

## Iron nanoparticles decorated on graphitic carbon nitride/ZIF-67 support: An electrocatalyst for the oxidation of methanol in fuel cell

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### Abstract

Iron nanoparticles (FeNPs) are the tiniest particle of iron metal with a large surface area and high reactivity. They are non-toxic. FeNPs have excellent dimensional stability and also possess high thermal and electrical conductivity, high surface area, and are highly magnetic. FeNPs can oxidize immediately when exposed to water or air and produces free Fe ions. There are numerous applications of FeNPs but the most promising one includes their role in drug delivery. Considerable attention is being paid to the utilization of computer-based and modeling optimization in fuel cell systems design. One advantage of this method is the positive effect on high cost and design cycle time savings, as well as its improved operation and design. The performance of optimum development depends primarily on the method by which the prototype is developed. It is crucial to identify the important factors and those that can be compromised without having an adverse effect on the design. Modeling is carried out to capture the designer's interest aspects of the fuel cell system. A mathematical model that represents particular fuel cell system aspects and estimates its characteristics can be in a form of algebraic equations, differential equations, or a process or subroutine based on a computer. The model can involve various alternatives to the design that can be achieved by changing parameters, variables, constraints or conditions. The principle explained in the preceding step contributes to the basis for comparing the various alternatives to design.

**Keywords:** Nitride/ZIF-67; Electrocatalyst; Iron Nanoparticles; Fuel Cell

### 1 Introduction

Nanotechnology is a revolutionary approach that involves the management of atoms and molecules at the nanoscale<sup>1</sup>. Nanotechnology has emerged as an exciting field of research in modern sciences and provides different types of products including nanoparticles, nanorods, or nanotubes with different dimensions. All these nano-sized products have different specific roles. They may vary according to their size and shape, chemical nature, and crystalline, amorphous, and solid-state of occurrence. Iron nanoparticles (FeNPs) are the tiniest particle of iron metal with a large surface area and high reactivity. They are non-toxic. FeNPs have excellent dimensional stability and also possess high thermal and electrical conductivity, high surface area, and are highly magnetic. FeNPs can oxidize immediately when exposed to water or air and produces free Fe ions. There are numerous applications of FeNPs but the most promising one includes their role in drug delivery .

Fuel cells have appeared as potential energy conversion devices which operate in the presence of the hydrogen or hydrogen-rich fuels with low CO<sub>2</sub> emissions. Among these, proton exchange membrane fuel cells (PEMFC) have gained more attention due to their superior properties such as high open-circuit potential, high energy conversion efficiency, limited fuel crossover effects, and efficient electrooxidation of organic molecules such as ethanol (DEFC), methanol (DMFC), formic acid (DFAFC), etc. at low-temperature. electrochemical reactions with solid electrodes. The main reasons

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which hinders the practical application of the MFC are the lower power output and high cost Pt-based catalysts. Therefore, various carbonaceous, metallic nanoparticles (NPs) as anode materials and carbonaceous, platinum-group metal and platinum-group-metal-free materials as cathode catalysts are used to improve the performance of the MFC along with lowering the cost [2]. The higher electronic conductivity of CPs compared to that of the conventional carbon-based catalyst support this higher attention during past two decades. Additionally, the higher surface area and unique synergistic effects with the metal NPs/metal oxide play an important role to improve the electrocatalytic activity of the catalysts and to stabilize fuel cell performance [3]. A significant effort has been made in the fabrication of Pt-free catalysts deposited on CPs, although loading of low-Pt nanomaterials on polymers is also used due to their high catalytic performance. V

## 2 General Fuel Cell Topics

In addition to developing the first fuel cell system to be used in a real application, the fuel cell research group at General Electric was also the first to publish a series of technical articles on fuel cells in the Journal. In addition to inventing and developing the PEFC, this group of researchers examined the thermodynamics of fuel cells and did a considerable amount of work on direct-hydrocarbon fuel cells, as well as direct-ammonia fuel cells. They also developed new electrode structures and examined new electrocatalysts for use with reformat fuels.[4] This group worked with an impressive array of low-temperature electrolytes; in addition to the ion-exchange membrane cells they used a variety of liquid acid electrolytes. An excellent review of this work, as well as a summary of the state of fuel cell technology at the time, is presented by two of the former GE workers, Liebhafsky and Cairns.

