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Proton Exchange Membrane Fuel Cell

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PROTON EXCHANGE MEMBRANE FUEL CELL

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http://dx.doi.org/10.5772/intechopen.69180 Edited by Tolga Taner

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First published in London, United Kingdom, 2018 by IntechOpen eBook (PDF) Published by IntechOpen, 2019 IntechOpen is the global imprint of INTECHOPEN LIMITED, registered in England and Wales, registration number: 11086078, The Shard, 25th floor, 32 London Bridge Street London, SE19SG – United Kingdom Printed in Croatia

British Library Cataloguing-in-Publication Data A catalogue record for this book is available from the British Library

Additional hard and PDF copies can be obtained from orders@intechopen.com

Proton Exchange Membrane Fuel Cell Edited by Tolga Taner p. cm. Print ISBN 978-1-78923-066-6 Online ISBN 978-1-78923-067-3 eBook (PDF) ISBN 978-1-83881-378-9

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Meet the editor



Dr. Taner is the head of the Department of Motor Vehicles and Transportation Technology at the Aksaray University since 2012 (starting date 2005). He received his BS degree in Mechanical Engineering in 1998 and his MS degree in Mechanical Engineering from Pamukkale University, Denizli, Turkey, and his PhD degree in Mechanical Engineering from the Gazi University of En-

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Preface

This is a book on PEM (Proton Exchange Membrane) fuel cell and technologies. Moreover, the research of PEM fuel cell can overcome many critical problems for an alternative resource energy. In addition, PEM fuel cells are also investigated for the technology application in the book. This book poses PEM fuel cell and technology in terms of enhancement with new technologies.

This book will encourage both academic research and industrial application processes. From concept to publication, this book took approximately 1 year to complete. I thank the publisher, InTechOpen, in particular the publishing process manager Ms. Renata Sliva for her support, help and guidance. I also thank all of the chapter authors for their huge works. Finally, I thank all my family, my wife Öznur and my daughter Özüm for their support.

I hope that this book will be helpful to people who read this book. Therefore, this book will make a scientific contribution to exergy workers, researchers, academics, PhD students and other scientists both in the present and in the future.

Dr. Tolga Taner, PhD Aksaray University Department of Motor Vehicles and Transportation Technology Turkey

General Information About PEM Fuel Cell

Introductory Chapter: An Overview of PEM Fuel Cell Technology

Tolga Taner

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71544

1. Introduction

Proton exchange membrane (PEM) fuel cells revive a significant state in the energy industry and others. Enhancement fuel cell design will solve many problems for the energy issues. However, some issues are waiting to be solved. Solving issues of the fuel cells will lead to enhance other new technologies. Thus, enhancement of alternative technologies can reply to human poverty. As a result, fuel cells and types were discovered since in the 1970s, institutions, scientists and industries executed many enhancements. These enhancements involve proton exchange membrane (PEM) and other fuel cells.

These developments have not finished yet because of some known issues. NASA and similar organizations provide support to fuel cells with the contribution of several organizations in Europe and the World. Parallel to targeted efforts aimed at solving fuel cell durability, energy and wastewater.

This book intends to provide the reader with a comprehensive overview of the fuel cells for an alternative energy results in the enhancement of the fuel cells as well as its use by finding solutions to these problems.

2. Brief of PEM fuel cell

Prior to the PEM fuel cell book chapters, brief technical information of PEM fuel cell has been given in this chapter. In addition, it is necessary to explain the working principle by defining what the PEM fuel cell means.

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The hydrogen activated to form the proton ion with the catalyst is injected in the Proton exchange membrane fuel cell (PEMFC). When the electron is forced to flow out, the proton passes through the membrane and produces electric energy. The electron interferes with the oxygen as the electron returns back to the cathode. The proton ion turns into water. **Figure 1** shows chemical reactions in every electrode [1, 2].

The reaction of anode can be activated in Eq. 1 as below:

$$H_2(gas) \rightarrow 2H^+ + 2e^- \tag{1}$$

The reaction of cathode can be activated in Eq. 2 as below:

$$\frac{1}{2}O_{2}(gas) + 2H^{+} + 2e^{-} \rightarrow H_{2}O$$
 (litre) (2)

Overall the reaction can be determined in Eq. 3 as below:

$$H_{2}(gas) + \frac{1}{2}O_{2}(gas) \rightarrow H_{2}O(litre)$$
(3)

Furthermore, PEMFC's advantages and disadvantages should be figured out according to the literature. PEM fuel cell's advantages are mentioned such as the heat and water waste management, the reaction of electrode kinetics, a power with high density, an alternative catalyst and a low study temperature [3–9].

Proton exchange membrane fuel cell's disadvantages are also mentioned such as a very high sensitivity, too expensive material, a gas diffusion layer (GDL) and flow field layer, catalyst issue, degradation and difficulties of production of membrane electrode assembly (MEA) [2–4, 10–12].

PEMFC's advantages and disadvantages should be known very well because of enhancement of alternative energy resources.



Figure 1. A general schematic drawn of PEMFC [1, 2].

In addition, a mass transport and water management is a very significant issue to be solved [13–16]. When mass transport and water management issues are solved, PEMFC will become an alternative energy resource in the future.

3. Conclusion

Alternative energy options have gained importance owing to the depletion of fossil fuels. These options require considerable experimental and prototyping efforts for realizing new energy resources. The enhancement of modeling and simulation of PEMFC are invented to find new alternative remedies. Therefore, PEM fuel cells might be investigated for enhancements of PEM fuel cell modeling and simulations. PEM fuel cell voltage, current, temperature, pressure, thickness and other parameters depend on the experimental run time. PEMFC with anodic or cathodic plates, which can be produced as a part of the cell's membrane electrode assembly (MEA), can take O_2 gas directly from the air by natural convection.

Its cathodic or anodic plates determine the performance of PEMFC. Due to these similar experiment study measurements, the effects of hydrogen feeding and performance-based optimizations were figured out by optimization of experimental works. The observed voltage, temperature, pressure, layer, current and other parameters are characterized all of similar experimental works. This study presents performance and efficiency enhancement methods for PEM fuel cells and developments related to the management of waste water in the fuel cell.

This book poses proton exchange membrane fuel cell and technology in terms of enhancement with new technologies. The main idea of this study is to scrutinize the performance efficiency and enhancement of modeling and simulations of fuel cells. Besides, the research of fuel cell performance can figure out many critical issues for an alternative resource of energy. Furthermore, compared to all types of fuel cells, advantage and disadvantage aspects of PEMFCs are also investigated. This book may be a model for future similar work because of the durability of PEM fuel cell, by discussing the energy production, waste water problems and the propose of solution.

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Improving the Performance of PEM Fuel Cell

Farqad Al-Hadeethi

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71928

Abstract

In order to develop a novel proton exchange membrane fuel cell (PEMFC), new materials were investigated in order to increase the water uptake of the membrane known commercially as "Nafion" by casting it with zirconium metal organic frameworks (MOFs) (i.e., MOF 801 and 808) to form a composite using sol-gel method. It was found that the water uptake of the composite membrane (NAF-MOF) was increased in a significant way, and ion exchange capacity was improved in comparison with the commercial membrane at various temperatures. Actual runs using PEM fuel cell at 80°C and Naf-MOF (801 and 808) membranes were performed to assure the efficiency of using these membranes.

Keywords: membrane, metal organic frameworks (MOFs), zirconium, temperature, flowrates

1. Introduction

At high temperatures, membrane dehydration and decrease in proton conductivity within PEM fuel cells (PEMFC) are significant issues. Basically, membrane dehydration causes shrinking, cracking, and loss of mechanical stability.

The ability of a polymer exchange membrane in a PEMFC to absorb and transport water is crucial to its function. Low water content in the membrane increases the ionic resistance of the cell, but too much hydration leads to excessive swelling. Huge literature related to water transport through an operating fuel cell is existing, but few research works concentrate on the materials research strategies that promote the net transport of water to the anode in order to offset the effects of dehydration of the anode and flooding of the cathode. The permeation of water through a membrane involves sorption, transport within the membrane, and desorption. Permeability can be determined by measuring the flux of water under a chemical potential gradient induced by a concentration or pressure gradient of water [1].



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Incorporating inorganic fillers such as metal oxides within Nafion improved the water uptake [2]. It was found that using the SiO_2 particles will increase the water uptake in the composite membrane due to the hygroscopic nature of metal oxides (SiO₂) [3, 4].

The composite membrane water uptake depends on membrane hydration; however, the increased hydration improves membrane proton conductivity and fuel cell performance. Moreover, temperature and water content strongly affect Nafion's viscoelastic response, which are of direct importance for operating PEMFC. Accordingly, it is expected that the composite membrane has higher performance than the commercial Nafion membranes [3].

In this work, new materials [i.e., zirconium (IV) metal organic frameworks (MOFs) (i.e., MOF 801 and 808)] were added to Nafion in order to produce composite membranes (Naf-MOF) and compare its water uptake at various temperatures with commercial Nafion membrane. In addition, actual runs using PEMFC at 80°C and Naf-MOF (801 and 808) membranes were performed to assure the efficiency of using these membranes.

2. Experimental work

The Nafion-zirconium (IV) metal organic frameworks (MOFs) membranes were casted from Nafion (sulfonated tetrafluoroethylene) dispersion, containing 4% by weight, supplied by Electrochem Co. using sol-gel method [5]. The isopropanol and Nafion dispersion were mixed at a certain volume ratio, and then, a significant weights of MOF (801 and 808) obtained from Yaghi group at University of California at Berkeley were added to the selected samples. These samples were kept in an oven at 100°C until all solvents were evaporated, and the polymeric ionomer formed a solid polymer membrane known as Naf-MOF composite membrane. Then, the formulated membrane film was activated using diluted H_2SO_4 at 80°C. Finally, it was rinsed in boiling distilled water for 1 h.



Figure 1. Adding the MEA to PEMFC.

The electrodes (anode and cathode) of PEMFC were prepared by dispersing carbon black mixed with iso-propanol on the surface of 5 × 5 cm carbon paper and then left in the oven at 100°C for 30 min in order to evaporate the isopropanol. Slurry of Pt–Ru (40–20% by wt.)/C, Nafion ionomer, PTFE, and iso-propanol was loaded over the carbon black layer in the form of continuous wet film using a brush, it was then dried in an oven for 30 min at 150°C. Nafion ionomer acted as a binder, while PTFE with pores at the cathode provided a network to expel water in order to minimize the occurrence of water flooding [3]. The water uptake of the Naf-MOF (801 and 808) composite membranes was investigated at (40, 60, 80, 100, and 120°C).

In order to investigate the performance of PEMFC using Naf-MOF (801 and 808) membranes at 80°C and counter current flow of air and hydrogen at 20 ml/min, an MEA (membrane electrode assembly) was sandwiched between graphite bipolar plates and gold-plated current collectors as shown in **Figures 1** and **2**. It is worthy of mention that the heaters connected to the PEMFC were connected to a temperature controller in order to keep the PEMFC stable at the desired temperature during the run.



Figure 2. Fuel cell setup used to conduct the needed experiments.

3. Results and discussion

The PXRD patterns of zirconium (IV) MOF 801 and 808 shown in **Figures 3** and **4** assure that the crystalline structure of these materials when added to Nafion dispersion forms Naf-MOF (801 and 808) composite membranes as shown in **Figures 5** and **6**. The SEM and polarized microscope images given in **Figures 7–10** revealed in a clear way the MOF particles within the polymeric ionomer.

Samples of Naf-MOF (801 and 808) composite membranes in addition to commercial Nafion membrane were kept inside distilled water containers for 1 h at various temperatures (40, 60, 80, 100 and 120°C) in order to investigate the water uptake of the mentioned membranes as shown in **Figure 11**. The results revealed clear ability of Naf-MOF (801 and 808) composite membranes in keeping water at 80 and 100°C in comparison with commercial Nafion membrane. Naf-Mof 808 showed an extraordinary ability in comparison with Naf-MOF 801 in keeping water at 120°C. It is worthy of mention that the water uptake of both Naf-MOF (801 and 808) composite membranes at 80°C is higher than Naf–SiO₂ composite membrane given in [3].

The results given in **Figure 11** are in agreement with the findings of Yaghi et al. [6] in which they showed that zirconium (IV) MOFs (i.e., 801 and 808) have the ability to keep water because they possess appropriate pore molecules for water adsorption.

On the other hand, actual runs using PEM fuel cell at 80°C and Naf-MOF (801 and 808) membranes were performed to assure the efficiency of using these membranes. Hydrogen and air



Figure 3. PXRD patterns of MOF 801.



Figure 4. PXRD patterns of MOF 808.

flow rates were equal to 20 ml/min for both membranes. It is clear from the results given in **Figure 12** that there is an obvious shift toward higher voltage and power in comparison with commercial Nafion membrane given in [7]. It is worth of mention that NAF-MOF 808 showed better performance in terms of currents, voltages, and power densities with time in comparison with NAF-MOF 801.



Figure 5. Image of Naf-MOF 801 composite membrane obtained from the sol-gel casting process.



Figure 6. Image of Naf-MOF 808 composite membrane obtained from the sol-gel casting process.



Figure 7. SEM image with magnification power (X 1700) of Naf-MOF 801 composite membrane after conducting the solgel casting process. The image reveals the shape of MOF particles within the polymeric ionomer.



Figure 8. SEM image with magnification power (X 11000) of Naf-MOF 801 composite membrane obtained from the solgel casting process. The image reveals the shape of MOF particles within the polymeric ionomer.



Figure 9. Polarized microscope image of Naf-MOF 808 composite membrane after obtained from the sol-gel casting process. The red circle shows the MOF particles within the polymeric ionomer.



Figure 10. Polarized microscope image of Naf-MOF 801 composite membrane obtained from the sol-gel casting process. The red circle shows the MOF particles within the polymeric ionomer.



Figure 11. Water content of Naf-MOF (801 and 808) composite membranes and commercial Nafion membrane at various temperatures (40, 60, 80, 100 and 120°C).



Figure 12. Polarization curves of NAF-MOF 801 and NAF-MOF 808 at 80°C, counter current flow of hydrogen and air = 20 ml/min.

4. Conclusions

- It was found that the modified Nafion composite membrane containing zirconium (IV) MOF 801 and 808 produced in situ is better than the commercial Nafion membrane in combating dehydration at 80, 100, and 120°C because the water uptake of the modified Nafion composite membrane containing zirconium (IV) MOF 801 and 808 is greater than the commercial Nafion membrane.
- **2.** The polarization curve obtained from the fuel cell using the modified Nafion composite membrane containing zirconium (IV) MOF 801 and 808 showed an obvious shift toward higher voltage and power in comparison with commercial Nafion membrane.
- **3.** NAF-MOF 808 showed better performance in terms of currents, voltages, and power densities with time in comparison with NAF-MOF 801.

Acknowledgements

The author would like to thank the Royal Scientific Society of Jordan for supporting the abovementioned work. The author would like also to thank Professor Omar M. Yaghi and his

research group at the University of California at Berkeley for providing the zirconium (IV) MOFs (i.e., 801 and 808) utilized during the research work.

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PEM Fuel Cell Technology

Robotic Technologies for Proton Exchange Membrane Fuel Cell Assembly

Vladimir Gurau, Devin Fowler and Daniel Cox

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71470

Abstract

Proton exchange membrane fuel cell (PEMFC) stacks and their components are currently being manufactured using laboratory fabrication methods. While in recent years these methods have been scaled up in size, they do not incorporate high-volume manufacturing methods. In this context, manufacturing R&D is necessary to prepare advanced manufacturing and assembly technologies that are required for low-cost, high-volume fuel cell power plant production. U.S. Department of Energy (DOE) has identified high-priority manufacturing R&D needs for PEMFCs. Along with efforts to develop technologies for high-speed manufacturing of fuel cell components, DOE identified the need for demonstrating automated assembly processes for fuel cell stacks. The scope of this chapter is to review current manufacturing R&D efforts in the area of automated processes for assembling PEMFC stacks, to present the current state of development, successful demonstrations, related technological challenges and the technical solutions used to overcome them. An emphasis of this review is on the design of tools used for robotic grasping, handling and inserting fuel cell components in the stack and on the use of design for manufacture and assembly (DFMA) strategies that enable the automated assembly process.

