatalyst although the support suffers serious corrosion problems under operating conditions. In this respect, many researches were focused on several nanostructured carbon materials. Taking into account the basic requirements for electrocatalyst support material (such as high electrical conductivity, electro-chemical stability, good interaction under FC operation conditions, corrosion resistance), the relevance of graphene base materials use in FC electrodes is fully understood.

FC performance is reflected in its polarization curve, representing the cell voltage versus current density. The decrease in performance in power density terms is associated with three main factors: (i) oxygen reduction reaction (ORR) kinetic losses of the cathode; (ii) ohmic resistance losses owing to interfacial resistances; (iii) mass transport overpotential at high current densities. In terms of gravity between them, the ORR kinetic losses are more challenging because an order of magnitude in ORR activity amendament would mark 60–70 mV in cell voltage increase, whereas the advancement in catalytic materials till now has recorded only 10 mV.

The catalyst layer, the part of the cell where the electrochemical reactions occur, has a complex microstructure based on carbon particles, Pt catalyst particles, an ionomer network and pores. Each of these components has its role in promoting the reactions. It would be desirable to reduce the Pt amount at cathode because it requires 2–3 times higher loading than anode, due to slow kinetic reduction rate. Since the oxygen reaction is typically the limiting reaction, the catalyst layer is described here in terms of the cathode. The catalyst layer must provide channels for allowing the transport of reactants and products, and must ensure conductive paths for the ions and electrons [4–6]. The ionomer network is the one that ensures the ion conductive paths for protons transport from the membrane to the reaction sites and acts as a diffusive medium for the humidified oxygen gas. The carbon particles conduct the electrons to the reaction site and provide a support for the platinum particles. The pores allow oxygen to flow through the layer and help in removal of the water produced. The oxygen dissolved into the ionomer for reaching the Pt particles can lead to mass transport resistance and

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further to overpotential losses. Also, the water generated at the cathode may be converted to either the liquid or gas phase. The liquid water can accumulates in the catalyst layer pores, blocking the access of the reactants to the active catalyst sites and decreasing the effective reacting surface area, hence leading to mass transport resistance and a reduction of cell performance in the concentration region of the polarization curve [7].

Until now, numerous attempts have been devoted to improve the stability and durability of supported Pt catalyst by taking into consideration the following main routes: (i) the use of chemical stable support materials with graphene the most likely candidate, due to high ordered structure, high surface area, excellent electrical and mechanical proprieties, (ii) the use of a nanocomposite co-catalyst [8–12].

Although it is expected that graphene-supported Pt catalyst should present an improved electrochemical stability and durability in comparison to carbon-supported Pt, nevertheless an additional modification of graphene layer structure is required in order to intensify the graphene support efficiency [13–17]. Thus, in order to avoid the graphene aggregation/nanoparticles agglomeration, two options are currently employed: the placing of one-dimensional carbon material as spacer and/or the introduction of oxygen-containing functional groups [18,19].

Several graphene base materials precisely nanocomposite with nonmetallic catalyst have received attention for PEMFC due to its basal plane structure with high surface area and high conductivity given by substrate and charge carrier mobility during ORR. Among them, the class of doped graphenes has received a particular consideration [20–26]. Carbon nanostructures have a low free carrier concentration, but important methods for modulating of electrical properties of graphene by chemical doping have been developed mainly through surface transfer doping and/or substitutional doping by different dopants. The mechanism of chemical doping in graphene takes after that of carbon nanotubes, however the former still remained disputed, especially in terms of pathway the mechanism works. The structure of graphene is not destroyed in the case of surface transfer doping, which is considered reversible. The substitution doping refers to the substitution of C atom in graphene lattice by atom with different number of valence e.g. halide. The incorporation of foreign atoms destroys the sp^2 hybridization of C atoms. The incorporation of iodine guest atoms into carbon nanostructures has been reported to significantly change the electrical resistivity or conductivity [27,28]. When iodine is introduced, it can react with edge or basal carbon atoms. Iodine demonstrated the tendency to form different charge transfer complexes even with weak donor like the π-electron cloud of carbon. The demand of a chemical stable and efficient catalyst for PEMFC, guided us to develop a new concept of electrode as alternative cathode. The recent application of I-doped graphene as electrode in FC has been recently recognized as an improved strategy for effective modification of cathode layer efficiency [29–31]. The significant interest caused by I-doped graphene is a result of its enhanced conductivity and improved catalytic activity for ORR with demonstrated effect in lowering of kinetic losses at cathode. The performed experimental studies revealed that the microporous layer (MPL) placed between catalyst layer (CL) and GDL have many advantages, among them we mention: keeps the hydration of the membrane and of the ionomer phase, prevents GDL flooding, especially at high current densities, forms a more intimate contact between CL and GDL.