It should be noted that after leaving GE, Elton Cairns Figure 1, has continued working on fuel cells at Argonne National Laboratory, Lawrence Berkeley National Laboratory, and at U.C. Berkeley. Elton Cairns is also an ECS Fellow and a past President of the Society.

### 2.1 Polymer Electrolyte Fuel Cells

PEFC Two major improvements have been made in PEFC technology since the Gemini program. The first was the development of perfluorosulfonic-acid membranes that are more stable than the hydrocarbon-based membranes used in the early PEFCs. These membranes, such as Nafion®, consist of a PTFE backbone with perfluorinated-vinyl-polyether side chains terminated by a sulfonate group. Nafion, and similar derivatives, are essentially fully fluorinated and therefore they do not suffer from rapid degradation in a fuel cell since CuF bonds are more stable than CuH bonds[5]

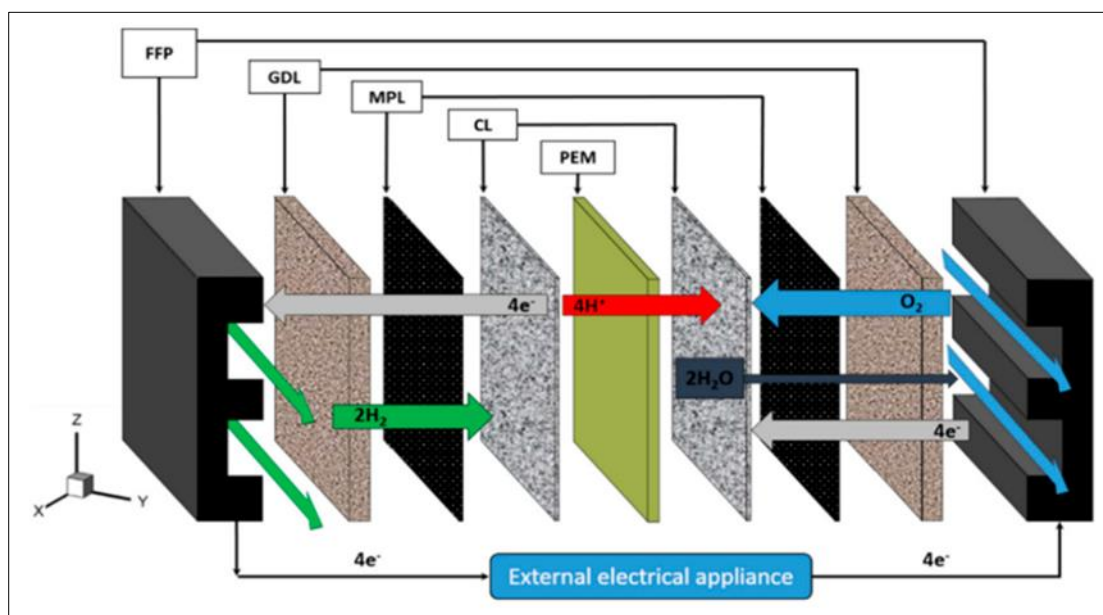


Figure 1 Main components in polymer electrolyte membrane fuel cells (PEMFCs)

### 2.2 Solid Oxide Fuel Cells

SOFc The “Nernst Glower” was the first use of a solid ionic conductor, demonstrated in the end of the nineteenth century.<sup>77</sup> In the 1940s Carl Wagner ~winner of the Society’s Olin Palladium Medal, 1951! explained the conduction

process, and the first article on a SOFC appeared in the Journal in 1962.78 This early work by Weissbart and Ruka was done at Westinghouse, which has continued to be a leader in SOFC technology to the present day. SOFCs are the only fuel cells that utilize a true solid electrolyte, and therefore electrolyte-management problems that are common to other fuel cell types are not a concern for SOFCs. ~Note that the membranes used in PEFCs must be hydrated to function well and therefore require careful management of the water within the cell.!