Keywords: proton exchange membrane fuel cell (PEMFC), automated fuel cell assembly, robotic assembly, end-effector, design for manufacture and assembly (DFMA)

1. Introduction

Fuel cells have been advocated as clean, energy-efficient alternatives to internal combustion engines in vehicles and as power sources in stationary and portable power applications. For transportation applications, current focus is on direct hydrogen fuel cells such as proton exchange membrane fuel cells (PEMFCs), in which on-board storage of hydrogen is supplied

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by a hydrogen generation, delivery and fueling infrastructure. In addition to the transportation fuel cell application, there is current support for distributed generation fuel cell applications with a near-term focus on fuel cell systems running on natural gas or liquid petroleum gas, as well as stationary, portable and auxiliary power applications where earlier market entry would assist in the development of a fuel cell manufacturing base [1].

Compared to other types of fuel cells, the PEMFC offers the advantages of delivering higher gravimetric and volumetric power density and for operating at lower temperatures, which result in a quick start up time and less wear on systems components. For these reasons, PEMFCs find today extensive applications in transportation and stationary uses. When compared to other types of fuel cells, PEMFCs dominated the market in recent years in both number of units and in total power shipped, accounting for over 65% of global shipments in 2015. PEMFCs generated a revenue over USD 2 billion in 2015 [2] and are expected to generate USD 12 billion in 2025 [3].

The PEMFC power plant consists of four main subsystems: (1) the fuel cell stack; (2) the balance-of-plant subsystem, which includes the water and thermal management modules, the air delivery module and the hydrogen generation/storage module; (3) the power conditioning subsystem and (4) system controls. The fuel cell stack and its components are currently manufactured using laboratory fabrication methods that have been scaled up in size but do not incorporate high-volume manufacturing methods. The entire fuel cell power plant is usually constructed by integrating its subsystems, but each subsystem is assembled separately by a labor-intensive process. In this context, manufacturing research and development is needed to prepare advanced manufacturing and assembly technologies that are necessary for low-cost, high-volume fuel cell power plant production. U.S. Department of Energy (DOE) has identified high-priority manufacturing R&D needs for PEMFCs. A summary of these needs include [4]: (1) to identify relationships between physical and manufacturing properties of fuel cell components, (2) to develop technologies for high-speed manufacturing of fuel cell components, (3) to identify the cost of PEMFC at several levels of manufacturing, (4) to develop agile, flexible manufacturing and assembly processes, (5) to develop automated processes for assembling fuel cell stacks, (6) to establish flexible automated manufacturing technology facility and (7) to develop production hardware for rapid fuel cell stack postassembly testing, including leak detection.

This chapter reviews the current manufacturing R&D efforts in the area of automated processes for assembling proton exchange membrane fuel cell (PEMFC) stacks and presents the current state of development, successful demonstrations, related technological challenges and the technical solutions used to overcome them. An emphasis of this review is on the design of tools used for robotic grasping, handling and inserting fuel cell components in the stack and on the use of design for manufacture and assembly (DFMA) strategies that enable the automated assembly process. Even though there have been demonstrated automated or semiautomated processes for manufacturing of some fuel cell components, this work is not intended to cover them. While the authors are not aware of any published or demonstrated automated technologies that integrate the automated manufacturing of fuel cell components with the automated assembly of fuel cell stacks, they will provide strategies for achieving this goal.

The PEMFC stack consists of several single (unit) cells connected in series (**Figure 1**) and clamped together between two end plates, usually using threaded components. A single cell

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Figure 1. Exploded view of a PEM fuel cell stack consisting of multiple single (unit) cells.

consists of a membrane electrode assembly (MEA) placed between two electrically conductive collector plates that have a network of channels (flow fields) fabricated into the planar surfaces (**Figure 2**). The MEA consists of five components: a proton conductive membrane bounded by two catalyst layers, one on each side of the membrane, and two porous gas diffusion layers (GDLs) bonded each on the other side of the catalyst layers. In a fuel cell stack, the



Figure 2. Components of a single (unit) cell.

collector plates have flow fields on both planar sides. One side serves as anode flow field for one single cell and the other side serves as cathode flow field for the adjacent single cell. In this case, the collector plates are called bipolar plates and have the additional role of connecting the single cells electrically in series. Each single cell is equipped with two gaskets placed on the peripheral area of each flow field, which are intended to prevent overboard reactant gas leaks or leaks between anode and cathode.

2. Justification for automated assembly of PEMFC stacks

Today, fuel cell stacks are assembled mostly manually in a lengthy process involving a repetitive work cycle in which human errors are common. A recent study of PEMFC system cost [5] based on application of standard DFMA analysis methods, including the *Boothroyd-Dewhurst DFMA®* software [6] estimated the time necessary to manually assemble PEMFCs to be between 0.64 and 0.83 minutes per cell. This result may support the conclusion that cost savings incurred by introduction of an automated stack assembly process are small compared to the overall PEMFC system cost. In the early stages of fuel cell prototype development, fuel cell stacks may be assembled manually, but the introduction of automated assembly processes becomes economically justifiable once the production quantity increases. Today, there are no fuel cell companies having the manufacturing capacity to produce more than a few hundred fuel cell systems per year. Three-to-four orders of magnitude increase in production rate will be needed for the transition to a hydrogen-based fuel cell transportation system [4].

Apart from an economic justification, there are other reasons for adopting automated processes for assembling PEMFC stacks. Fuel cell manufacturers must increase the production volume to continually reduce costs while improving quality, reliability, performance and safety. A justification reason for adopting automated assembly technology is related to the objective and subjective effects on the worker and on the product quality associated to the monotony of repetitive work cycles characteristic to assembly of fuel cell stacks consisting of large number of cells. A recent study [7] showed that a manual assembly process of a 20-cell PEMFC stack lasted on average 50% longer than the robotic assembly process. The delays in the manual operations, as compared to the operations performed by the robot, were in part due to periodic breaks necessary for the human operator performing a repetitive work cycle. These delays are expected to increase significantly as the size of the fuel cell stack increases. Automated fuel cell assembly processes are further justified when integrated into larger automation lines in which the fuel cell components are produced as well using automatic technologies.

3. Technological challenges

One of the most significant technological challenges represents the difficulty to align accurately the fuel cell components in the stack when the assembly process is executed by a robot
that has limited accuracy and repeatability and no joint flexibility (lack of compliance) [7, 8]. Assembly of fuel cell stacks requires perfect indexing and aligning of bipolar plates, MEAs and gaskets. Misalignment of components generates overboard leaks or leaks between anode and cathode of the reactant gasses during fuel cell operation. GDLs must fit within the central, open area of the peripheral gaskets without overlapping them. A minimum clearance between GDLs and gaskets must allow them to expand in-plane during the application of the compression load. In order to avoid component misalignment during a manual fuel cell assembly process, it is a common practice to use steel alignment pins mounted in one end plate along with positioning holes in the fuel cell components that are used to guide them along the pins.

Nevertheless, when the fuel cell components are inserted along rigid alignment pins that have a certain tolerance to position, straightness and parallelism by a robot arm with limited accuracy and repeatability and no joint flexibility (no compliance), this method alone will result in jamming and breaking the fuel cell components during their insertion process. The challenge of precisely aligning the fuel cell components in the stack increases with stack length, which is determined by its number of cells. Earlier research on robotic assembly of PEMFC stacks [9, 10] attributed these failures to a low bearing ratio (positioning hole diameter to component thickness ratio) characteristic to thin fuel cell components and to warping of flexible MEAs and gaskets. Later successful demonstrations of fuel cell robotic assembly processes [7, 8] were made possible by a careful selection of a combination of allowances between the alignment pins and positioning holes and between the GDLs and the peripheral gaskets, by using flexible alignment pins and end-effectors possessing passive compliance.

In an automated assembly process, a second significant challenge represents the diversity of fuel cell components that need to be grasped and handled by robot end-effectors. These components include graphite bipolar plates, thin, flexible rubber gaskets and membrane electrode assemblies (MEAs). Initial demonstrations of robotic assembly processes [9, 10] were based on expensive workcells using multiple robots, each equipped with a different type of end-effector for grasping and handling specific fuel cell components.

4. Design for manufacture and assembly of fuel cell components

A deterrent to successfully demonstrate automated assembly technologies for fuel cells has been an insufficient use of DFMA principles in designing components. There have been attempts to demonstrate robotic assembly processes using off-the-shelf fuel cell components that were not designed for an automated assembly [9, 10].

To reduce the manufacturing cost and shorten the product development time, DFMA principles must be considered in the earliest design stages of fuel cell components [11]. The fuel cell components must include design features that allow an accurate engagement and component alignment during pickup and release operations, as well as compensate for the robot limited accuracy, repeatability and lack of compliance [7, 8, 12, 13]. The *Boothroyd-Dewhurst*

DFMA analysis method [6] provides systematic procedures for evaluating and improving the product design for ease of assembly and quantifies the time and cost of the assembly process based on component design features.

Before analyzing DFMA recommendations and design solutions that address them, one must consider design restrictions specific to fuel cell components. The most important are: (i) PEMFC components are flat, thin parts. Their planar area may range from 1 cm² to a few hundred cm² while their thickness ranges from submillimeter-scale (gaskets and MEAs) to a few millimeters (bipolar plates). (ii) Most PEMFC components have no symmetry. The anode and cathode sides of MEAs have different catalyst loadings (mgPt/cm²) and often have different catalyst types. The anode and cathode flow fields of bipolar plates are not identical, their design depending on the required mass flow rate of gas and on special requirements for removing liquid water from the flow field. The orientation of the PEMFC components in the stack is important. (iii) Some fuel cell components (gaskets and MEAs) are flexible, having the tendency to bend or warp during their handling and insertion operations.

We will discuss next DFMA recommendations for robot assembly [6] that are specific to fuel cell components and will present design solutions that address these recommendations:

- i. Reduce part count. This is a major strategy for reducing assembly and manufacture cost. Often, MEA manufacturers readily integrate GDLs in the MEA assembly, but GDLs may be assembled separately in the stack. GDLs are thin, porous layers that are difficult to be handled by end-effectors equipped with vacuum cups. *KUKA Robot Group* demonstrated a robot assembly [14] of PEMFC stacks in which GDLs were picked and inserted in the stack as separate components. Peripheral gaskets are usually assembled as separate components, but they can be integrated with the bipolar plates. This solution reduces the gasket material waste. *ZSW (Center for Hydrogen and Solar Technology* in Ulm, Germany and *Zentrum für Brennstoffzellentechnik* in Duisburg, Germany) demonstrated automated PEMFC assembly lines in which liquid rubber was applied directly on the peripheral areas of bipolar plates and MEAs using a syringe [15] or screen printing technique [16] and then the rubber was allowed to cure before final assembly.
- ii. Include features such as leads, lips and chamfers that make parts self-aligning in the assembly. Due to limited accuracy and repeatability of robots, this is a vitally important method to ensure fault-free part insertion in the stack. Designs [17] of self-aligning bipolar plates using protrusions and recesses have been proposed (Figure 3). Due to MEA and gaskets tendency to warp, this technical solution may require holding down the components and securing them using special purpose fixturing that must be activated by the robot controller. This solution may add the assembly cost significantly. A successful solution for aligning and securing the components in the stack after insertion is the use of alignment pins mounted on the base end plate (Figure 4) and positioning holes in the fuel cell components. The clearance between the alignment pins and positioning holes must be equal or less than the clearance between the gaskets and the GDLs. This prevents the gaskets from overlapping the MEAs after insertion. As described earlier, since the alignment pins have a certain tolerance to

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Figure 3. Design features used for self-aligning bipolar plates [17]. Source: United States Patent and Trademark Office, www.uspto.gov.



Figure 4. Component presenters and PEMFC stack (second from left) equipped with flexible alignment pins made of poly(tetra)fluoroethylene and used for locating component during pickup and release operations; reproduced from [7].

position, straightness and parallelism and since robots have limited accuracy, repeatability and no flexibility, components tend to jam and break during the automated insertion process. A demonstrated solution to this problem [7, 8, 12, 13] is the use of flexible alignment pins instead of rigid pins made of steel. When they are made of a polymer, the pins do not need to be extracted from the stack at the end of the assembly process, reducing thus the assembly cost. For ease of component insertion, pins can be designed with large chamfers. Alignment pins made from polymers are easier to cut to size and chamfer than steel pins. In addition to this solution, the end-effector may be designed with passive or active compliance.

iii. Design features such that components do not require to be secured after insertion. The alignment pins discussed above locate the components after insertion even when MEAs and gaskets have the tendency to warp.

Other DFMA recommendations for robot assembly [6], such as designing products that can be assembled in a layer fashion directly from above, or avoiding the need for reorientation of the partial assembly, are generally satisfied by the PEMFC configuration and do not require special design.

5. End-effectors for manipulation of PEMFC components

The design of robot end-effectors must be integrated with the design of fuel cell components. They must be able to compensate for the robot's limitations in accuracy, repeatability and lack of compliance. To minimize the number of robots needed for assembly, to reduce the assembly cost and to enable designs of flexible robot workcells, it is preferable to design end-effectors capable of grasping and handling most types of fuel cell components. In addition, it is preferable to design end-effectors capable of assembling fuel cell stacks of any size (number of cells).

Initial demonstrations [9, 10] of robot workcells for automated assembly of PEMFC stacks used robots with different types of end-effectors, including double-acting finger grippers for clamping bipolar plates from their lateral surfaces and pneumatic end-effectors for manipulating gaskets and MEAs. Due to the thin configuration of fuel cell components, finger grippers designed for clamping them laterally and grasping from presenters require additional equipment such as feeders or feedback vision systems to determine their location at submillimeter scale and their speed appropriate for indexing during pickup and release operations.

Designs of inexpensive, more flexible end-effectors capable of manipulating all fuel cell component types have been demonstrated [7, 8, 12, 14]. They are equipped with vacuum cups and are designed to grasp the components from their top planar surface. Suspension mechanisms used to provide a soft touch and to reduce the machine need for indexing when picking up and releasing fuel cell components can be provided. The suspension mechanisms reduce the need for accuracy when approaching the component presenters or the stack and eliminate the need for expensive feedback visual systems (**Figure 5**).

To compensate for a general robot's limited accuracy, repeatability and lack of joint flexibility, end-effectors with passive compliance have been demonstrated [7, 8, 12].

The end-effector shown in **Figure 6** consists of three subassemblies connected to each other by two miniature linear blocks and rails oriented at 90° relative to each other. They allow the lower subassembly that grasps the fuel cell components and the top subassembly that attaches the end-effector to the robot wrist assembly to have a relative motion along the X and Y axes between them. Stoppers delimit each block's travel to about 3 mm along the rail. These linear blocks and rail system offer the end-effector a reliable passive compliance capability that compensates for the robot's limitations in accuracy, repeatability and lack of joint flexibility.

In addition to this, the linear blocks and rail system allow the end-effector to slide the positioning holes on the fuel cell components along the alignment pins when the latter have a certain tolerance to position, parallelism and straightness. This compliance system along with the conical tip of the alignment pins (**Figure 4**) may compensate for misalignments as large as a few millimeters, which are much larger than the usual limitations in a robot's accuracy and repeatability. The lower subassembly of the end-effector (**Figure 6**) has the role to pick up and release the fuel cell components and to align them along the alignment pins on one fuel cell end plate. Four level compensators equipped with suspension mechanisms and vacuum Robotic Technologies for Proton Exchange Membrane Fuel Cell Assembly 29 http://dx.doi.org/10.5772/intechopen.71470



Figure 5. End-effectors used for PEMFC components manipulation: (a) double-acting finger gripper; reproduced with permission from [9]; (b) pneumatic end-effector with suspension mechanism; reproduced from [14]; (c) end-effector with vacuum cups and suspension mechanism used in [7]; (d) pneumatic end-effector; reproduced from [16].

cups are mounted on the lower subassembly to provide a soft touch and to reduce the need for machine indexing when the fuel cell components are picked up and released in the stack. The four vacuum cups are pneumatically connected through tubing and fittings mounted on the level compensators to a miniature vacuum pump controlled by the robot. The lower subassembly is also equipped with a winglet with two positioning holes that align with the positioning holes on the fuel cell components during pickup and release operations. The top subassembly connects the end-effector to the robot wrist-assembly. The intermediate subassembly has the only role of interconnecting the lower and the top subassemblies through the miniature linear blocks and rails and to provide passive compliance to the end-effector. To enable robotic assembly of fuel cell stacks consisting of any large number of cells, the interface component of this end-effector that attaches to the robot wrist-assembly is off-centered relative to the suspension mechanisms and vacuum cups, preventing the fuel cell stack from interfering with the robot wrist-assembly during pickup and release operations.



