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A stable and active iron catalyst supported on graphene nano-flakes for the oxygen reduction reaction in polymer electrolyte membrane fuel cells

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ABSTRACT

Two of the major challenges for the commercialization of automotive fuel cells are cost and durability. Cost estimations indicate that at a large production rate, the majority of the stack component cost comes from the catalyst ink. Decreasing this cost depends on finding a durable cost-effective platinum-free electrocatalyst. In this work, pure graphene nano-flake (GNFs) powders are produced by plasma decomposition. The GNFs are composed of 5–20 layers of stacked graphene sheets, a structure that appears to be closely associated to catalyst stability and durability. Additionally, the large number of attachment sites for nitrogen and atomic iron functionalization provide an avenue for improving activity. The GNFs were nitrogen functionalized and then used to support atomic iron to create the active sites for a non-noble catalyst. Iron was successfully incorporated at a value of 0.28 at% on the surface of the catalyst structure. The catalyst was used on the cathode side of a polymer electrolyte membrane fuel cell (PEMFC) and showed stability over 100 h. The performance of the catalyst demonstrates, to our knowledge, the first proof of a stable strictly iron-based fuel cell catalyst.

1. Introduction

Currently, the catalyst for polymer electrolyte membrane fuel cells (PEMFCs) is exclusively platinum, an expensive metal ($56.44 USD/g [1]) found in low abundance. In order for PEMFCs to become a viable alternative as an energy source for the transportation industry, production costs must be significantly reduced. In scale up studies on the number of PEMFC units produced, essentially half of the production costs can be associated to the catalyst ink and more particularly the platinum loading itself [2]. One way to reduce production costs is to develop a corrosion resistant non-noble metal substitute to the platinum-based catalysts currently being used. Functionalized carbon nanomaterials have already been acknowledged as a potential alternative [3–6].

In work published by Pristavita et al. in 2011, carbon black powders composed of layers of graphene sheets were produced [7,8]. The powders, referred to as graphene nano-flakes (GNFs), were functionalized to achieve nitrogen sites. Iron was adsorbed onto the surface of the functionalized GNFs to form catalytic sites.

This paper presents the nitrogen and iron composition on the surface of the GNFs, shown throughout the synthesis steps. A report on the crystallinity parameters (purity, crystallite size, and average length of graphene plane) is also included. Finally, the results proving the stability of the catalyst in a PEMFC are given.

2. Background

The PEMFC is based on reverse electrolysis with hydrogen and oxygen as fuels, its main components being the electrolyte membrane, catalyst layers, diffusion layers, bipolar plates with fuel canals, current collectors, and end plates (Fig. 1). The electrolyte membrane has high ionic conductivity and selectivity, is an electronic insulator, and has mechanical, chemical, and heat stability [9]. The membrane is squeezed between the two catalyst layers, which are usually multicomponent metal composites based on platinum on a carbon support structure.

The oxygen reduction reaction (ORR) occurring at the cathode is particularly problematic; this reaction has sluggish kinetics resulting in the need for roughly 80% of the platinum that is used in a PEMFC. For the cathode side, every square centimeter of catalyst area carries typically about 0.1–0.5 mg of the costly platinum metal. The proposed non-noble metal catalyst studied here is targeting the ORR with the objective of replacing platinum.