Additionally, the high operating temperature, typically about 1000°C, makes the SOFC much more tolerant of reformed fuels and, because water is generated on the anode, in-cell reformation of hydrocarbon fuels is feasible.[7] SOFCs are also potentially capable of very high electrical efficiencies in a co-generation system ~e.g., integrated with gas microturbines

Zeolitic imidazolate frameworks (ZIFs) are porous crystalline materials consisting of well-ordered pores [8]. They have high surface area, specific adsorption capacities and often exhibit high thermal, chemical and hydrothermal stability [9]. These properties make them attractive materials for many applications such as gas storage, separation, catalysis, drug delivery and chemical sensors [10]

### 2.3 ZIF-67 and ZIF-8

In order to minimize the dosage of noble metal Pt and maximize the surface area (active sites) of electrocatalysts; zeolite imidazole

frameworks are therefore applied. ZIF-8 and ZIF-67 are the first choices, due to their simplicity of synthesis, low-cost precursors and the existence of highly electroconductive Zn or Co metals that benefit the electrons transfer during HER [11]. Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal organic frameworks (MOFs, also known as porous coordination polymers).[12]

### 2.4 Application . ZIF-67 and ZIF-8

This review explores the features and corresponding application of ZIF-67 and its derivatives. Thermally and chemically stable zeolitic imidazolate framework (ZIF) materials have received extensive research and application interest. In particular, ZIF-67 can be synthesized by a facile and environmentally friendly organic synthesis method. The nanostructures and mean particle sizes of ZIF-67 can be adjusted by controlling experimental conditions carefully. The resulting ZIF-67 possesses the characteristics of a tunable pore aperture, highly stable structure, catalytic activity and so on. Furthermore, by combining the advantages of ZIF-67 and various components or structures, the resulting compounds have a potentially better performance than pure ZIF-67.[13] Therefore, ZIF-67 and its derivatives have aroused great interest of scientists and have the potential to be applied to gas adsorption, molecular separation, electrochemistry, catalysis and so on.

### 2.5 Characterization and properties of ZIF-8 and ZIF-67

A novel Zn/Co zeolitic imidazolate framework (ZIF) has been constructed by an easy and straightforward room temperature technique. Several characterization techniques such as SEM, TEM-EDX, single-crystal XRD and ICP have been applied to confirm that the structure formed is a sodalite (SOD) cage type structure. The Zn/Co-ZIF possesses a high nano-crystallinity and porosity with a large surface area. By tuning the amount of Co and Zn in the Zn/Co zeolitic imidazolate framework, the physical and chemical properties have been improved compared with those of the single metal frameworks (ZIF-8 and ZIF-67).

Consequently, the Zn/Co-ZIF was investigated for two different applications; gas adsorption (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>) and catalysis (CO<sub>2</sub> conversion to cyclic carbonates) and the obtained results were compared with the performance of previously reported single metal frameworks (ZIF-8 and ZIF-67). Additionally, hydrolytic stability tests under ambient conditions and immersed in water at 75 °C were performed and pointed out that Zn/Co-ZIF exhibits a higher stability. Moreover, based on these results, the Zn/Co-ZIF demonstrates better properties compared with ZIF-8 and ZIF-67.[14]

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## 3 Materials and Procedures

### 3.1 Fuel Cell Types and Development

The fuel cell is an energy conversion system that can transform chemical energy into heat and electrical energy. The anode, cathode, electrolyte, and external circuit known as the load are the only main components of a typical fuel cell

system. Despite its complex construction, the fuel cell system is fairly simple to operate. The cathode is fed with the oxidant in the air while the anode is continuously fed with hydrogen fuel.