Figure 6. Partially exploded view of an end-effector with passive compliance; reproduced from [7].

6. Workcell design for automated assembly of PEMFC stacks

There have been successful demonstrations of automated assembly technologies for PEMFC stacks using special-purpose automation lines [15, 16], workcells consisting of multiple general-purpose robots [9, 10] and workcells consisting of a single robot [7, 8, 14]. There are two strategies to accomplish the automated assembly process: (i) assemble first single (unit) cells, fasten them, test them and then assemble the single cells in the final stack and (ii) assemble the entire stack directly by repeatedly adding bipolar plates, gaskets and MEAs.

The first strategy enables testing and servicing single cells, without disassembling the entire stack, but has additional manufacturing operations. It was demonstrated by *ZSW* [15] and *ZBT* [16] both in Germany. The workcells consist of special-purpose automation lines comprising multiple stations for assembling single cells, including stations for application of liquid rubber as sealant, for curing the rubber, for application of the MEA, for fastening the cell and testing it for gas leaks. The single cells are transported between stations by conveyors. *ZSW* assembly line [15] uses a KUKA robot for assembling the single cells in the stack.

The second strategy was demonstrated using general-purpose robot workcells. The Center for Automation Technologies and Systems (CATS) at Rensselaer Polytechnic Institute [9, 10] demonstrated a workcell consisting of three KUKA robots surrounding a moving shuttle cart and dedicated part bins (**Figure 7a**). Each robot is dedicated to a single stack component and assembly is accomplished on the shuttle cart that moves between robots. Other components to this workcell include a control center, a vision system and subsystems consisting of a shuttle cart with decrementing Z parts feeders and robotic end-effectors.

KUKA Robot Group [14] (**Figure 7b**) and Kent State University [7, 8, 12, 13] (**Figure 7c**) demonstrated flexible, inexpensive workcells consisting of a single general-purpose robot equipped with universal end-effectors capable of manipulating all fuel cell components. In both workcells, fuel cell components are stacked in presenters from which the robot picks components and inserts them in the stack. These workcell arrangements eliminate the need for conveyors,



Figure 7. General purpose robot workcells for assembly of PEMFC stacks: (a) workcell consisting of 3 KUKA robots with 6 DOF (degrees of freedom); reproduced with permission from [9]; (b) workcell consisting of a single KUKA robot with 6 DOF; reproduced from [14]; (c) workcell consisting of a single Fanuc robot with 6 DOF used in [7].

indexing mobile shuttle carts on which the fuel cell stack is built, component feeders or feedback visual systems. The workcell demonstrated at Kent State University consists of a Fanuc S 420F robot, three presenters containing bipolar plates, gaskets and MEAs and the end plate with alignment pins on which the fuel cell stack is built (**Figure 7c**). The presenters where the fuel cell components are picked from consist of support plates with two poly(tetra)fluoroethylene (PTFE) alignment pins each similar to the alignment pins on the fuel cell end plate. The presenters and the fuel cell end plate are mounted on an aluminum extrusion framing attached to the workbench. The presenters are permanently mounted to the frame. Every time a new stack is assembled, a fuel cell end plate is attached to the frame using locators and clamps (see also **Figure 4**). The locators allow the new end plate to be mounted every time in the same position.

7. Future work

All automated assembly processes presented here use special-purpose automation lines or general-purpose robots that pick fuel cell components from presenters and insert them in the stack. The fuel cell components in presenters are all oriented in the same position, for example, the bipolar plates with the anode flow field, and the MEAs with the cathode oriented upward. To integrate an automated assembly process into a larger line in which the fuel cell components are also produced using automatic technologies, intermediate stations are required, where the position of components is analyzed and the components are reoriented and then stacked in presenters all with the same orientation. These complex tasks require in addition to automated quality control operations, collaborative robot activities and image analysis. These complex tasks remain to be demonstrated.

Acknowledgements

Preparation of this chapter was made possible with funds from Georgia Southern University.

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Perspective Non-Fluorinated and Partially Fluorinated Polymers for Low-Temperature PEM FC

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71250

Abstract

The main requirement to the materials used to make membranes polymer electrolyte membrane fuel cells (PEM FC) is the combination of high proton conductivity and resistance to the FC operation conditions. Thus, the search for inexpensive and high-performance non-fluorinated or partially fluorinated materials for use as FC membranes is an actual task today, since the use of membranes based on perfluorosulfonate acid has a number of disadvantages limiting their application. The aim of this study is the investigation of sulfonated polyimide (SPI) and materials for use as FC membranes. The relevance of research stems from the fact that the use of the SPI will allow to increase the resistance of the membrane to the constantly changing environment in which PEM operates. The objects of research are sulfonated polyimides. SPIs, especially aromatic SPIs, are attractive to researchers, because of the possibility of obtaining a wide variety of chemical structures and also due to their excellent thermal, mechanical properties and high resistance to aggressive media. The results of this study will be methods of obtaining and evaluating the advantages and disadvantages of SPI-based materials. For the first time, special attention will be paid to advanced development based on SPI with the addition of crown-ether fragments.

Keywords: polyimides, poly(imide-siloxane), polyimidesters, polyimide matrix, fuel cell, proton-exchange membrane, proton exchange

1. Introduction

Fuel cells (FC) are chemical sources of current. They perform direct conversion of fuel energy into electricity, avoiding combustion processes and conversion of thermal energy

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into electrical energy. In an ideal fuel cell, electrolyte and electrodes are not consumed and do not undergo any changes during the operation process – the chemical energy of fuel is converted directly into electricity.

The FC device is similar to the device of the galvanic cell. The main part of any fuel cell is the membrane-electrode assembly (MEA), which is a solid electrolyte layer with the applied electrodes. One side of the membrane (similar to liquid electrolyte in the galvanic element) is applied to the cathode and the other anode catalytic layers. Most often, the catalyst of the anode, molecular hydrogen dissociates and loses electrons. Cations of hydrogen are conducted through the membrane to the cathode, but the electrons are given to the external circuit because the membrane does not pass electrons. On the catalyst of the cathode, the oxygen molecule joins with an electron supplied from an external communications and with arrived proton to form water, which is the only product of the reaction. The current collecting at the cathode and anode sides, a supply source of reagents and withdrawal of the reaction products is carried through the porous gas diffusion layers (GDL), is usually made of carbon materials.

There are several different types of fuel cells classified according to the type of electrolyte. The type of the electrolyte depends on the most parameters of the FC, such as operating temperature, size, energy output, etc.

Fuel cells based on polymer electrolyte (proton-exchange) membrane (PEM) is designed to become compact sources of energy and replace petrol and diesel engines. These systems operate at relatively low temperatures up to 100°C. They quickly go on working power, and are compact, which is advantageous for use in transport. The main, and still not overcome the disadvantage of this type of FC is a weak resistance of the membrane to constantly changing environment in which operate PEM.

Membrane PEM FC works in conditions of constantly changing temperatures, high humidity, organic reagent and the formation of peroxides. The main requirement to the materials used to make membranes is the combination of high proton conductivity and resistance to the conditions of the FC. An important criterion is also the low cost of their production.

The first electrolytic membrane, which was developed by General Electric in the USA in the late 1960s to FC used in spacecraft of the Gemini, was sulfonated copolymer poly-(styrenedivinylbenzene). This polymer was not sufficiently resistant to oxidation under operating conditions of FC. A major breakthrough in technology proton-conducting membranes for fuel cells was the emergence of perfluorosulfonate acid (PFSA) Nafion – DuPont product obtained in the 1970s and Nafion counterparts from other firms, for example, Flemion[®] (Asahi Glass), DowMembrane[®] (Dow Chemical) and Aciplex[®] (Asahi Chemical).

However, the own proton conductivity of such membranes is extremely small, and effectivity proton transfer is determined by the presence of adsorbed atmospheric moisture. Moreover, the market value of the Nafion membranes is 700-800 /m².

Despite the fact that PFSA are still excellent materials for membrane fuel cells, yet they have several significant shortcomings that limit their widespread application. These factors stimulate

the interest of researchers to finding cheap and high-performance alternative materials for use as membranes, fuel cells. Such polymers, as polyetherketone, polyetheretherketone, polysulfone, polyether sulfones and polyimides are particularly attractive for researchers. Due to the large diversity of possible chemical structures, including partially fluorinated, they have a high mechanical strength, chemical and thermal stability.

One of the most promising materials for the fabrication of membranes FC are the aromatic polyimides. Polyimides have high heat resistance, the most heat-resistant polyimides based on dianhydride pyromellitic and 1,4,5,8-naphthalenemethanol acids.

These polyimide films are hydrophilic and do not have proton conductivity. Therefore, to ensure high proton conductivity in polyimide chain introduce acidic groups (most often sulfonic – SO_3H , sometimes phosphoric). The membranes based on sulfonated polyimides (SPIs) (containing the main chain and/or branches of the group SO_3H), gas permeability for hydrogen is about three times lower than that of Nafion.

2. Perspective non-fluorinated and partially fluorinated polymers for low-temperature PEM FC

One of the advantages of fuel cells with polymer electrolyte membrane (PEM FC) indicate a high efficiency of conversion of fuel energy into useful energy, compared with current alternative systems, based on heat engines, whose efficiency is limited by Carnot cycle. It is believed that efficiencies can be over 80%. In practice, however, the efficiency of fuel cells with a polymer membrane is about 50%.

The main difference between fuel cells from other chemical current sources is the possibility of continuous fuel injection and continuous weaning current for potentially unlimited period of time. In practice, however, there is a severe degradation of all components of the MEA, which leads to a monotonous decrease of the voltage on the plates of FC (hence reduced efficiency) when fixing the subtracted current [1].

The "heart" of the MEA is a polymer electrolyte (proton-exchange) membrane (PEM). Typically, the proton-exchange membrane is a film of polymer with a hydrophobic main chain and the acid groups in the side chains. Water in contact with polymer is clustered close to the acid groups, forming nano-sized hydrated cluster. In this area, in addition to water contain various hydrated forms of the movable proton. Thus, the hydrophilic part of the polymer provides efficient proton transport, while the hydrophobic part stabilizes the morphology of the membranes and ensures their mechanical strength [2].

The hydrophobic part of the polymer usually contains aliphatic, aromatic, fluorinated or nonfluorinated fragments. As acid groups generating protons, sulfonates are most often used, more rarely acid residues of phosphoric acid. It is believed that the sulfonated polymers are more efficient in the presence of water vapor, while the more phosphorylated heat-resistant polymers and their conductivity is less dependent on humidity. To improve the conductivity, the hydrophilic portion of the proton-exchange membrane is often injected with a water-soluble proton-generating additives (usually strong acid), nanoscale oxides or solid electrolytes. Sometimes the proton-generating additive is injected into a non-conductive polymer matrix. In this case, the hydrophilic part is formed by the coordination of water around the introduced additives with subsequent separation of phases.

The main function of proton-exchange membrane is to transfer the cathode area of a proton, resulting in ionization of hydrogen at the anode. Therefore, the membrane should have a maximum conductivity. The conductivity at the level of 10^{-1} – 10^{-3} s/cm is considered adequate for use in FC. Because ideally, the work of FC need to carry in conditions of significant fluctuations of temperature and humidity as fuel and oxidizer, it is desirable that an efficient proton transfer occurred under these conditions. In order to avoid electrical losses, the electronic component of conductivity should be minimal (at least 2–3 orders of magnitude lower than the ionic component) [3].

In addition, the proton-exchange membrane plays a role of gas separation: it cuts off the anode side of the MEA, which contains hydrogen, from the cathode, where air or oxygen is blown. The low gas permeability when using hydrogen under high pressure is especially important. The permeability of the membranes of less than 10^{-2} ml/(min cm²) is considered sufficient for long-term operation of the fuel cell.

The proton-exchange membrane is subject to a number of requirements. For the efficient operation of the fuel cell, ohmic losses in the membrane should be minimal, and the proton conductivity of the membrane is high. The membrane must have mechanical strength sufficient to pressing on the electrodes to the membrane and operation at elevated pressures of the reactants.

Since the formation of extremely reactive hydrogen peroxide on the cathode is possible, in addition to water, the membrane should possess high chemical stability to oxidation and hydrolysis. The water released at the cathode during the fuel cell works is partially absorbed by the membrane, leading to its swelling. This process is most noticeable when using the humidified air. Excessive swelling of the membrane with subsequent drying, after repeated enabling/disabling of the fuel cell, is extremely undesirable process that leads to destruction and exfoliation of the thin active layer and deterioration of the characteristics of the fuel cell. To prevent direct chemical (not electrochemical) reaction of the reactants on one of the electrodes is necessary that the membrane was gas-tight. Penetration of hydrogen on the cathode side equivalent leakage current and should be minimized in order to increase the efficiency of the fuel cell [4].

2.1. Main requirements for PEM

In order for the materials to be used in PEM fuel cells, they must have a number of conflicting requirements such as in Ref. [5]:

- **1.** Low cost.
- **2.** Good film forming ability.

- 3. Sufficient proton conductivity (≥100 MS/cm), weakly dependent on relative humidity.
- 4. The ability to retain moisture at high temperature.
- 5. Thermal, oxidative and hydrolytic stability.
- 6. Low permeability to fuel, for example, methanol <10⁻⁶ mol (min cm)⁻¹.
- **7.** Preservation of the strength properties at operation temperatures of FC (80–200°C) within the required time.
- 8. The possibility of disposal of spent membranes by standard methods.

It should be noted that the functional characteristics of membranes need to be optimized in the complex, because they are fundamentally interrelated. Indeed, it would not be quite correct to improve, for example, the proton conductivity of the membrane material, without regard to the mechanical properties and the stability of the membrane as a whole. A simple way to increase proton conductivity of the polymer sulfonic acid is, for example, to increase the number of sulfonate groups per unit volume (i.e., decreasing equivalent weight), but this path inevitably leads to obtaining material with poor mechanical properties, excessive swelling or even dissolving in water, which is the product of the reaction. Similarly, the phosphorylation or the increase of doping of polybenzimidazole by phosphoric acid leads to soft gel consistence, incapable of effective separation of reactants between cathode and anode.

On the other hand, losses in the membrane are determined by not specific but general resistance. This means that the transition to more durable membranes that could efficiently separate the reagents, being more delicate, with a mild deterioration in its conductivity could be an advantageous. In practice, however, the general principle is that an increase in mechanical stability of the membrane and reducing its permeability toward reactants, for example, by chemical linkage, always leads to the inevitable drop in conductivity.

2.2. Polymers used as proton-exchange membranes

The first electrolytic membrane, which was developed by General Electric in the USA in the late 1960s to FC used in spacecraft of the Gemini, was sulfonated copolymer poly-(styrenedivinylbenzene). This polymer was not sufficiently resistant to oxidation under operating conditions of fuel cells [6]. A major breakthrough in technology proton-conducting membranes for fuel cells was the emergence of perfluorosulfonate acid (PFSA) Nafion – DuPont product [7, 8].

2.2.1. Commercial proton-exchange membrane

Currently the most common membrane is a perfluorinated ion-exchange membrane Nafion developed by DuPont in the 1970s, there were also a number of analogous Nafion – products companies Asahi Glass (Flemion), Asahi Chemical (Aciplex), Dow Chemical, 3 M, FuMA-Tech (Fumapem), etc., wherein minor variations in the structure of side chain polymer molecules (**Figure 1**).



Figure 1. Structure of the Nafion membranes [2].

Membrane Nafion is a copolymer of tetrafluoroethylene and a possible co-monomer having a side chain of perfluorinated vinyl ether with end sulforaphanes.

Materials based on such polymers are high-tech, and able to get a pretty high-performance at operating temperatures up to 90°C. However, the own proton conductivity of the membranes is extremely small, and effective the proton transfer in them is determined by the presence of adsorbed atmospheric moisture, Therefore, these membranes are FC only work under conditions of constant wetting and hydrostatic, which requires the introduction of additional devices and increase rates of electrochemical generators [2, 9].

It is known that platinum catalysts are very sensitive to the purity of fuel. Negative impact on the catalyst may be present in such hydrogen as impurities hydrogen sulfide. Therefore, the preparation of fuel for low-temperature FC must include expensive phase removal of sulfur compounds and CO [9]. Increasing the operating temperature can in principle improve the efficiency of platinum catalysts. So, the permissible content of CO increases from 10 to 20 ppm at 80°C to 1000 ppm at 130°C. This significantly reduces the cost of the fuel. In addition, increasing the operating temperature allows for more effective heat dissipation and disposal of heat (the latter increases the total fuel efficiency).