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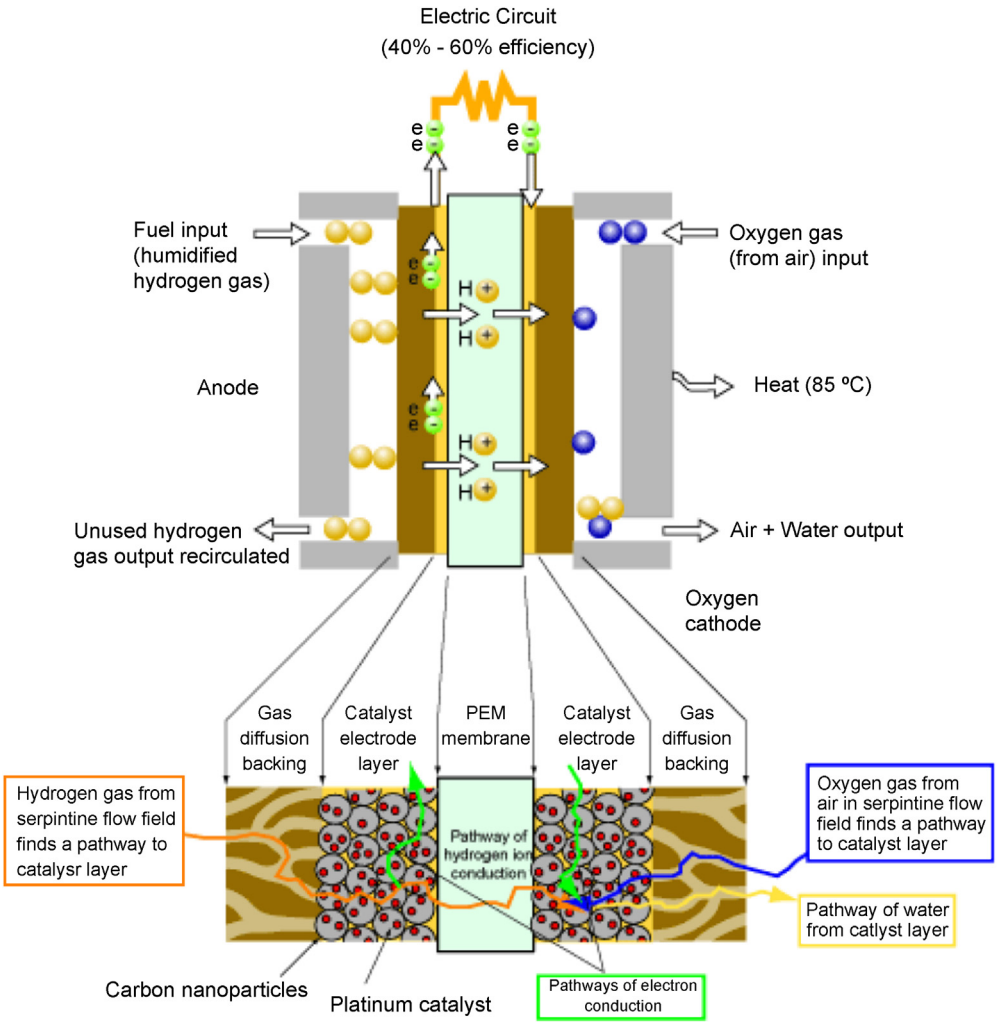

Fig. 1. Fuel cell anatomy [10].

The catalyst layer must have high electrochemical activity, high poison tolerance, corrosion stability, and mechanical and heat stability. Another requirement of the catalyst is to have a large surface area of catalytic activity per unit volume of the catalyst layer; therefore, in current developments catalyst nanoparticles are typically used and fixed onto carbon substrate particles [4,5,11]. For many research teams working on platinum, the goal in creating some catalyst layer morphology is not only to maximize the available area, but also to achieve uniformity of platinum particles on the carbon support and prevent agglomeration of the particles that would decrease the activity [4,5,12]. This paper attacks both the problem of platinum replacement and enhancement of catalyst area through the generation of iron-based catalytic sites, with iron being made available at the atomic level as discussed by Lefèvre et al. [6].

The catalyst structure used in this study to potentially replace platinum as the PEMFC catalyst is iron coordinated to pyridinic nitrogen within graphitic domains (Fig. 2). This active site is very similar to heme (Fig. 3), an iron porphyrin structure found in the hemoglobin of blood and modified by Jasinsky [13] to create an active site for the ORR using cobalt phthalocynanine (Fig. 4).

Ideally, the carbon nano-powder support should have a large amount of pyridinic nitrogen on its surface as more pyridinic nitrogen enhances the possibility of forming iron coordinated catalytic sites. A high crystallinity such as that obtained in graphene based structures is not only advantageous for stability in the acidic environment of the fuel cell, but should also help in providing the edge structures for nitrogen/iron-functionalization as illustrated in Fig. 2.

GNFs were produced recently as a pure product with uniform size distribution using thermal plasma technology, their structural size being typically between 5 and 20 atomic layers of roughly 50–100 nm sheets [7,8]. The plasma decomposition of a carbon-containing feedstock such as methane is used to trigger particle generation using a well controlled homogeneous nucleation field. As indicated, pure graphene nano-flakes can be produced without generating carbon dioxide while only generating trace amounts of impurities. Additionally, since the graphene nucleation occurs at very high temperatures within the plasma system, it is possible

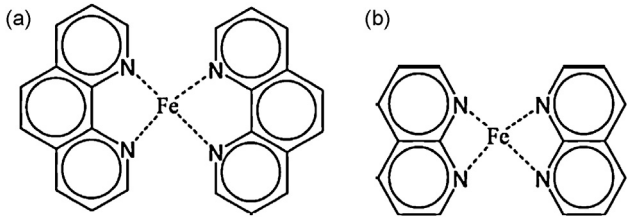

Fig. 2. Schematic of the hypothesized catalyst sites in an (a) 'armchair' and (b) 'zig-zag' graphene structure [14].

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