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Direct growth of carbon nanofibers on carbon-based substrates as integrated gas diffusion and catalyst layer for polymer electrolyte fuel cells

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ABSTRACT

One-dimensional carbon nanostructures are considered promising for application as catalyst support in polymer electrolyte fuel cells, replacing the most widely used carbon black, due to their physico-chemical properties and high surface area. Different morphologies of carbon nanofibers, by varying the graphene layers orientation with respect to the fibre axis, exhibit different amount of available open edges that can act as anchorage site for catalyst nanoparticles. CNF are grown on graphite paper by a controlled plasma enhanced chemical vapour deposition and then used as substrates for Pt electrodeposition. The CNF direct growth on carbon paper allows having single layer electrodes with both diffusive and catalytic layer function. Moreover, the replacement of conventional ink deposition methods with electrodeposition for platinum dispersion, allows greatly reducing the catalyst load, increasing at the same time its utilization and performance. The innovative electrodes are characterized by field emission gun scanning electron microscopy and X-ray photoelectron spectroscopy to assess the morphological properties, and by cyclic voltammetry in H_2SO_4 and $H_2SO_4 + CH_3OH$ to determine the electrocatalytic activity and long term stability. The comparison with an electrode made of conventionally deposited Pt catalyst by ink method on commercial carbon black shows better performance for the developed Pt/CNF electrodes.

Introduction

In recent years all topics related to the development of reliable clean and renewable energy sources are of great interest and relevance, due to the current energy crisis, the problem of waste disposal and pollution and the risk of depletion of traditional energy sources. The need to reduce the dependence on fossil fuels and the generation of heat by the power sources is increasingly strongest, so the use of alternative and environmentally friendly energy sources is a topic of much current research. Fuel cells meet the requirement to develop

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an energy conversion technology that is inherently clean, efficient and compatible with renewable sources of energy. As a matter of fact, these devices convert directly to electrical energy the chemical energy stored in the fuel, with high efficiency and with water as the only by-product (when the fuel is methanol there is actually also a small amount of CO_2, but it is negligible compared to traditional combustion systems). Moreover, they offer other benefits, such as the wide variety of installed power, low noise and excellent energy efficiency. Polymer electrolyte fuel cells, both proton exchange (PEFC) and direct methanol fuel cells (DMFC) are very promising from this point of view [1,2]. They are being applied in three main areas: transportation, stationary and portable power generation. They have the potential to reach an efficiency as high as 60% in electrical energy conversion and overall 80% in cogeneration of electrical and thermal energies with >90% reduction in major pollutants [2]. Despite all the research efforts, there are still some critical issues for PEFC and DMFC penetration into the market that must be overcome to make these devices economically competitive with conventional energy sources. The main bottlenecks are the high cost, mostly related to the use of Pt-based catalyst and electrode assembly process, and the long term stability, especially due to the Pt agglomeration and poisoning by CO [1]. The current status of $61/kW (2009) for transportation fuel cell is still over 50% higher than the target of the US Department of Energy (DOE), i.e. $30/kW by 2015, in order to compete with the conventional technology of internal-combustion engines. In addition, a durability lifetime of 2500 operating hours (for transportation PEM fuel cells) was achieved in 2009, yet still needs to be doubled to meet the DOE's target, i.e. 5000 h durability by 2015 with 60% efficiency for transportation [2].

The catalysts most frequently used for PEFC and DMFC are Pt or Pt-alloy nanoparticles supported on activated carbon with high specific surface. A Pt loading of about 0.3 mg cm^{-2} has been achieved in demonstration units, but the target set by DOE is 0.2 mg cm^{-2} by 2015. The fuel cell cost breakdown highlights that it has been greatly reduced in the past decade, but it is still far from the DOE target [2]. One primary portion of a fuel cell cost is due to the membrane electrode assembly (MEA), to which the catalyst gives the biggest contribution. New materials development is, therefore, one of the main focus of fuel cells performance improvement and cost reduction.

The conventional electrodes are made of two different layers for diffusive and catalytic function, both obtained by spray deposition of the specific ink. For the catalytic layer the ink is prepared by an impregnation–reduction method [3–9]. Using this technique, however, a significant Pt amount is not fully exploited because the nanoparticles remain isolated and not simultaneously in contact with feeding gas, carbon support and proton exchange membrane [10].

To improve the Pt utilization is theoretically necessary to reduce the nanoparticles size. The optimal size reported in the literature is between 2 and 6 nm [11–14]. Catalytic nanoparticles of this size, however, have a surface atoms percentage of only 25–50%, because more than half of the used catalyst is not active for the electrochemical reactions. A further nanoparticles size reduction is not a viable solution because catalyst particles smaller than 2 nm are easily incorporated into the micropores of the support material and, consequently, become inaccessible for the electrochemical reactions due to the lack of three-phase boundary [15–17]. Attempts have been also devoted to the development of non-Pt-based catalysts, but the results are still not satisfactory [1,18].

In addition, materials other than carbon black (surface area of about 250 m^2g^{-1} for Vulcan XC-72), consisting of near-spherical graphite particles (<50 nm in diameter) coalesced into aggregates and agglomerates of around 250 nm in diameter, have been investigated as catalyst support. As a matter of fact, carbon black is widely used but it contains organo-sulphur impurities acting as Pt poisoners, and micropores that can trap the catalyst nanoparticles making them inaccessible to reactants thus reducing the catalytic activity.

The use of carbon-based nanomaterials, especially monodimensional morphology [19,20], as catalyst support is attractive with the aim to reduce the noble metal amount improving its utilization and activity. Nanostructured supports enable fast electron transfer and high electrocatalytic activity, having properties like high specific surface area, high electrical conductivity and good stability. Several works in the literature show how the use of carbon nanotubes (CNT) allows an increase in the catalyst performance [21–23]. However some authors report that CNT tend to form bundles reducing their specific surface and bind the catalytic particles only with weak interactions because of their relatively inert surface [24].

Many studies have also been aimed at the possibility to replace commercial nanocarbon with carbon nanofibers (CNF) [25], that are characterized by a negligible content of micropores in which the catalyst nanoparticles may remain closed with consequent reduction of electrochemical active surface.

Carbon nanofibers are commonly classified into different structural forms, depending on the angle that graphene layers form with the fibre axis [26,27]: the graphene layers are perpendicular to the fibre axis in the platelet CNF (pCNF), oriented at an angle between 50° and 70° in the herringbone CNF (hCNF) and parallel to the fibre axis in the tubular CNF (tCNF). Since the properties of graphite are anisotropic, graphene layers orientation strongly affects the resulting material properties such as electrical and thermal conductivity, mechanical strength and stiffness.

The basic difference between CNT and CNF, especially pCNF and hCNF, comes from their structure. CNT are rolled up co-axial sheets of graphene exposing predominantly basal planes, while CNF have an abundance of dangling bonds and defects resulting from the exposed edge planes. For this reason CNF present a lot of potential catalyst anchoring sites.

Tubular CNF have been studied as a possible substrate for Pt electrocatalyst showing higher performance compared to commercial Vulcan carbon substrate [27]. The fibres were preliminarily purified and such treatment induced the presence of oxygen-containing functional groups that facilitate the subsequent deposition of the catalyst. The benefit of the presence of containing oxygen functional groups is controversial [21,25,28]: on one hand the functionalization improves dispersion and anchorage of catalyst particles, on the other it causes the decrease of some properties such as electrical conductivity. Moreover, some authors state that oxygen-containing functional groups are responsible for corrosion of carbon-based substrate [29,30]. Among CNF morphologies, the structures with a great number of edges plane are characterized by high