Temperature rise of FC is also significantly accelerates the electrode reaction, therefore, can be expected to reduce necessary for the efficient operation, of the quantities of the noble metal in the electrodes. However, the proton conductivity of Nafion-type membranes at temperatures above 90°C is drastically reduced (**Figure 2a**), making their use impossible at elevated temperatures. Obtaining membranes themselves are extremely time-consuming and the cost of quality of membranes of this type are large.

Another commercially available system that may be used at temperatures up to 200°C, are membrane based on PBI, doped with phosphoric acid (**Figure 3**).

Phosphoric acid forms an acid-base complex with a polymer matrix (membrane brand the company PEMEAS Celtec Division) [10]. The significant superiority of such membranes in comparison with the Nafion membranes is their high proton conductivity in the absence of moisture (**Figure 2b**) and high thermal stability (up to 600°C). The working temperature range for the MEA on the basis of such membranes is 160–180°C. The fuel cell in this temperature region enables the use of hydrogen with high co content.

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Figure 2. Dependence of proton conductivity for the membranes Nafion-117 (a) and on the basis of polybenzimidazole (PBI), doped with phosphoric acid (b), the temperature [4].



Figure 3. The structure of polybenzimidazole.

The main problem with membranes is that they are "afraid" of liquid water, in contact with which is destroyed in an acid-base complex and the phosphoric acid is washed out in the area of catalytic and diffusion layers, leading to partial blockage of the gas pores, degradation of bipolar plates and the gas-feed system. The removal of phosphoric acid from the polymer matrix reduces the proton conductivity of the membrane. To avoid condensation of water vapor in the cathode area using relatively time-consuming procedure for stopping the fuel cell, which consists of the removal of loading, purging dry argon to remove water vapor, sealing and cooling. Of course, such a laborious procedure requires additional equipment, which significantly increases the cost of electrochemical generators of the MEA on the basis of the membranes of PBI/phosphoric acid.

2.2.2. Non-fluorinated polymers

Due to the high cost of perfluorinated polymer sulfonic acids and also because of their high permeability toward methanol, great attention to various hydrocarbon polymer sulfonic acid was given in recent years. At a lower cost of production, those acids could be a substitute Nafion [5].

Typical examples of hydrocarbon polymers used as membranes, fuel cells are sulfonated polyetheretherketone, polyarylene, polysulfone and polyimides.

In general, in comparison with National, hydrocarbon polymers are characterized by both advantages and disadvantages. Typically, the synthesis of carbohydrate polymers of the least

costly than the synthesis of fluorine-containing polymers. The permeability of the hydrocarbon polymers on oxygen and methanol is lower than polyfluorinated polymers. Because of lower hydrophobicity of the macromolecules of hydrocarbon polymers in General, the sensitivity of their proton conductivity to the degree of hydration of the reactants supplied to the fuel cells is not as pronounced as perfluorinated sulfonic acids. This simplifies the control of water balance in the MEA during the work. The less pronounced hydrophobic properties of hydrocarbon polymers molecules are also allowing to retain water at high temperatures, which increases the possible working temperature range of the FC – in comparison with FC-based membranes Nafion and its analogs. However, the balance of conductivity and mechanical properties of hydrocarbon polymers is worse, in general, than for the perfluorinated polymeric sulfonic acid.

2.2.2.1. Sulfonated polystyrene and its analogs

The first real working generator on fuel elements, was the generator of General Electric power of 1 KW, which was used as a source of electricity and drinking water for astronauts participating in the Gemini project in the mid-1960s. However, the working life of this installation was limited due to the chemical degradation of the membranes based on sulfonated polystyrene under the action of peroxides, formed at the cathode. For such membranes the company Ballard Power Systems has developed a new series of sulfonated copolymers of α , β , β -trifluorostyrene and substituted α , β , β -trifluorostyrene.

Such polymers are known under the brand name Ballard Advanced third generation Membrane (BAM3G) and have a chemical structure shown in **Figure 4**.

Alternative and relatively cheap way of obtaining proton-exchange membranes is the method of grafting of ionogenic groups in the fluorinated polymer matrix. The method of radiation grafting is well known as a method of modification of polymers to modify their physicalchemical properties [11–16]. Radiation-grafted membranes get based on existing commercially



Figure 4. Structural unit of sulfonated polystyrene.

available films in three stages. In the first stage, a polymer film is irradiated with an electron beam or gamma radiation for the formation of free radicals in the polymer material. Next, to the polymer backbone sutured to the lateral pendants, which are then sulfonated. It is argued that the process of obtaining such membranes more economical than the manufacture of Nafion. Using this method you can modify the fluorine-containing materials in [17–20], but comparison of these materials with each other is difficult due to different sample conditions and different degree of grafting.

Most radiation-grafted membranes contain polystyrenesulfonic acid in side chains (Figure 5).

As a polymer backbone, a variety of fluoro-substituted polymers include polyvinylidene fluoride, a vinylidene fluoride copolymer with hexafluoropropylene with a different molar ratio of comonomers, a copolymer of tetrafluoroethylene with hexafluoropropylene, etc. [20–22].

The values of proton conductivity of the obtained membranes at high degrees of grafting are compared with Nafion up to 0.11 s/Cm under 100% humidity and room temperature. The same can be said about the permeability of hydrogen [22]. The value of proton conductivity is directly related to the ability of the membrane to absorb water, which in turn substantially depends on the properties of the polymer matrix. Usually, a significant disadvantage of these membranes is their high degree of swelling, greatly exceeding the values for Nafion [20, 21].

2.2.2.2. Sulfonated polyphenylquinoxalines

Ballard Advanced Materials has been researching this group of polymers over the past 10 years. The first series of polymers based on polyphenylquinoxalines (PPQ), named BAM1G, was obtained by direct sulfonation of the PPQ (**Figure 6**).

BAM1G membrane different thickness (40–120 μ m) has good mechanical properties in dry and wet conditions. The characteristics of these membranes with equivalent weight of 390–420 is comparable to Nafion-117, however, the duration of work in the fuel cell before the



Figure 5. Structure of the polymer with sulfonated styrene in the side chain. The main chain is hydrophobic.



Figure 6. The structural unit of sulfonated polyphenylquinoxaline.

onset of degradation is low, averaging 350 h [23]. It is obvious that they are not able to make real competition perfluorinated membranes.

2.2.2.3. Sulfonated polyarylethersulfones

The basis of polyarylethersulfones is phenyl rings, separated alternately by ether and sulfonic groups. The most researched commercially available Udel polyarylethersulfones (PAES) (**Figure 7**) μ and Victrex polyethersulfones (PES). PAES can be partially fluorinated, like Ballard Advanced Materials BAM2G membranes.

The processes of sulfonation of PAES have been studied in detail in [24, 25] and it is shown that for the case of PAES it is impossible to obtain a polymer containing more than one sulfogroup per monomer unit. The use of a softer sulfonating agent (methylsilylchlorosulfonate), in contrast to a rigid sulfurating agent (chlorosulfonic acid), avoids the destruction or crosslinking of the polymer. A disadvantage of sulfonation under mild conditions is the limited degree of sulfonation [26].

Direct sulfonation of PAES, depending on the conditions, leads to two different variants of the arrangement of the sulfogroups in the ortho position to the ether bridge of bisphenol-A (**Figure 7a**) see [27] or to the diarylsulfonic part (**Figure 7b**) see [28], which is most resistant to hydrolysis. In the first case, membranes based on sulfonated PAES are water-soluble at sulfonation degrees of more than 30%, which does not allow their use in fuel cells.

When sulfonated in the diarylsulfonic part, the membranes become water-soluble only at degrees of sulfonation greater than 65% [28]. Attempts have been made to cross-link such membranes in order to reduce solubility in water [29]. However, the cross-linked membranes become brittle at low humidity and show unsatisfactory results when tested in a fuel cell.

Membranes based on sulfonated PES (Figure 7d) are insoluble in water. In the case of PES, proton conductivity at the Nafion level is reached at degrees of sulfonation of the order of 90%, however,

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Figure 7. Various polyarylethersulfones: PAES, sulfonated to the ortho position to the ether bridge of bisphenol-A (a); PAES, sulfonated to the diarylsulfonic part (b); polymer BAM2G (c); sulfonated PES (d) [24, 25].

such membranes have a high degree of swelling (three times greater than Nafion at room temperature), which increases significantly with increasing temperature to 80°C and impairs the mechanical properties. To overcome this problem, the membranes were cross-linked with diamines, which reduced not only the degree of their swelling, but also the conductivity [27].

Membranes based on sulfonated fluorinated PAES that are insoluble in water show better performance when tested in a fuel cell compared to Nafion-117 and Dow membranes see [28], but their service life is limited to about 500 h.

2.2.2.4. Sulfonated polyetheretherketones (S-PEEK)

PEEK is a class of aromatic semicrystalline polymers based on phenyl rings separated by ether and carbonyl (-CO-) groups (**Figure 8**).

These polymers have a high thermal stability, chemical resistance and have limited solubility in organic solvents. With the introduction of sulfogroups into the main chain of polymers, their crystallinity decreases and the solubility increases [30, 31].

These non-sulfonated polymers are stable up to 500°C, and sulfonated polymers are stable up to 240°C. There are various procedures for sulfonation of PEEK [32, 33]. Since the sulfonation reaction proceeds by the electrophilic mechanism, in the case of PEEK, the sulfogroup is successfully introduced only into the aromatic nucleus between the two ether bonds because of the high



Figure 8. Structural units of PEEK: Basic PEEK (a) and sulfonated (S-PEEK) (b).

electron density in this nucleus. It is possible to add only one sulfogroup to the monomer unit. In the case of PEEK, the use of chlorosulfonic acid as a sulfurizing agent destroys the polymer see [34], therefore concentrated sulfuric acid is used for this purpose [35, 36]. It is possible to achieve a degree of sulfonation of 30–100% without cross-linking and polymer degradation. However, in the sulfonation of PEEK by sulfuric acid under heterogeneous conditions, it is impossible to achieve a random sequence of sulfonated and non-sulfonated polymer units with a sulfonation degree of less than 30% [37]. Successful control of the arrangement of the sulfogroups in the polymer chain can be achieved by using a precursor polymer obtained by copolymerization of amenable and non-sulfonated monomers, followed by sulfonation of the resulting random copolymer [38]. Similar methods of directed design of molecular structure prevent additional and sometimes unpredictable macromolecular reactions in the process of sulfonation.

The solubility of these polymers directly depends on the degree of sulfonation. Thus, with a degree of sulfonation of more than 30%, the polymers are soluble in DMSO, DMF, N-methylpyrrolidone. With an increase in the degree of sulfonation up to 70%, the polymer dissolves in methanol, and at a degree of sulfonation more than 70% – in water. The absorption of water by membranes based on S-PEEK at a degree of sulfonation of 65% and humidity of 100% is 8%. With the same degree of sulfonation and humidity, the conductivity of S-PEEK is small – about 10⁻⁵ S/cm [39]. At high degrees of sulfonation, membranes based on S-PEEK have high degrees of swelling. To reduce swelling, chemical cross-linking of macromolecules or the addition of agents forming strong hydrogen bonds are used [40]. For example, in Ref. [41] membranes based on mixtures of S-PEEK with amine derivatives of polyarylester sulfone, polyamides and poly-facets were obtained. The degree of swelling of such membranes can be reduced by strong hydrogen bonds between the polymer molecules or the formation of polysols, which, however, results in partial blocking of the sulfogroups and a decrease in the proton conductivity of the membranes.

2.2.2.5. Sulfonated polyphosphazenes

Polyphosphazenes (**Figure 9** in Ref. [42]) are a new class of polymers that are promising for use in FCs due to their thermal and chemical stability and the ability to easily vary the chemical structure of the polymer over a wide range by introducing various side chains into the main chain.

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Figure 9. The structural link of polyphosphazene basic (a), sulfonated (b) [43].

Proton-exchange membranes based on sulfonated polyphosphazenes may well act as an alternative to perfluorinated membranes. However, there are only a limited number of papers devoted to obtaining and investigating the properties of such membranes. Difficulties are associated with obtaining water-insoluble polymers and matching their hydrophilic/hydrophobic properties [44]. One of the main methods for the synthesis of these polymers is the reaction of polydichlorophosphazene with various nucleophilic agents to form organic polymeric derivatives with a high molecular weight, the properties of which depend to a large extent on the nature of the side substituents. The sulfonation of aryloxy- and arylaminophosphazenes with concentrated sulfuric acid was carried out in Ref. [45]. It is also possible to use 1,3-propanesulfone as a sulfurizing agent, however, the degree of sulfonation is low enough. Aryloxypolyphosphazenes can also be sulfonated with sulfur trioxide in dichloromethane. It is also possible to use 1,3-propanesulfone as a sulfurizing agent, but the degree of sulfonation is low enough [46]. Aryloxypolyphosphazenes can also be sulfonated with sulfur trioxide in dichloromethane. It was shown in Ref. [47] that at the molar ratio of SO₃ to the amount of monomeric units, only C-sulfonation is observed and the polymer chains attack with the formation of the = $N \rightarrow SO_3$ complex, while increasing the amount of SO_3 there is not only C-sulfonation.

2.3. Proton-conducting membranes based on polyimides

One of the promising materials for the manufacture of membranes TE are aromatic polyimides (PI). Polyimides are characterized by high heat resistance, and the most heat-resistant polyimides based on pyromellitic dianhydride and 1,4,5,8-naphthalenetetracarboxylic acids, which practically do not soften before the beginning of thermal decomposition, and their thermal decomposition temperature is more than 500°C (**Figure 10**).

However, the heat resistance of polyimides is well regulated by varying the nature of the monomers and is usually 300–430°C [48]. Most aromatic polyimides are insoluble in most organic solvents, are inert to the action of oils, and also hardly change under the action of dilute acids.



Figure 10. General scheme for the preparation of polyimides. For the preparation, one dianhydride and one or more diamines are used, therefore Q, most often aromatic, and X, Y, Z may be different or identical, both aromatic and aliphatic.

With the introduction into the side chain of various substituents, especially card groups (phthalide, phthalimidine, fluorene and anthrone), the solubility of polyimides is substantially improved. Thus, poly (pyromellitimide) of dianylinophthalein (I) dissolves in DMF, m-cresol, sim-tetrachloroethane, hexafluoro-2-propanol, polyimides 3,3', 4,4'-benzophenone tetracarboxylic (II) or 3,3', 4, 4'-diphenyloxydetracarboxylic acid (III) and dianilinfluorene are also dissolved in methylene chloride, chloroform [49].

By themselves, polyimide films have very low proton conductivity. Therefore, to ensure high proton conductivity, acid groups are introduced into the polyimide chain (most often sulfonic acid – SO_3H). In membranes based on sulfonated polyimides (containing in the main chain and/or in the branches of the group SO_3H), the gas permeability for hydrogen is approximately three times lower than for Nafion-117 [50].

The use of polyimides for the manufacture of membranes is hampered by their extremely poor solubility. Fortunately, this problem can be solved, as shown above, by the chemical structure of the polymer, for example, when a 2,2'-diamino-3,4'-diphenyl ether is used as the unsulfonated diamine, a polymer soluble in m-cresol can be obtained.

Polyimides exhibit different resistance to the action of water vapor in different ways. Since polyimide chains in membrane materials will be responsible for mechanical strength and resistance to fuel cell (FC) conditions, it is necessary to choose such structures of monomers (aromatic tetracarboxylic acid dianhydrides and aromatic diamines) that will yield polyimide matrices that are stable under the action of water vapor.

2.3.1. Stability of polyimides in an water environment

It is necessary to consider what determines the stability of polyimides in water environment. Pure water under normal conditions for polyimide films does not work, however, when boiling in water, the films gradually lose their high mechanical properties [51]. In strongly alkaline (pH > 12) or strongly acidic (pH < 2) media, hydrolysis accelerates sharply, and the film is completely destroyed. This phenomenon is associated with the destruction of imidic bonds. Resistance to hydrolysis depends most strongly on the chemical structure of the dianhydride component of the unit. In particular, polypyromellitimides are among the least resistant to hydrolysis of polyimides [52]. The authors suggest that the hydrolysis of polyimides in neutral environment proceeds through tetrahedral compounds according to the scheme (**Figure 11**).

