Nitrogen self-doped electrocatalysts synthesized by pyrolysis of commercial polymer fibers for oxygen reduction reaction

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ARTICLE INFO

ABSTRACT

In this study, metal-free electrocatalysts were obtained from the pyrolysis of commercial Kevlar™ and Twaron™ carbon fibers (pKf and pTf, respectively). An easy and low cost synthesis method was developed. The obtained electrocatalysts have a significantly lower cost than conventional platinum based electrocatalysts. Synthesis of the electrocatalyst was made by pyrolysis treatment of the carbon fibers, under nitrogen atmosphere, followed by an activation treatment under carbon dioxide atmosphere. Properties and electrochemical performance of pyrolyzed (pKf, pTf) and activated (aKf and aTf) samples were compared. The electrocatalysts obtained have surface areas of up to 1000 m^2/g after the activation treatment. Morphology and structural characteristics were studied by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Raman Spectroscopy and X-ray photoelectron spectroscopy (XPS). The electroactivity of these electrocatalysts was evaluated by the oxygen reduction reaction (ORR) in acid media by rotating disk electrode technique. Carbon fibers showed an improvement in the ORR after receiving the activation treatment.

Introduction

The development of fuel cells is a very promising alternative to solve the problem of clean energy generation with high efficiency [1,2]. However, one of the main challenges to achieve a large-scale production of fuel cells is to reduce production costs due to the high cost of platinum. Several alternatives have been proposed, mainly focused on reducing the platinum amount without affecting the performance of the fuel cell, e.g. enhanced support and platinum dispersion [3], to reduce particle size in order to increase the active area of platinum and using bimetallic systems as co-dopants that protect platinum from poisoning [4]. However, these methods

do not report a significant decrease in costs, and in some cases the cost could be higher in bimetallic systems. Platinum-free systems have attracted the interest of several research groups. The first metal-free electrocatalysts studied were nitrogen-doped carbon nanotubes (N-CNTs) and nitrogen-doped graphene (N-Gs) [5–7]. Generally, these carbon nanostructures are characterized by a highly ordered carbon lattice [8]. However, the introduction of heteroatoms (N, B, P, S, etc.) modifies the graphite lattice generating defects, consequently modifying their electronic properties. Mousavi and Moradian [9] and Kotakoski [10] used nitrogen and boron as dopants of carbon materials. Both groups noted that depending to the type of dopant, the properties of doped carbon nanostructures may vary showing a metallic or a semiconductor character. Su et al. [11] synthesized N-CNTs and N-Gs for use as metal-free heterogeneous catalysts. N-CNTs showed N or P-type semiconductor properties and N-Gs exhibited metallic conductivity. Previous studies reveal that N-doping could change the band structure of graphene, shifting its electronic properties from metallic to semiconductor [8]. Since 2009, Kuanping Gong et al. [12] reported the use of nitrogen-doped carbon nanotubes as metal-free electrocatalysts, the reported activities were very close to platinum for the cathodic oxygen reduction reaction (ORR) for PEM fuel cells. Methods commonly used for the synthesis of nitrogen-doped carbon nanostructures are methods such as laser ablation, electric arc-discharge, chemical vapor deposition (CVD) and plasma, all of the above using a nitrogen precursor [13]. The materials synthesized by conventional methods share disadvantages, such as the use of toxic precursors for CNTs, graphene and the usually highly corrosive nitrogen precursors, causing serious damage to the environment, additionally most of these methods require the use of expensive equipment [14]. On the other hand, recent studies have found that nitrogen-doped carbon materials with short and medium range of order in their lattice (carbon fibers and carbon black), have similar electrocatalytic activity to N-CNTs and N-Gs for the ORR [15,16]. There are several advantages of using these carbon materials over CNTs and Gs: i) synthesis methods are more environmentally friendly, ii) use less toxic and cheaper precursors and, iii) methods of synthesis are less complex [17].

Aramid fibers are polymers made up of long chains of poly para-phenyleneterephthalamide. These fibers exhibit outstanding strength-to-weight properties, high stiffness, low elongation to break, resistance to organic solvents and good resistance to abrasion and cutting, among others [18,19]. The chemical structure of aramids contains nitrogen bonded to benzene groups, when they are pyrolyzed said nitrogen is integrated to the graphitic lattice. Studies on pyrolyzed Kevlar™ fibers using Fourier Transform Infrared spectroscopy (FTIR) by Mosquera et al. [20] show the possibility to form heterocyclic aromatic compounds as quinolones [21]. Moreover, Bradley et al. [22] evidenced the stability of nitrogen–carbon bonds using the X-ray photoelectron spectroscopy (XPS) technique during CO_2 activation process. Lee et al. pyrolyzed carbon fibers and subjected them to a further activation treatment using carbon dioxide to use them as a supercapacitor electrode where the specific surface area and specific capacitance were enhanced [23]. Thus, the study on the electrocatalytic activity of commercial aramid carbon

fibers is attractive because these materials could be used as metal-free electrocatalysts for the ORR.

In this paper, commercial aramid carbon fibers (Kevlar™ and Twaron™) were pyrolyzed and activated by environmentally friendly methods. Textural and morphological properties were obtained in order to track nitrogen–carbon bonding after both treatments. The materials were evaluated for oxygen reduction reaction as potential metal-free electrocatalysts for the ORR in fuel cells.

Experimental

Fiber preparation

Commercial aramid fibers Kevlar™ (DuPont Co) and Twaron™ (Teijin Aramid) were used as raw material for the synthesis of metal-free electrocatalysts. Through a simple synthesis method, the fibers changed their properties becoming electrocatalysts. First the fibers were pyrolyzed by an inert atmosphere treatment with a nitrogen flow rate of 300 ml/min, heating ramp of 20 °C/min up to 800 °C, isothermal during 2 h. The activation process was then performed by replacing the nitrogen atmosphere by carbon dioxide with a flow rate of 300 ml/min during 40 min, keeping the same temperature. All the thermal treatments were performed in a tubular furnace with a quartz tube to keep the atmospheres. The nomenclature used to identify the samples was prefixing *p* and *a* corresponding to the pyrolyzed and activated samples, respectively. The tag **Kf** is for Kevlar™ fibers and the tag **Tf** is for Twaron™ fibers.

Characterization

Fiber morphology and microstructure was characterized by scanning electron microscopy (SEM, JEOL JSM-6010LV operated at 10 kV), an elemental analyzer (CHONS Carlo Erba USA) was used to determine the chemical composition. Structural properties were analyzed by X-Ray diffraction (XRD) of powders, the patterns were collected from 5° to 80° 2θ with step size of 0.2°/s (Bruker D8 advance with Cu Kα as radiation source, λ = 0.15406 nm). Textural properties of pyrolyzed and activated fibers were measured with Autosorb-1C Quantacrome Instruments, at 77 K. All samples were degassed at 250 °C for 3 h prior to measurement. The specific surface area was calculated using the Horvart-Kawazoe (HK) technique. The Raman spectrometry was performed with a Micro Raman Horiba Labranhr Vis 633 with a He–Ne laser source. X-ray photoelectron spectroscopy (XPS) spectra were collected on Thermo Scientific model Escalab 250Xi spectrometer equipped with a monochromator.

Electrochemical evaluation

Electroactivity measurements were performed by cyclic voltammetry and linear sweep voltammetry in a rotating disc electrode (RDE) Pine Research Instrumentation rotator model AFMSRCE. A conventional three-electrode cell was used at 25 °C coupled to a Princeton Applied Research potentiostat model VersaSTAT 3. The working electrode was prepared