The hydrogen that is delivered to the anode is split into two types: hydrogen positive ions, or  $H^+$ , and hydrogen negative ions, or  $H^-$ . Electrolyte theoretically divides the channel between the anode and cathode. The electrolyte's presence only permitted the transport of  $H^+$  ions from the anode to the cathode and, by acting as an insulator, prevents the movement of  $H^-$  ions. The following equations [15] reflect the three primary chemical stages that take place at the anode and cathode in the fuel cell system

### 3.2 Membrane Electrode Assembly (MEA)

Membrane electrode assembly (MEA) includes a multi-layer structure. MEA is considered as the DMFC core component system, functioning to host the main oxidant and fuel electrochemical reactions to produce electricity.

A typical configuration of MEA consists of a polymer electrolyte membrane (PEM), cathode and anode catalyst layers (CLs), gas diffusion layer (GDLs), and microporous layer (MPLs) that are also known as backing layers. MEA structure is delicately built with porosity in micro/nano-scale due to its ability to control many transportation processes in DMFC's electrochemical reactions. There are several methods available for producing MEAs using various procedures and materials. MEAs' durability and performance depend on the manufacturing process under certain conditions.

### 3.3 Solid Oxide Fuel Cells (SOFCs)

Since the 1990s, research has been done and scientific reports have been made regarding the SOFCs' potential to serve as a sustainable energy source. lists both the advantages and disadvantages of SOFCs. The most recent focus has been on SOFCs, high-temperature fuel cells, for use in cooling, heating, and power production systems. Both oxygen ion-conducting (SOFC-O<sub>2</sub>) and proton-conducting (SOFC-H<sup>+</sup>) electrolytes are used in SOFCs thermal compatibility with electrolyte materials in addition to strong chemical stability

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## 4 Conclusion

The fuel cell system design can be seen as a decision-making process that comprises of identifying potential design alternatives and selecting the most appropriate one. It can be classified as good design if it meets the design specifications as well as a trade-off between the various design goals. The specifications and goals for a fuel cell system consist of performance, dimension, which is weight and size, emissions, output power, rapid start-up and rapid response to changes in load, lifetime, and operability in intense environments and noise, which will be important in certain applications.

Considerable attention is being paid to the utilization of computer-based and modeling optimization in fuel cell systems design. One advantage of this method is the positive effect on high cost and design cycle time savings, as well as its improved operation and design. The performance of optimum development depends primarily on the method by which the prototype is developed. It is crucial to identify the important factors and those that can be compromised without having an adverse effect on the design. Modeling is carried out to capture the designer's interest aspects of the fuel cell system.

A mathematical model that represents particular fuel cell system aspects and estimates its characteristics can be in a form of algebraic equations, differential equations, or a process or subroutine based on a computer. The model can involve various alternatives to the design that can be achieved by changing parameters, variables, constraints or conditions. The principle explained in the preceding step contributes to the basis for comparing the various alternatives to design.

Then, the prototype can be combined with a numerical optimization algorithm to produce improved designs iteratively. This can lead to one or more optimal solutions. Modeling and optimization will assist the designer in further consideration of shortlisting the designs. However, optimization will not always produce a better design appropriate for manufacturing. In this situation, the iteration of the preceding points is required to confirm that suitable fuel cell phenomena are captured in the model and exact governing equations are employed, the assumptions' validity employed in modeling is analyzed, as well as to confirm that the design specifications and goals are modified and altered if necessary. The final design will result in either a final prototype or an improvement of an existing design to be developed in the future.

## Compliance with ethical standards

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### *Disclosure of conflict of interest*

The authors have no conflicts of interest to declare.

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