Further, an amide bond is broken. The limiting stage is the first, namely, the breaking of the imide cycle. The mechanism of alkaline hydrolysis in the example of polypyromellitimides was considered in Ref. [53]. A polyimide film when immersed in a 4 M water solution of KOH at 20°C swells, turns pale, and after few hours becomes colorless while retaining strength and flexibility. After treatment with hydrochloric acid and heating for 30 min at 140°C, this film, according to the results of IR spectroscopy and its physical properties, becomes similar to the original one. In the described conditions, the polyimide regenerates.

To study hydrolytic stability, the authors in Ref. [54] synthesized and studied less stable phthalic (I) polyimides, compared to naphthalic (II) polyimides (**Figure 12**). The resistance of polyimides to hydrolysis was investigated by IR spectroscopy. Thermal stability, proton conductivity, water absorption and ion-exchange capacity of polyimides were also measured.

Comparing the IR spectra of both series of polyimides after aging in water at 80°C for 4 h, the intensity of 1784 cm⁻¹ peaks characteristic for the C = O bond in the case of a series of



Figure 11. Scheme of the first and second stage of hydrolysis of polyimides in a neutral environment.



Figure 12. Phthalic (I) and naphthalic (II) series of sulfonated polyimides (where X: -O- or -CH₂-).

naphthalic polyimides was higher than in the case of phthalic polyimides. In addition, in the case of naphthalic polyimides, the peaks characteristic of the S = O bond did not decrease or disappear. Similarly, naphthalic polyimide films retained their mechanical integrity even after 3 days of soaking. Phthalic polyimides disintegrated after 52 h.

The presence in the polymer structure of a binaphthalic dianhydride fragment and benzophenone groups in the meta-position toward the imide ring should additionally increase the hydrolytic stability of the polyimide [55–58].

The best hydrolytic stability of naphthalic polyimides appears to be due to steric hindrance, which hinders the approach of water to attack the carbonyl carbon atom of the imide ring (see **Figure 11**).

The influence on the hydrolytic stability can also be exerted by diamine, by increasing (decreasing) the electron density (decrease (increase) in the electrophilicity) of the carbonyl carbon of the imide cycle, for example:

- **A.** The introduction of a voluminous aliphatic fragment into the diamine structure both into the main chain and as side branches [59, 60].
- **B.** The introduction of bridging electron-donor sulfur atoms or phenoxy groups into the main polyimide chain, in addition to substantially reducing the electrophilicity of carbonyl carbon, significantly increase the hydrolytic stability [61–64].
- **C.** Membranes that are made from polyimides, with sulfonated side branches are more stable than similar membranes, where sulfogroups are in the main chain [65].
- **D.** In contrast, the introduction of trifluoromethyl groups, which have a strong electronwithdrawing effect, would threaten the stability of the imide group [66].
- **E.** The hydrolysis reaction of imide rings is reversible, this assumption was confirmed by the fact that cross-linked SPI, with a different chain length of cross-linker, is much more resistant to hydrolysis than non-cross-linked and resistance to hydrolysis increased in proportion to

the reduction of the length of the chain of the cross-linking agent [67]. Thus, the main chain of polyimide can be restored provided that the fragments are closely spaced [68].

F. It was recently discovered that membranes based on porous spongy, non-sulfonated polyimides (matrices), the pores of which were filled with different SPIs, showed higher hydrolytic stability than membranes obtained from the same SPI, but not in the PI matrix [69].

2.3.2. Solubility of polyimides

The solubility of polyimides strongly depends on the chemical structure of the polymer. Two key factors in the development of soluble polyimides are the decrease in the regularity (repeatability of the links) of the main chain and the minimization of the density of imide rings along the main chain. Progress in solving these problems was achieved using fluorine-containing dianhydrides, such as 4,4-(hexafluoroisopropylidene) diphthalic anhydride, or by including oxygen atoms in the diamine (e.g., oxydianiline). In addition, aliphatic side chains were included in diamines to reduce the interaction between polyimide chains and increase solubility. In the previous decades, a large number of structural changes were undertaken, including the inclusion of thermally stable, flexible or asymmetric bonds in the main chain and the introduction of bulky substitutes. Polyimides containing bulky triphenylamine units along the polymer backbone are amorphous and have good solubility in many solvents, excellent film formation and high thermal stability [49].

2.3.3. Sulfonated polyimides (SPI)

It is shown [50] that the sulfonated naphthalic (six-membered imide cycles in the circuit) polyimides when working in the fuel cell demonstrate results comparable to Nafion, at least when working up to 3000 h. At the same time, the characteristics of the membranes based on sulfonated phthalic (five-membered imide cycles in the circuit) of the polyimides is significantly deteriorated after 70 h of operation. It has been suggested that in the process of hydrolysis of phthalic imide structure, there is a rupture of the polymer chains and the membrane becomes brittle. Since six-membered cycles of naphthalic polyimide are much more stable to hydrolysis, their chemical structure meets the requirements for FC membranes. The permeability of methanol through the membrane SPI is much lower than for PFSA membranes [70].

The use of SPI as proton-conductive membranes was first demonstrated in Ref. [71]. The main driving force for the development of SPI research was the search of cheaper alternatives to commercially available Nafion developed by DuPont. Very soon it was discovered that, although SPI swell in high humidity conditions needed to operate fuel cells, however, they showed high values of proton conductivity comparable to Nafion. The water absorption and the coefficient of osmotic pressure are not significantly changed in a wide range of temperatures in contrast to Nafion. Such features make SPI preferred for use in fuel cells operating at medium-temperature range, also SPI less membranes degrade when enabling/disabling FC and also better retain water on the anode side of the MEA.

While the first generation of the SPI electrolytes showed values of conductivity of $2 \cdot 10^{-3}$ s/cm, up to $4 \cdot 10^{-2}$ Sm/cm in [72, 73] which were significantly lower than the conductivity of Nafion, the next generation SPI electrolytes gave satisfactory values of conductivity to 1.67 Cm/cm at 120°C in Ref. [74] and 1201 Cm/cm at 80°C for SPI/graphene composite material.

These materials are currently considered promising candidates for the use as FC with PEM, working in the temperature range from 40 to 100°C. In addition, SPI membranes exhibit a permeability to methanol is several times lower than in Nafion, particularly at elevated temperatures [75, 76].

Tests made on FC based on the membranes from variety of SPI showed that the operating time of FC is strongly dependent on the temperature regime of its work. FC on the basis of SPI with sulforaphane in the side chains, in general, worked longer than FC based on SPI with sulfonate groups in the main chain, but still inferior to Nafion. Although testing of SPI membranes was carried out in a real working environment, working time of FC is depended not only on the stability of the membrane, but also on the quality of the connection of electrodes to the membrane [77, 78].

2.4. Proton-conducting membranes with block structure based on polyimides

According to Ref. [5] there are not so much easily synthesized structures of dianhydride aromatic tetracarboxylic acids giving during polymerization of imide cycle naphthalic type. It should be noted that obtaining of the diamines is much easier than dianhydrides and almost all the variety of polyimide structures is achieved through various diamines. However, not all structures of aromatic diamines are easily synthesized and allow you to obtain a sulfonated polyimide with satisfactory hydrolytic stability [79, 80].

Copolymerization is one of the most common and successful ways of preparing new materials with the necessary properties arising from the presence of several structures with different chemical or physical properties in one polymer chain. In order to increase the efficiency of FC operation, it is necessary to develop polymeric electrolyte membranes of block structure (block copolymers) that each repeating polymer block will perform a certain function and to give the final materials unique properties that are inaccessible to conventional polymers.

The most common type and appropriate type of units for inclusion in the PI circuit are polysiloxane, see [81], its characteristics of linear organosilicon polysiloxane meet the requirements of the PEM FC. One of the most common polysiloxane – polydimethylsiloxane (PDMS) among all synthetic polymers has the very high flexibility of the polymer chain. Another important advantage of polysiloxanes is their heat resistance and oxidation resistance.

Figure 13 shows the process of obtaining such block polymers [82].

Polyimide chains of block copolymer are sufficiently rigid formations, sulfonate groups 3,3'-benzylisothiocyanate provide high proton conductivity. Experimental fuel cells, constructed with the use of such membranes showed output current, comparable to the FC based on Nafion [83]. Siloxane blocks are in them as a fragment, which increases the mobility and hydrophobicity of the chain, which ensured the formation of a large number of proton-conducting channels in the membrane [84]. Stitching also gives the membrane additional mechanical strength. Perspective Non-Fluorinated and Partially Fluorinated Polymers for Low-Temperature PEM FC 53 http://dx.doi.org/10.5772/intechopen.71250



Figure 13. Synthesis of sulfonated poly(imide-siloxane).

Modification of polyimide chains of inclusions of crown ethers, may also improve mechanical properties and increase the solubility, reducing the rigidity and the regularity of polyimide chains. In addition, the size of the cavity of some crown ethers correspond to the diameters of the channels, these inclusions can provide additional ion conductivity, provided they are aligned properly for the formation of conducting channels [85].

3. Conclusion

Emerging market of FC is the main driving force pushing the scientific community for the development of inexpensive and high-performance membrane materials. That is, the cost of manufacturing proton-conducting membranes contributes most to the value of FC and, as a consequence, the cost of the produced energy. FC running on methanol are the most promising for transportation and portable electronic applications because of the serious problems associated with the storage and use of hydrogen.

Despite the fact that PFSA are still excellent materials for membrane fuel cells, their prices are still consistently high and they do not fully satisfy all of the requirements of PEM, in particular on the permeability of methanol. These factors stimulate the interest of researchers to finding cheap and high-performance alternative materials for use as membranes, fuel cells.

Polymers such as polyimides, despite their poor solubility and hydrolytic stability, are attractive to researchers due to the wide variety of possible chemical structures. Polyimides,

including partially fluorinated, have high mechanical strength, chemical and thermal stability. In addition, naphthalic polyimides, when operating in a fuel cell, exhibit results comparable to Nafion, at least when operating up to 3000 h.

One of the solutions to overcome the shortcomings of the PI, would be the development of PEM block structure (block copolymers), polyimide-based, where each repeating polymer unit performs a specific function, which together lead to the satisfaction of all conflicting requirements of PEM. However, development of such PEM is complicated by the fact that improving one characteristic (e.g., increasing the number of groups-proton acceptors in polymer chains), thereby deteriorating the other parameters (in this example, the deterioration of the mechanical stability, swelling and the formation of a non-conductive gel). On the other hand, improving the mechanical parameters of the PEM (e.g., cross-linking of the polymer) often leads to a deterioration of proton conductivity. Therefore, modeling of the PEM design must be complex. It is necessary to select the block structure of the copolymer a way to find the optimum implementation of the requirements of PEM FC. In view of the extremely high thermal stability of the polyimide base, the potential for the use of materials should not be limited to low-temperature FC only. Due to the possibility of introducing imidazole-containing blocks, and phosphoric acid groups, it is also possible to develop materials for medium-temperature phosphoric acid FC.

Our group has developed laboratory techniques for the preparation of monomers for the production of membranes based on SPI, as well as inclusion blocks, to improve their properties. According to the developed methods, experimental samples of monomers and inclusions were made. The properties of the experimental samples are investigated and characterized. A laboratory procedure for the production of SPI films and block copolymers based on them has been developed. According to the developed methods, experimental membrane samples were prepared. Research and adjustment of the properties of experimental samples are being carried out.

Acknowledgements

Applied researches are carried out with state financial support represented by the Ministry of Education of Russia under the Agreement on granting subsidies No. 14.625.21.0036 of October 27, 2015. Unique identifier for Applied Scientific Researches (project) RFMEFI62515X0036.

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Degradation in PEM Fuel Cells and Mitigation Strategies Using System Design and Control

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.72208

Abstract

The rapid miniaturization of electronics, sensors, and actuators has reduced the cost of field sensor networks and enabled more functionality in ever smaller packages. Networks of field sensors have emerging applications in environmental monitoring, in disaster monitoring, security, and agriculture. Batteries limit potential applications due to their low specific energy. A promising alternative is photovoltaics. Photovoltaics require large, bulky panels and are impacted by daily and seasonal variation in solar insolation that requires coupling to a backup power source. Polymer electrolyte membrane (PEM) fuel cells are a promising alternative, because they are clean, quiet, and operate at high efficiencies. However, challenges remain in achieving long lives due to catalyst degradation and hydrogen storage. In this chapter, we present a design framework for high-energy fuel cell power supplies applied to field sensor networks. The aim is to achieve long operational lives by controlling degradation and utilizing high-energy density fuels such as lithium hydride to produce hydrogen. Lithium hydride in combination with fuel-cell wastewater or ambient humidity can achieve fuel specific energy of 5000 Wh/kg. The results of the study show that the PEM hybrid system fueled using lithium hydride offers a three- to fivefold reduction in mass compared to state-of-the-art batteries.

Keywords: sensor networks, degradation, design, control systems, hydrogen storage

1. Introduction

Field sensor networks have many important modern-day applications. This includes monitoring, exploration and mapping of inaccessible and pristine environments. Field sensor networks have deployed for monitoring climate-change, including air quality, water quality and soil erosion (**Figure 1**) [1]. These devices are emerging as important tools in

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disaster prediction, including measuring winds in a hurricane, measuring rising seawater from storm surges, inland flooding, sea-erosion, monitoring spread of forest fires, monitoring avalanches, earthquakes, volcanoes and tsunamis [1]. Field sensor networks may also provide timely real-time field data that may feed into computer models for advanced prediction, planning, including timely efforts to evacuate a population and provide postrecovery damage assessment.

Field sensor networks have important applications in the emerging field of precision agriculture (**Figure 1**), where hundreds or thousands of sensors provide periodic monitoring of soil humidity, plant growth, health, and soil nutrition to provide accurate predictions for harvest, enable healthier, higher return on crops and mitigate plant diseases and loses.

In the field of security, field sensor networks have important applications in securing borders, by providing continuous monitoring of border regions including above, below and at ground, for illegal entry, smuggling of people, goods and controlled substances (**Figure 1**, right). There are similar needs to monitor high-security facilities for intruders. For security applications, several hundreds or thousands of modules might be deployed over large areas, including border regions and wirelessly report their data to a base-station.

Another new emerging application is Space Situational Awareness (SSA). There is an evergrowing need to continuously monitor incoming objects from space, including spacecraft debris re-entering the earth's atmosphere and meteors. For this, a camera is mounted to a robotic telescope that scans and tracks incoming objects of interest. Using this footage, it is possible to determine where the object will land and impact the ground and determine its origin/source.

To be practical, once deployed, field sensor network modules need to operate unattended, ideally for years. A key to making these sensor systems practical and ready for wide-scale use is the need for high-energy power supplies.

Significant advancements have been made in the miniaturization of electronic devices, sensors, actuators and radios. However, current power supplies typically depend on rechargeable



Figure 1. Field sensor networks have important applications in environmental monitoring and precision agriculture including monitoring of water, air and soil health (left). They are playing a critical part in continuous observation with emerging applications in border security (right) and space situational awareness.

battery technology and in rare instances, primary non-rechargeable batteries. Current battery technology alone does not meet the needs of many of these field systems due to their low specific energy. This is despite the fact that conventional batteries have made substantial improvements over the past 30 years in terms of specific energy, overall reliability and power density. Furthermore, rechargeable batteries have made significant advances in terms of charge-discharge cycle-life and shelf-life. For long life applications, batteries need to be recharged or replaced often. This presents a major challenge in remote environments with limited accessibility. Significant work is being done to address the energy limits of current batteries [2, 3] but current trends show that batteries cannot meet the high-energy requirements of long duration field sensor networks.

Photovoltaics are another source of power for field sensors but they are bulky, require periodic maintenance such as cleaning of panels and require high solar insolation throughout the year. However, plummeting market prices of solar panels from the late 1990s onwards make them one of the leading options for powering environmental sensors. The challenges remain in powering the sensor when sunlight is not available, including during inclement weather and night time. Another alternative is a wind generator. Wind generators have become attractive due to their low-cost of construction compared to other renewable power sources. Wind generators maybe practical in certain natural environments such as coastlines, mountain passes and flat plains. Due to their large footprint and need for periodic maintenance, they are only promising for certain field applications and climate conditions.