In spite of all reasonable performances, the long-term FC operation under dynamic load conditions becomes extremely important to cope with prospective FC commercialization, thus going further, the stability/durability tests are required.

The main objectives of this work are to improve the ORR electrode by including the nanostructured I-doped graphene and to prove the lifetime of the developed cathode in long term PEMFC operation conditions. Worth mentioning, that no paper has been reported in respect to the long-term stability of the PEMFC containing I-doped graphene. In view of these facts, the purpose of this work is to provide valuable information about the recommendation of I-doped graphene as innovative cathode in PEMFC, based on performances obtained in stability test (as catalytic material) and durability test in long-term FC operation conditions (as ORR electrode).

2. Experimental

2.1. Materials

Graphite powder, $K_2S_2O_8$, P_2O_5, conc. H_2SO_4, HI were purchased from Sigma-Aldrich. $KMnO_4$, H_2O_2 and HCl were obtained from Oltchim SA Romania. Carbon paper gas diffusion layer (GDL, SGL), membrane (Nafion-212), ionomer solution (5 wt% Nafion) were purchased from Ion Power, USA. Commercial catalyst (HISPEC 4000 Pt/C 40 wt%) was purchased from Alfa Aesar. The purity of reactants (H_2 and O_2) was 99.999%.

2.2. Catalysts preparation

I-doped graphene electrocatalyst was synthesized via a facile process described in detail elsewhere, through nucleophilic substitution of graphene oxide (GrO) by reduction with hydroiodic acid. (HI) catalyzed by AlI_3 [29,30]. Briefly, the graphite oxide (GO) was prepared starting from graphite powder by a modified Hummers method including specific steps, as follows. The pre-oxidation was used to prepare the pre-oxidized GO, namely the graphite (7.5 g), $K_2S_2O_8$ (6 g), and P_2O_5 (6 g) were introduced into conc. H_2SO_4 (50 ml) and P_2O_5 (50 g), under continuously stirring at 80 °C. The product was washed, filtrated, dried at 60 °C. The as pre-oxidized GO was mixed into conc. H_2SO_4, and then $KMnO_4$ (45 g) was slowly added during stirring and cooling in water-ice bath. The suspension was stirred at 40 °C until it became brown, and then was diluted using de-ionized water. H_2O_2 30 wt% (50 ml), solution was slowly introduced. The yellow mixture was centrifuged, washed with a 1:10 HCl aqueous solution in order to remove residual metal ions. The obtained GO solution was dispersed by stirring using an IKA Ultraturrax T 25 (2 h), and ultrasonic bath (ELMA T 490DH model) at 110 W/40 kHz and 35 °C (4 h). Graphene oxide (GrO) 4 g L^{-1} was obtained. Taking out a share-part of as-prepared GrO dispersion, the hydroiodic acid HI 55 wt% (170 g) was added (in 4 h) at 80 °C, as reduction agent and precursor iodine dopant. The obtained mixture was washed using de-ionized water for several times, dried to constant weight at 50 °C (more than 8 h), and grated to powder. The final step was the elemental iodine removal by repeated extraction in acetone using a Soxhlet extractor.

2.3. Catalysts characterization

The microstructure and morphology of prepared samples were evaluated by using the facilities of following equipments: Field Emission Scanning Electron Microscope (FESEM SU 5000 Hitachi) equipped with EDS-energy dispersive X-ray spectroscopy and WDS-wavelength dispersive; X-Ray Photoelectron Spectroscope (XPS, Quantera SXM equipment), with a base pressure in the analysis chamber of 10^{-9} Torr and X-ray source Al K_α radiation (1486.6 eV, monochromatized) and the overall energy resolution estimated at 0.65 eV by the full width at half maximum (FWHM) of the $Au4f_{7/2}$ line; Fourier transform infrared (FTIR) spectrometer (Nicolet Impact 410, Thermo Fisher, USA); Autosorb IQ (Quantachrome, USA) with adsorption and desorption experiments performed at 77 K after initial pretreatment of the samples by degassing at 115 °C for 4 h; X-Ray Fluorescence spectrometer (XRF, Rigaku ZSX Primus II), equipped with an X-ray tube with Rh anode, 4.0 kW power, with front Be window of 30 μm thickness