Daily variabilities experienced by both photovoltaic systems and wind power generators, mean that these generators need to be coupled with a battery to store excess capacity and kickin when there is an input power shortage. However, these rechargeable batteries increase the cost, complexity and reduce system robustness. These rechargeable batteries cannot provide power when there is a prolonged power shortage. Hence, the system needs to be designed to predict these shortages and have sufficient battery capacity to handle them.

Energy harvesting using piezoelectric generators has been another popular choice proposed for field sensors, but have yet to be practically applied. These generators require a steady source of vibrations and are suitable only for a limited number of low-power applications. These limitations identify the need for a high-energy power supply that can provide a steady source of power, rain or shine for long durations, in the order of years.

Here we consider use of fuel cells as high-energy power supplies for low-power field sensor networks. Fuel cells are electrochemical energy conversion devices that convert chemical energy directly into electrical energy [4, 5]. **Table 1** shows common fuel cell technologies. Unlike a battery, fuel cells must be constantly fed with fuel and oxidizer to produce electricity. There are different types of fuel cells based on operational temperature, type of electrolyte, fuel and oxidizer used. Some of the fuel cells listed utilize low-cost fuels such as natural gas, methanol and gasoline. However, they operate at high temperatures and produce CO_2 . This makes them unsuitable for use in pristine environments and indoors. Alkaline, Polymer Electrolyte Membrane (PEM) and Direct Methanol Fuel Cells (DMFC) all operate at low temperatures. It

Fuel cell	Electrolyte	Operating temperature (°C)	Electrical efficiency (%)	Fuel oxidant
Alkaline fuel cell (AFC)	Potassium hydroxide solution	15–90	20–60	H ₂ O ₂
Proton exchange membrane fuel cell (PEMFC)	Proton exchange membrane	15–80	40–70	H ₂ O ₂ /Air
Direct methanol fuel cell (DMFC)	Proton exchange membrane	15–130	20-40	$\rm CH_2OHO_{2'}Air$
Phosphoric acid fuel cell (PAFC)	Phosphoric acid	160–220	55	Natural gas, bio gas, $H_{2'}$ O ₂ , Air
Molten carbonate fuel cell (MCFC)	Molten mixture of alkali metal carbonates	620–660	65	Natural gas, bio gas, gasoline, H ₂ ,O ₂ , Air
Solid oxide fuel cell (SOFC)	Oxide ion conducting ceramic	800–1000	60–65	Natural gas, bio gas, gasoline, H ₂ , O _{2,} Air

Table 1. Common fuel cell technologies.

should be noted that there exist high-temperature PEM fuel cells [6]. However, Alkaline fuel cells operate at lower efficiencies and require an electrolyte which requires relatively large containers/casing. However, Alkaline fuel cells are known to be reliable having been used as a power source on several spacecrafts [7]. It is the bulky size and low-operating efficiencies that makes Alkaline fuel cells less attractive for sensor networks.

However, two of the remaining technologies including, PEM fuel cells and direct-methanol fuel cells are both attractive for sensor networks. Both operate at low-temperatures and are quiet. PEM fuel cells are relatively more mature and can operate at cell efficiency as high as 60–65%. They react with hydrogen and oxygen to produce electricity. The storage and release of hydrogen is typically a challenge. However, there are new practical solutions that are simple, that offer high specific-energy, low-temperature solutions. Oxygen is obtained directly from the air or pressurized storage tanks or chemical sources.

Direct methanol fuel cells use methanol and oxygen from the air to produce electricity. They tend to have lower efficiencies than PEM, longer start-up times and produce carbon dioxide and water. However, direct methanol fuel cells are attractive, because methanol is relatively easy to produce, store and has higher energy densities that conventional hydrogen storage methods. The main challenge with direct methanol fuel cells is an inherent limitation with the fuel-cell design compared to PEM. Direct methanol fuel cells produce CO_2 as a waste product. This requires an effective ventilation system to prevent build-up of CO_2 . CO_2 can build-up in the fuel cell and dissolve in the water to form carbonic acid, a mild of source of corrosion and degradation of fuel cell components including the membrane and carbon support layer. A second source of CO_2 induced degradation is from the formation of CO from high enough concentrations of CO_2 around the fuel cell. Together, these sources can cause high rates of cross-over resulting in lower operating efficiencies and unreliability. PEM fuel cells using hydrogen and oxygen is more attractive compared to the other fuel cell technologies for sensor network applications.

However, PEM fuel cells are not widely used in field applications because they face significant hurdles. Firstly, PEM fuel cells are faced with the problem of degradation of their components that result in shortened lives and lower reliability compared to batteries. A second major challenge is the storage of hydrogen [8]. Conventional methods of hydrogen storage are bulky and inefficient, providing only a marginal advantage over current batteries. A third major challenge is that the fuel cell produces lower power compared to batteries. A fourth challenge is that PEM fuel cells have high capital and operating costs. Significant progress is being made in all these areas. Our research addresses the first three challenges.

In this chapter, we present PEM fuel cells as a promising solution to powering sensor networks for long duration. The PEM fuel cell power supply is implemented as a fuel-cell hybrid system, held under controlled conditions to maximize life, maximize cell operating efficiency and minimize component degradation. This method enables the fuel cell power supply to achieve conversion efficiencies of 60–65% and lives of 3–5 years. The fuel cell is supplied with hydrogen fuel from a water activated lithium hydride hydrogen generator that freely extracts water vapor from the air. This method offers a theoretical specific energy of 5000 Wh/kg, more than 40 times conventional lithium ion batteries [9–11]. Our experimental studies show specific energy of 4200 Wh/kg being achieved. Through several case studies, we show that through effective design and control a fuel cell power supply can be superior to conventional batteries for field sensor network module applications.

The remainder of this chapter is organized as follows. Section 2 presents background and related work. Section 3 presents power management, air management and fuel management design and control of the PEM fuel cell power supplies to achieve long life. Section 4 presents several case studies and compares conventional fuel cells technologies and batteries to the proposed technology followed by conclusions in Section 5.

2. Background

In this section, we analyze the major challenges facing fuel cells in order to effectively apply them for field sensor network applications.

Fuel cells have been proposed as power systems for sensor networks. An important factor in their selection addressed earlier in the chapter is that they are clean, are efficient, offer high energy density and are quiet [4, 5]. Most of these properties make them suitable for deployment in sensitive, pristine environments. In contrast, conventional primary batteries pose concern of leakage into the environment. This makes fuel cells a credible choice for environmental sensing. Proposed technologies for powering sensor networks in the field include polymer electrolyte membrane (PEM) fuel cells (**Figure 2**), direct methanol fuel cells (DMFC) and microbial fuel cells [4, 5, 12–14].

2.1. PEM fuel cell applications

PEM have been proposed as low-power sources for use in the field [10, 15–17]. Impressively, MEMs scale PEM fuel cells have been fabricated and tested for this purpose [18]. These



Figure 2. A Polymer Electrolyte Membrane (PEM) fuel cell and its major components.

systems integrate several components of a fuel cell power supply into a chip sized wafer, including the fuel and oxygen source. These fuel cells have been shown to operate for a few hundred hours, though long-life experiments have yet to be tested.

Further, this system trades-off small size for performance, including current density. Control of these fuel cells is performed typically using passive systems that self-regulate fuel dispensation and oxygen flow. Another work by Chraim and Karaki proposes uses of PEMs for sensor networks [15]. One of the major challenges in the implementation of PEM fuel cells for field applications is the storage of hydrogen. Several works have proposed use of metal hydrides from canisters. One approach involves utilizing an ambient power sources to electrolyze water into hydrogen and oxygen [16]. The stored hydrogen and oxygen are fed to a fuel cell providing continuous power [16]. Another proposed application [19] demonstrates a hybrid system where a fuel cell recharges a battery that is in turn used to power a sensor network. The fuel cell in this system is used to keep the battery topped up. Our work identifies some of the additional benefits of this technology particularly to avoid oscillations in fuel cell voltage that limits life.

2.2. Large scale and stationary backup power generation

Current PEM fuel cell control techniques are designed for stationary [20], large-scale power generation applications and use conventional feedback control, gain-scheduling and set-point-tracking approaches towards operating fuel cells [21]. In these configurations, the fuel cell voltage may vary drastically depending on the power demand. Large variation in fuel cell voltage according to our models can substantially shorten life [11]. Fuel cell battery hybrid systems are a promising solution to this problem. In our proposed approach, the fuel cells are small, low-power and operate at constant operating voltage. The fuel cell constantly charges a battery that handles the high and varying loads. The battery protects the fuel-cell from external oscillations

in load that shorten life. In addition, the battery provides a burst of high-power depending on the load demand. A constant operating point simplifies air, fuel and water management, instead of requiring active control methods as in [21].

2.3. Microbial fuel cells

Microbial fuel cells [12] use microbes and their metabolism to generate electricity. They are well suited for swamps, ponds and even reservoirs containing waste water. Although the power density tends to be low, the system benefits from its relative simplicity [12]. A key challenge though is the maintaining the well-being of the microbial organisms to ensure sufficient power is generated. Death of a microbial colony due to disease or change in environmental conditions can have a significant impact on the microbial fuel cell and hence requires periodic human oversight/tending [12].

2.4. PEM fuel cell degradation

PEM fuel cells became the focus of our interest in high-energy power supplies because it is one of the more mature technologies and shows significant potential for both high-energy and long-life applications [4, 5]. A PEM fuel cell membrane electrode assembly (MEA) has several major components that are all subject to degradation (**Figure 2**). They are the gas diffusion layer (GDL), bi-polar plates, the membrane and catalyst layers. The GDL facilitates transfer of input gasses to the anode and cathode. The bi-polar plates have an important role in distributing the reactant gasses to the anode and cathode, conduct electrical current within the cell and help to remove heat from the active area, while preventing leakage of gasses [22]. The anode catalyst layer facilitates the oxidation of hydrogen molecules into protons while the membrane allows for the transport of protons from the anode to the cathode. The cathode catalyst layer facilitates the assembly of protons and oxygen molecules into water via a reduction reaction.

2.4.1. Gas diffusion layer (GDL) degradation

Extensive research has been done to identify the mechanisms that degrade fuel cell components. GDL degradation affects the ability of the cell to absorb reactants. This degradation includes loss of hydrophobicity of the cathode that results in flooding [23] causing loss in performance. Degradation of the GDL can reduce or block gas passageways resulting in choking of the fuel cell. A major source of GDL degradation has been due to mechanical compressions resulting in stress and strains that reduce the micro-pore regions [24]. This reduces gas transport and thus reduces the effectiveness of the GDL. Freeze thaw cycles are well known to damage the GDL as freezing water expands and damages the micro-pores. Another source of damage to the GDL is the loss of polytetrafluoroethylene (PTFE) [5, 24]. PTFE is used to maintain gas passages by repelling water using its hydrophobic properties. The PTFE is weekly bonded to carbon fiber material and therefore high-temperature and humidity can slowly attack and damage the carbon support holding the PTFE. Corrosion of the carbon layers due to oxidation and due to dissolution of the platinum catalyst can slowly erode the PTFE layers. For long duration fuel operations, the major degradation mechanism ends up being GDL degradation particularly the gradual loss of the PTFE [5, 24]. The erosion of the PTFE results in accumulated flooding in the fuel cell [24]. Flooding is known to cause corrosion of various components of the fuel cell including the catalyst [25]. Structural damage, such as from freezing [26], mechanical stress, wear and tear of a GDL can reduce the cell's ability to absorb fuel or oxidizer [27] and thus reducing a cell's performance and resulting in catalyst degradation. However, it should be noted that many of these sources of GDL degradation can be prevented by avoiding such conditions as structural damage, flooding or freezing.

2.4.2. Membrane degradation

Membranes are also subject to degradation and can be classified into three categories, thermal, mechanical and chemical [27–30]. An important source of membrane degradation is due to mechanical stress and strain. The root cause of this degradation is flooding [31]. Membranes once weak are prone to formation of pinholes that result in fuel cross-over and significant reduction in power generated. This is followed by catastrophic failure of the fuel cell [28, 32]. Mechanical stress and strain is known to occur due primarily to humidity and temperature cycling [32]. Humidity is known to impact the mechanical properties of the membrane. With too high a humidity, the membrane curls up and with too little humidity the membrane hardens and dries out. The impact of relative humidity cycling can be severe. It has been shown that a membrane cycled between a Relative Humidity of 30 and 80% faces structural failure after only 100 cycles [32]. A second source of membrane degradation is due to chemical attack [28]. The result from chemical attack is reduced strength of the membrane leading to structural failure.

In addition, membranes can degrade due to migration of impurities, particularly catalyst particles that deposit in the membrane. This can result in local structural weak points that cause pinholes, permitting cross-over of reactant gasses and their direct combustion of the reactants causing loss of power, rapid increase in temperature and fuel cell death [32]. The root cause of the above failure is the particles produced by catalyst degradation in the cathode. Hence in many cases platinum catalyst degradation in the cathode is an important factor in fuel cell durability and life [27]. One cause of catalyst degradation is the dissolution of the platinum particles into ions [27]. The ions either redeposit on large platinum particles (similar to Ostwald ripening) or dissolve and migrate away from the catalyst layer and into nearby regions [33]. Sustained degradation reduces the available catalyst surface in the anode and cathode resulting in loss of power.

2.4.3. Catalyst degradation

In many cases, platinum catalyst degradation in the cathode is an important factor in fuel cell durability and life [27, 34]. One cause of catalyst degradation is the dissolution of the platinum particles into ions [25, 27, 34, 35]. The ions either redeposit on large platinum particles or dissolve and migrate away from the catalyst layer and into nearby regions [33]. Sustained degradation reduces the available catalyst surface in the anode and cathode resulting in loss of power. It also weakens the carbon support structure that holds the platinum and vice-versa through corrosion of the carbon particles [33, 36].

Carbon corrosion is another important source of degradation in a fuel cell [25]. The carbon structure breaks into particles that migrate into the membrane and GDL. The migrating platinum catalyst and carbon particles weakens the membrane structure as discussed above, causing irreversible structural damage ultimately resulting in tears and pinholes. The fuel cell catalyst is impacted by the oxidation of the platinum particles. Oxidation of the platinum particles results in the formation of surface films of platinum oxide that effectively reduces the available catalyst surface area resulting in loss of power. While oxidation of platinum reduces the surface area, it is also known to protect platinum particles beneath the oxide layer from dissolution.

Early empirical models attempted to capture the effect of catalyst degradation and the resultant power loss based on hours of operation [37]. These models are incomplete and do not account for the fuel cell operational factors that results in catalyst degradation. Several models of fuel cell electrochemical interactions account for platinum catalyst degradation [34, 38]. They capture the physics of the rate of dissolution and oxidation of the platinum particles. These models show the significant effect of fuel cell operating voltage on catalyst degradation [34, 38]. In these studies, the fuel cells are analyzed for conditions where the fuel cell's output voltage is varied in a square wave oscillating between 0.87 and 1.2 V. These conditions are intended to represent oscillatory voltage conditions relevant for PEM fuel cell powered automobiles [34]. It should be noted that voltage oscillation experiments have strong influence on the fuel cell cathode than the anode due to the slower reaction and reciprocal higher resistance of this electrode.

We focused on developing a physical model of fuel cell catalyst degradation that matches existing experimental data, enabling us to make long term predictions of life and performance under field conditions [17, 34]. As discussed above, PEM fuel cells are delicate and require balancing various system parameters such as fuel flow rate, temperature, humidity and operating voltage within a narrow operational window. Operation outside of this narrow window can result in irreversible damage to a fuel cell.

2.5. Hydrogen storage

Another major challenge as noted earlier is hydrogen storage. High pressure and cryogenic storage of hydrogen are clearly impractical for small, low power applications such as sensors networks. A third practical option is the use of metal hydrides. Conventional reversible metal hydrides release hydrogen through changes in pressure or temperature. An alternate option is the use of chemical hydrides that release hydrogen through chemical reaction [39]. While reversible hydrides are valued because of their ability to be recharged with hydrogen, they are not ideal for long-life field applications because they normally have low hydrogen storage densities (defined as the weight of hydrogen divided by the total weight of the hydride) on the order of 1-2% [40]. However, there exists other higher hydrides with much higher yield but they require much higher temperatures, in the order 200–700°C. Achieving such high temperatures for small, low-power devices limits the potential field applications and increases complexity.

Hydrolysis is the reaction of chemical hydride with water to produce hydrogen [10, 39]. However, popular water activated metal hydrides including sodium borohydride (NaBH₄) [41] and magnesium hydride (MgH₂) [42] have low hydrogen content, low-reliability and require expensive catalysts. Alternatives such as calcium hydride do not require catalyst but have low yield. Our research has focused on lithium hydride (LiH) which has higher net hydrogen content by mass than calcium hydride. Hydrogen can be released by exposing lithium hydride to



Figure 3. Lithium hydride hydrolysis reaction with water. The reaction can achieve reaction completion [10].

water releasing the hydrogen from the hydride and stripping water of its hydrogen. Lithium hydride unlike other water activated hydrides requires no complex mechanisms or catalysts to start, control and complete the hydrogen release reaction [10, 39]. Our experimental studies show that water activated lithium hydride can achieve 95–100% reaction completion rates with excess of water (**Figure 3**) [10].

3. Fuel-cell design for sensor networks

3.1. Fuel cell degradation

Fuel cell degradation is an important factor in the design of the fuel cell power supply. Fu cell degradation is impacted by operating conditions, including operating voltage, temperature, humidity and voltage oscillations [17]. Using the catalyst degradation model developed in [11, 17], we determine the effect of operating conditions on fuel cell life.

The model is run and we quantify the effect of each operating condition on fuel cell life, while keep other conditions constant. Use this model; we obtain life predictions for the fuel cell. Next, we fit an analytical expression to these life prediction curves and use the expression to extrapolate fuel cell life under field conditions.

Figure 4 shows that fuel life exponentially increases for lower voltages. To achieve 3 years of life, the fuel cell would have to operate at 0.8 V or less. According to the model, increased voltages accelerates dissolution of the platinum catalyst, thus reducing its electrochemically active surface area. However, operating at high voltages increases the fuel cell conversion efficiency, but also results in less power output. These conflicting factors need to be considered to determine a suitable operating voltage.

Typically, all but the simplest of electrical devices have varying electrical loads. The work in [17] analyzed the effect of voltage fluctuations on fuel cell life. The results show a linear



Figure 4. The predicted effects of operating voltage on fuel cell catalyst life (cathode humidity 50%, temperature 25°C).

reduction in catalyst life for a linear increase in voltage oscillation amplitude. To understand the full impact of voltage oscillations, the percentage reduction in life needs to be multiplied to the expected life in **Figure 5** to obtain an absolute effect on life.



Figure 5. The predicted effects of voltage oscillation on fuel cell catalyst life.

The effect of temperature on fuel cell performance is critical for field devices, where temperatures will vary over the course of a day and over seasons. The effect of temperature on fuel cell catalyst life is shown in **Figure 6**. For increased temperature, an exponential decrease in life is predicted by the model. For example, operating at 0.8 V, the life of the catalyst is 4.5 times shorter operating at 60°C than for 15°C. Low temperatures decrease catalyst degradation and increases life, but can produce other problems such as increased condensation resulting in flooding.

Humidity is an important operating parameter for fuel cell catalyst life. The effect of cathode humidity on the catalyst life of an air breathing PEM fuel cell is shown in **Figure 7**. As seen, life is significantly shortened when the relative humidity approaches 0, while a peak occurs at 10% relative humidity. Further increase in humidity is less substantial.

This result is caused by varying rate of platinum oxide formation due to cathode humidity.

Based on the degradation models we produce a combined equation to predict the effect of fuel cell catalyst life. This equation for τ_{clife} in years presumes each operating variable has an independent effect on the life of the fuel cell catalyst. The equation is given below:

$$\tau_{clife} = a_V e^{-k_V V} a_T \cdot e^{-k_T T} \cdot \left(a_h \ln h + k_h \right) \cdot \left(1 - a_\lambda \lambda \right) \tag{1}$$

The equation considers the effect of operating voltage, operating temperature, operating humidity and voltage oscillations. The list of variables used and their respective values are shown in **Table 2**.

For field applications, ambient temperature and humidity may change over the course of a day and over the seasons. Next, we model the impact of humidity and temperature oscillations on



Figure 6. The predicted effects of temperature on fuel cell life.

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Figure 7. The predicted effects of humidity on fuel cell life.

the life of the fuel cell membrane. A second degradation phenomenon modeled is degradation of the membrane due to humidity cycling given below. Based on the experiments from [32] and others, the PEM fuel cell membrane can only withstand a finite number of humidity cycles that result in stress loading culminating in mechanical failure of the membrane.

$$\tau_{mlife} = \Delta t_{hosc} \cdot \frac{b_{memb}}{RH_{max} - RH_{min}}$$
(2)

where Δt_{hosc} is the humidity cycling period, b_{memb} is a membrane specific constant and is 0.02 for Nafion NR111 [32], RH_{max} and RH_{min} is the maximum and minimum relative humidity.

The total life of the fuel cell is then modeled as the following:

$$\tau_{life} = \min(\tau_{clife'}, \tau_{mlife}) \tag{3}$$

where τ_{life} is the expected life of the PEM fuel cell. In summary, the expected life is the minimum of the catalyst life presented earlier and life of the membrane due to humidity cycling. These factors independently impact the fuel cell. Catalyst degradation begins with performance degradation of the catalyst and finally results in catastrophic loss, while membrane degradation results in mechanical damage to the membrane that results in the formation of pinholes and ends up in catastrophic loss.

Variable	Value
a _v	3.11×10^{14}
a _T	7.67 years
a _h	-3.37×10^{-1}
a _x	4.173 V ⁻¹
k _h	2.77
k _v	-4.48 V ⁻¹
k,	$-3.75 \times 10^{-2} \text{ C}^{-1}$

Table 2. Fuel cell catalyst life model parameters.

Figure 8 shows the maximum and minimum daily temperatures expected throughout the year in Negev, Israel. **Figure 9** shows the maximum and minimum daily humidity expected in Negev. Using these varying temperature and humidity conditions, we can predict the net effect on life of a fuel cell power supply in the field. We presume the fuel cells operating at 0.78 V and voltage oscillations are at 0.2 V. Using ambient temperature and humidity (in other words no environment control) the expected fuel cell life is 0.27 years (**Table 3**).

Next, we set the fuel cell to operate at 10% humidity and operate the power supply 5° above dew point. The annual maximum and minimum dew point in Negev, Israel is shown in **Figure 10**. By effectively lowering the operating temperature and humidity, we expect to increase the life of the fuel cell. In addition, lower operating humidity also reduces the chances of flooding. The resultant fuel cell life is 2.2 years (**Table 2**).



Figure 8. Annual daily maximum and minimum temperature in Negev, Israel.

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Figure 9. Annual daily maximum and minimum humidity in Negev, Israel.

Furthermore, we can reduce voltage oscillations experienced by the fuel cell system to 0.02 V. Our studies show that we can minimize oscillations to 0.02 V further extending life to 12.2 years (**Table 2**). By effectively controlling the humidity, temperature, operating voltage and voltage oscillations we can extend the operating life of the fuel cell.

In the following section, we describe how we implement fuel cell control systems to achieve long life. A block diagram of the fuel cell power supply is shown in **Figure 11**. The fuel cell power supply consists of several important components, a hydrogen generator system, fuel cells, humidity and temperature control, air management system and power management and control. In the following section, the power management system will be analyzed.

3.2. Power management

The proposed fuel cell power supply consists of a fuel cell-battery hybrid system. The fuel cell constantly charges a battery and the battery/fuel cell system periodically powers an electrical load. By having several fuel cells in series, the net voltage can be set high enough to charge a battery without use of additional electronics. Otherwise, a step-up DC-DC convertor is required. The DC-DC typically introduces voltage oscillations that can by our analysis result in degradation of the fuel cell power supply [11, 17]. It also decreases the efficiency of the system due to voltage conversion loses.

Conditions	Predicted fuel cell life (years)
Operating voltage 0.78 V, 0.2 V oscillation, No environment control	0.27
Operating voltage 0.78 V, 0.2 V oscillation, 15% Humidity, +5°C dew point	2.2
Operating voltage 0.78 V, 0.02 V oscillation, 15% Humidity, +5°C dew point	12.2

Table 3. Fuel cell catalyst life comparison for field sensor network.



Figure 10. Annual daily dew point temperature in Negev, Israel.

Without the DC-DC convertor, the system is simpler and more efficient. In addition, a variable resistor circuit is included in the circuit. This variable resistor circuit is activated and used during start-up and shutdown, to ensure the fuel cell is at proper voltages at all times and to avoid fuel starvation. The variable resistor ensures the fuel cell maintains a constant voltage during start-up and shutdown. Finally, an electrical load is connected to the circuit and periodically turned on at a set duty cycle or on-demand.

First, the average power required of the fuel cell needs to be determined. Second, an operating voltage range must be selected for the cells. For sensor network applications, we wish to maximize both the life and fuel cell conversion efficiency to minimize hydrogen fuel consumption. The operating efficiency of a fuel cell given as a function of voltage is [4, 5]:

$$\lambda_{FC} = 0.81 \, \mathrm{V} \tag{4}$$

A third constraint is that the fuel cells need to have matching output voltage to charge the battery. This is to avoid a specialized battery charging circuitry. A battery charging circuitry would add additional complexity to the system, and be a source of voltage oscillations and it will further reduce system efficiency due to conversion losses. However, the trade-off is that the fuel cells need to be designed to be in a matching series configuration, with a high enough voltage to charge the battery.

A battery needs to be selected that has enough capacity so that when the load is powered, it does not result in a substantial voltage drain from the battery. This is once again to avoid voltage oscillations that degrade the fuel cell. This expected change in voltage due to loss of charge can be calculated from integrating a voltage-battery charge curve.

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Figure 11. Proposed fuel cell power supply.

A power control system monitors the fuel cell output voltage and the battery (see **Figure 12**). Once the voltage drops just below operating voltage range, the control system would divert output power from the fuel cell to charge the battery until the net voltage reaches the upper boundary of the operating voltage range.

3.3. Air and water management

The purpose of the air and water management system is to ensure oxygen is delivered to the fuel cell cathode and ensure inert gasses such as nitrogen don't build-up in the anode. We assume that air-breathing PEM fuel cells are used; hence the oxygen is freely extracted from the air. However, it is critical that the air entering the cathode maintains a proper humidity to ensure smooth operation of the fuel cell. This requires that the air humidity not be too low or



Figure 12. Proposed fuel cell voltage control system.

too high. Improper water management can result in loss of performance, prolonged flooding and shortened life [31, 43]. The effect of humidity on catalyst degradation from [11, 17] is shown here. The results show that humidity needs to be well above 10% to avoid accelerated degradation. However, the humidity also cannot be too high, otherwise this might cause flooding that blocks pores in the GDL and result in reduced power output due to fuel starvation, oxygen starvation or both. In addition, excess flooding may cause damage to the membrane and GDL [43]. For the micro-fuel cells considered here, this maximum humidity cannot exceed 70%. It is found that most of the waste water from the fuel cell exits the cathode. Therefore, this waste water needs to be carefully disposed to prevent the cathode from reaching the maximum humidity.

A second objective as noted earlier is to prevent build-up of inert gasses such as nitrogen in the anode. The fuel cells as noted earlier are configured in a dead-end anode mode. This typically maximizes fuel utilization, but at a cost of build-up on nitrogen on the anode. If this is left uncontrolled, a fuel cell will starve of hydrogen and drop in voltage. The net effect is that this degrades the fuel cell catalyst and limits life. A conventional method of removing the nitrogen is using a purge valve that is actively controlled. The valve periodically opens and closes to dispose of the nitrogen build-up according to a predetermined schedule [21]. However, this requires active electronics and valves and results in some loss of hydrogen, between 10 and 15% for small scale systems. For low power systems, methods to avoid the active electronics and valves can both simplify the system and increase overall efficiency.

In our work, we focused on designing a passive membrane to continually purge nitrogen. This is done using sufficiently thick foam, which lets nitrogen through but also some hydrogen. The thickness of the foam is varied using empirical methods to let out enough nitrogen. This is done by varying the foam and its thickness to ensure minimal voltage drops in dead-end mode.

Through this design process, our work suggests, that nitrogen can be effectively purged in small scale systems with estimated hydrogen leakage losses of up to 5%.

3.4. Thermal management

As noted earlier, maintaining the fuel cell at a controlled temperature can substantially decrease fuel cell degradation. It avoids build-up of hot-spots, drying and reduction in

humidity. In our studies, we presume the fuel cell power supply is at above freezing temperature. The proposed thermal controller is shown in **Figure 13**. In this controls approach, a thermal switch is introduced. The system works by operating within a temperature setpoint band. In an active setup, a temperature sensor is used to take readings and feed the signal to a thermal-switch actuator, while in a passive setup; thermal expansion of the material is used to close the switch. When there is too much heat, the thermal switch is closed and is used to radiate the heat to an external radiator. When the switch is open, internal heat generated from the fuel cell is recirculated.

3.4.1. Thermal storage system for cold environments

For cold environments, the field sensor module needs to be specially designed to capture excess heat during the daytime and release this heat during night-time. This strategy keeps the field sensor module at or above the operating temperature at all times. In Polar Regions, there is lack of daylight for several months at a time and hence an effective thermal storage system will need to have captured ambient heat a few months in advance. Our own experience in developing photovoltaic sensor networks for measuring snow height in Greenland shows that an effective low-risk strategy is to run the sensor module in a hibernate mode and conserve as much heat as possible [44, 45]. However with a fuel cell power supply, our Greenland sensor network would have operated unhindered even during the dead of winter. These operational limitations encourage efforts to develop practical thermal storage solutions.

In **Figure 14** we present a Thermochemical Energy Storage System (TESS) that we have demonstrated in the laboratory. TESS captures external heat from the environment during daylight and releases it during the night time, when the external temperatures plummet. One potential material for thermal storage is lithium chloride (LiCl). Dry LiCl is exposed to stored waste water from the fuel cell. The waste water is absorbed and forms a hygroscopic solution with the LiCl. This process releases heat which is used to keep the sensor module within operating temperatures. The lithium chloride salts maybe reused for thermal storage simply by exposing the lithium chloride water solution to high external heat. The water boils off and the



Figure 13. Proposed fuel cell thermal control system.



Figure 14. Proposed thermochemical energy storage system.

lithium chloride salt remains and can once again be used to release heat. The control system for TESS can be made entirely passive which eliminates additional electronics and sensors, but is typically less efficient and less precise in maintaining a desired operating temperature.

The feasibility of this thermal control system depends on controlling the reaction rate. This mechanism will control the rate of heat production. The system will have a flow control valve and a micro-pump. Similar to the conventional system, a control system will check the temperature sensor data. In this system, temperature sensors will actuate the flow control valve. The water vapor flows onto the dehydrated salt bed and will give the necessary heating effect. Once the set point temperature is reached, the processor will stop the flow control valve.

3.5. Humidity management

As noted earlier, maintaining a fuel cell at a suitable humidity can decrease fuel cell degradation [11, 17]. Humidity needs to be maintained at a set-point to minimize humidity cycling which decrease membrane life. However, the humidity needs to be high enough to ensure membrane conductivity but low enough to avoid flooding. Flooding of the cathodes can disrupt fuel cell operations or cause long-term membrane structural damage. In our studies, we presume the fuel cell power supply and sensor network module maintains an internal temperature above freezing. The proposed humidity controller is shown in **Figure 15**. In this controls approach, a humidity controller constantly monitors the cathode humidity using humidity sensors. Once the humidity reaches beyond a set-point threshold, a vent opens to release the excess humidity into a dry environment. This control approach just like the thermal control system described

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Figure 15. Proposed fuel cell humidity control system.

earlier can be made passive utilizing humidity sensitive material that can expand or contract (i.e. open or close) a vent. However, our laboratory studies shown these methods are unable to achieve humidity control within ±10% relative humidity.

3.6. Fuel management

Here it is shown that lithium hydride is ideal for storage and release of hydrogen. Hydrogen can be released by exposing the hydride to water, releasing the hydrogen from the hydride and stripping water of its hydrogen according to the following reaction:

$$LiH + H_2O \rightarrow LiOH + H_2$$
(5)

Lithium hydride unlike other water activated hydrides requires no complex mechanisms or catalysts to start, control and complete the reaction [10, 39]. Our experimental studies show that water activated lithium hydride can achieve 100% reaction completion rates (see **Figure 3**). Another appealing feature of water activated lithium hydride, for PEM fuel cells is that in theory, it produces enough waste water for activating the lithium hydride. When exhaust water from a fuel cell is reused for producing more hydrogen using a lithium hydride generator, the reaction achieves a theoretical 25% hydrogen storage efficiency or 5000 Wh/kg specific energy [9–11] (40 folds higher than lithium ion batteries).

Based on the experiments performed, a semi-empirical model is developed of the hydrolysis of thick layers of lithium hydride for design of a lithium hydride hydrogen generator [10]. The model predicts the total volume of hydrogen produced at a given time, for a given humidity, volume, and exposed surface area of lithium hydride. Using this model, we have developed a lithium hydride hydrogen generator design that can achieve reaction completion.

3.7. Control of hydrogen generator

Several control strategies have been developed to produce the required hydrogen at high operating efficiencies. Active control strategies had been initially pursued to achieve a desired hydrogen pressure. A small peristaltic pump drawing an average power of 10⁻² mW is used

to periodically dispense droplets of water exposed to the hydride to produce hydrogen for a 50 mW system (**Figure 16**). However, for low-power sensor network applications there is a need to simplify the system and increase its reliability by minimizing control electronics and actuators. Our work focuses on passive lithium hydride hydrogen generators, that are simpler and more appropriate for low-power because they don't have active control components that would otherwise require electrical power.

A passive control system works by exploiting the physics of a material or structure to perform control (**Figure 17**). The proposed concept is to control the output hydrogen pressure. The mechanism works by letting in water vapor through NafionTM membrane layer that produces hydrogen, which increases hydrogen pressure. The NafionTM lets water vapor cross from a point of high vapor pressure to a point of lower partial pressure, but prevents the escape of hydrogen. The partial pressure of water vapor inside the chamber is low because it readily reacts with lithium hydride to produce hydrogen. This setup in effect allows the lithium hydride to passively extract water vapor from the surrounding. Once the unit reaches the target pressure, a latex diaphragm expands and seals the NafionTM preventing further transport of water vapor.

A cross-section view of a passive lithium hydride generator is shown in **Figure 17**. (A) Generator consists of two opposing compartments that allow for pressure communication between them. (B) Water vapor either produced at the fuel cell's cathode or from the environment enters through the Nafion[™] sheet. (C) The water vapor reacts with the lithium hydride. The generated pressure travels to the upper chamber and inflates the latex membrane. (D) The rate limiting mechanism occurs when the latex membrane presses against the Nafion[™], greatly reducing the amount of water vapor entering the system. (i) Latex membrane fully contracted, allowing water vapor to enter the system. (ii) Latex membrane fully expands at target pressure stopping any more water vapor from entering the system.

The passive hydrogen generator is designed not to carry water on board. Instead, it extracts water vapor from its surroundings. This design is tested for long duration to produce hydrogen for a fuel cell power supply in [10, 11]. The generator was designed to not carry water on-board. While passive lithium hydride generators relying on liquid water have been developed, this generator is unique in its ability to use water vapor from the atmosphere or fuel cell exhaust [9, 10].



Figure 16. Active control system used to control hydrogen generation and hydrogen pressure at 1.1 Bar [10].

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Figure 17. Passive lithium hydride hydrogen generator design.

Additionally, lithium hydride generators have not been experimentally validated for long periods of time or with a hybrid PEM fuel cell system. Based on the lessons learned, an experimental system was built to demonstrate the fuel cell power supply for field sensor networks.

4. Application case studies

Consider a ball shaped sensor network node (Figure 18) with a 10–20 cm radius [11]. The node consists of four interchangeable modules, a central CPU module containing electronics and wireless-radio, a power module consisting of either fuel cells or batteries and a payload module to house sensors. The payload module may contain temperature, humidity/moisture, vibration, accelerometers, chemical, light sensors and cameras. These nodes periodically communicate to neighboring nodes and a central base station. Hence, they will be low-power devices that intermittently operate at high power to operate their payloads or communicate data. Each node will require a minimum 10 mW for standby power. It is assumed the sensor modules consume 500 mW average. These nodes need to operate for 3–5 years unattended, without any periodic maintenance and have a mass less than 30 kg, so that it may be easily carried and deployed on site.

It is assumed that the field sensor is deployed in a temperate, desert or tropical location, operating continuously, where the temperature varies between 15 and 40°C and humidity varies between 0.15 and 1.0. In colder climates, the sensor node will require heaters to maintain the fuel cell temperature at 15°C or higher.



Figure 18. Layout of field sensor nodes for application in border security (left) and environmental monitoring (right).

Figures 18 and **19** shows the sensor node assembled in two different configurations for three different applications. These applications include (1) Environmental monitoring of air quality and pollution readings, (2) Border security for illegal crossing and smuggling and (3) Space Situational Awareness (SSA) monitoring of incoming falling objects and meteorites from the sky in remote locations.

For these three different applications, there are different payload sensors. The key difference between the three applications is the operational duty cycle. For environmental monitoring, the duty cycle can be low, utilizing environmental sensors (air, $CO_{2'}$ temperature, humidity, soil moisture) that are typically low power devices with data being gathered periodically at duty cycles of 0.1 or less. For border monitoring and security applications, the power supply needs to be fully operational and sensors constantly operating thus requiring a high duty cycle. These sensors may have an infrared range finder, ultrasonic range finder and cameras.



Figure 19. Layout of field sensor for applications in space situational awareness.

It is presumed that a state-of-the-art field system is developed consuming an average power of 0.5 W. However, the actual peak power consumed maybe higher and dependent on the choice of sensors and applications. For SSA, a camera sensor needs to be active and enter a high frame-rate mode when an incoming object is detected.

4.1. Battery

First batteries are considered as power supplies for these nodes. Batteries self-discharge, where stored energy is lost at a fixed rate modeled as a geometric series. It is further assumed that the last 20% of the stored energy cannot be used. The mass of a battery power supply required is:

$$M_{bat} = \frac{\alpha E(T)(1 - r^{T})}{\rho_{bat}(1 - r)}$$
(6)

Where, M_{bat} is the total mass of the battery power supply required for *T* years of life, α is the capacity margin, *r* is the self-discharge rate, ρ_{bat} is the energy density of the battery, E(T) is the energy required to power a payload device for *T* years according to a given duty cycle. The energy densities, self-discharge rates and mass of the battery power supplies are shown in **Table 4** [11].

A sensor module weighing more than 30 kg or more lacks scalability to hundreds or even thousands of modules owing to the high cost and logistics required for deploying/moving them and installing them. Ideally, the sensor module and power supply needs to have low mass that enables them to be carried in backpacks, mules and deployed in off-grid environments.

4.2. PEM fuel cell

Next, the proposed PEM fuel cell power supply concept is compared against batteries [11]. The mass of the fuel for the PEM fuel cell power supply is given by:

$$M_{fuel} = \frac{E(T)}{\rho_{fuel}r} \cdot ln \left| \frac{0.5 - \frac{1}{r}}{T + 0.5 - \frac{1}{r}} \right|$$
(7)

where M_{fuel} is the total mass of the fuel for T years of life, ρ_{fuel} is the specific energy of the fuel, E(T) is the energy required to power a payload device for T years for a given a power profile, r is the power degradation rate of the fuel cell power supply for a specified operating point. In addition, the dry mass of the power supply excluding the structural shell is given in **Table 4**.

Technology	Specific energy (Wh/kg)	Self-discharge/degradation (% per month)
Alkaline	110	0.5
Lithium ion	140	5
Lithium CR	270	0.17
Lithium thionyl chloride	420	0.08
LiH fuel cell	5000	0.12

Table 4. Power supply technology characteristics.

The lithium hydride fuel has a volume of 0.7 g/cm³. Based on these factors, the shell consists of two aluminum spheres, 1 and 1.5 mm thick, each with enough internal volume to hold the lithium hydride fuel.

The energy density of the fuel is given as follows:

$$\rho_{Fuel} = \rho_{LiH} \cdot \lambda_{FC_EH2} \cdot \eta_{LiH_RC}$$
(8)

Where, σ_{LiH} is the usable quantity of hydrogen energy released from the lithium hydride hydrolysis reaction (presuming water reuse), $\eta_{LiH_{RC}}$ is the percentage reaction completion of the lithium hydride reaction and $\lambda_{FC EH2}$ is the efficiency of the fuel cell system.

The total efficiency of the fuel cell is calculated from the following:

$$\lambda_{FC_EH2} = \lambda_{FC} \cdot \lambda_{FC_stack} \cdot \lambda_{Purge}$$
(9)

Where λ_{FC} is the chemical to electrical efficiency of the individual fuel cells and is related to the operating voltage of the cell, $V/V_{LHV'}$ where V_{LHV} is 1.23 V, λ_{FC_stack} is the fuel cell stack efficiency and is 0.95, λ_{purge} is the losses due to nitrogen purging and is 0.95. Our work shows that operating each cell at 0.78 V, giving it a λ_{FC} = 0.63 is a good trade-off between efficiency, life and power output. To supply peak system power and avoid oscillatory voltage seen by the fuel cell, the battery handles the high and varying power of the load.

To generate the average power required this requires 5 fuel cells. This design vastly simplifies the fuel cell control electronics. The fuel cells are assembled in this configuration to avoid a DC-DC convertor. With each fuel cell operating at 0.78 V, 5 are assembled in series to obtain a nominal volt of 3.9 V. Note, that the mass calculated accounts for the extra fuel required due to losses from degradation and to ensure the fuel cell provides the energy required at the end of *T* years. **Table 5** shows the mass breakdown of the fuel cell power supply. The power supply consists of the fuel cell, lithium hydride fuel storage system, power control electronics and other components for air and water management. The lithium hydride fuel produces hydrogen with the addition of water extracted from the air.

4.3. System comparison between batteries and fuel cells

We first compare the proposed system with batteries. **Figure 20** shows the mass of the power system vs. average power of 0.5 W for 5 years of operation at 100% duty cycle. For very low power, batteries provide an advantage, because of the additional overhead mass required for

Component	Mass (grams)
Fuel cell and electronics	100
Sensor payload	80
Computer	50

Table 5. Dry mass breakdown for fuel cell powered sensor module.

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Figure 20. Comparison of field sensor power supply technologies for up to 5 years of operation, 0.5 W and 100% duty cycle.

the fuel cell power supply. The advantage for the fuel power supply is apparent when the system requires high energy. Fuel cells using lithium hydride shows a 50-fold advantage in terms of mass compared to lithium ion batteries, a seven fold advantage over Lithium CR batteries and a threefold advantage versus lithium thionyl chloride batteries. It should be noted that the rechargeable batteries weigh tens or hundreds of kilograms. For a network of hundred or thousand nodes, most of the batteries considered are not feasible.

We also compare the proposed fuel cell power supply with previously reported fuel cell storage technologies (**Figure 21**). These previously reported numbers are extrapolated to the required energy for mission lifetime. This includes a PEM fuel cell powered using sodium borohydride and direct methanol fuel cells (DMFC). For these comparisons, the dry mass for these fuel cell configurations is assumed to be the same as the concept fuel cell system presented here. In addition, the operating efficiency of DMFC is lower at 40% and it outputs carbon dioxide that needs to be vented. DMFC offers a simpler approach to fuel storage; however, challenges exist with fuel cell life, due to build-up of carbon monoxide and low operating efficiencies. We presume these challenges have been overcome. The major difference is the mass and volume of the fuel and container.

Overall, for high duty cycle applications (see **Figure 22**), the proposed fuel cell power supply offers a compelling advantage over other energy storage technologies. A LiH fuelled PEM fuel cell power supply of 78 kg can be fully operational for 5 years at 100% duty cycle and supply



Figure 21. Comparison of fuel cell and battery technologies for field sensor power supply. The system is compared for up to 5 years of operation, 0.5 W and 10% duty cycle.

2 W of power. In comparison, a lithium thionyl chloride primary battery system would weigh 360 kg. Overall, the proposed power supply offers a 4.6-fold mass advantage over the best battery technology and 5.25-fold advantage over DMFC.



Figure 22. Comparison of leading fuel cell and battery technologies for field sensor power supply. The system is compared for up to 5 years of operation with 100% duty cycle.

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Figure 23. Comparison of leading fuel cell and battery technologies for field sensor power supply. The system is compared for up to 5 years of operation at 5% duty cycle.

In another scenario (**Figure 23**), we consider powering a field sensor at 5% duty cycle for 5 years. This is equivalent to operating a sensor for 3 seconds every minute. The proposed fuel cell power supply can power a 20 W field sensor and have a total mass of 51 kg. In comparison, the lithium thionyl chloride battery would have a mass of 173 kg. The advantage of the lithium hydride fuel cell system is reduced mass for long duration missions. Overall, the presented lithium hydride fuelled PEM fuel cell offers a substantial advantage over conventional batteries and other fuel cell and hydrogen technologies. These results present a promising pathway towards field testing and evaluation of the proposed concept. For higher duty cycle applications, the proposed system shows an increased advantage over conventional technology. The mass advantage approaches nearly fivefolds over lithium primary batteries. This shows the promise in this technology for high-energy, remote, off-grid applications.

5. Conclusions

Field sensor networks are being applied to environmental monitoring, border security and infrastructure monitoring tasks. Current sensor modules rely on solar power augmented by rechargeable batteries. These systems are bulky and due to extended inclement weather may stop working. Fuel cell power supplies offer a compelling alternative. They can keep a sensor network fully powered for years at a time, utilizing very little fuel and is clean, quiet and highly efficient. We present a fuel cell design framework for achieve long-life operations by minimizing the effects of catalyst degradation, while maximizing operating efficiency and performance. Using these techniques, we identified operating conditions that will enable fuel

cells designed in a hybrid system to achieve more than 5 years of life, by performing temperature, humidity and voltage management. We then extrapolated the capabilities of this proposed fuel cell technology and compared them to state-of-the-art fuel cell and battery technology. The results show that the proposed technology requires substantially less mass and can be enabling for several applications, where hundreds or thousands of modules need to be deployed in the field.

Acknowledgements

The author would like to gratefully acknowledge Prof. Steven Dubowsky (MIT), Prof. Paolo Iora (Univ. of Brescia/Politecnico di Milano), Dr. Daniel Strawser (MIT), Dr. Daniele Gallardo (formerly RPI), Dr. Ling Ling Deng (Harbin Institute of Technology) and Kavya Manyapu (Boeing) and for being instrumental in the development of this work. The author would also like to gratefully acknowledge the critical support and helpful discussions of Israel's MAFAT, Basic Science Office including Dr. Igal Klein and Prof. Alex Schecter of Ariel University. In addition, the author would like to acknowledge Caltech/NASA Jet Propulsion Laboratory (JPL) for supporting this work.

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Many Different Applications of PEM Fuel Cell

Chalcogenides and Carbon Nanostructures: Great Applications for PEM Fuel Cells

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71994

Abstract

Nanostructured metal chalcogenides (NMCs) and carbon nanostructures (CNS) are attracting significant attention due to their features such as high stability in an acidic environment, especially if they have a significant oxygen reduction activity and remarkable superconducting properties. The broad range of CNS exhibits novel physicochemical properties, and thus it is triggering intense research about carbon nanoscience with numerous applications. In this context, new synthesis routes are designed under moderate conditions, which are definitely needed in order to simplify the process, reduce costs, and allow the production of NMCs at lower temperatures and CNS whose size and shape can be controlled. Some related studies about Pt based on sulfides and selenides, transition metal chalcogenides (TMCs), and carbon nanostructures (nanotubes and graphene) are revealed here; however, they show promise for fuel cells that these NMCs, CNS, or even NMC-CNS materials have been applied for other energy devices. Until now, a good response for cathodic reactions is employing TMCs based on tungsten and CNS without metal. According to experimental results and in terms of catalytic activity, durability, and chemical/electrochemical stability, much more research is required to produce commercially valid non-noble catalysts, electrocatalysts, or supports; however, one approach on this field is metal-free CNS.

Keywords: chalcogenides, nanostructures, carbon, catalyst, solar, fuel cells, oxygen reduction, transition metals, electrocatalyst

1. Design considerations for electrocatalysts

Several advantages on the design of proton exchange membrane (PEM) fuel cells are the costeffective and innovative synthesis methods, which are necessary for new catalyst discovery

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and catalyst performance optimization. In addition, the carbon support functionality should be emphasized in terms of the active surface increase, the coordination effect of catalyst and support, and the distribution of active catalytic sites.

The main focus is the oxygen reduction reaction (ORR); this electrochemical reaction plays an important role in the operation of fuel cells. Nevertheless, due to its complexity, we are far to reach a full comprehension about the mechanisms involved in these systems. The development and study of novel materials that have useful electrocatalytic properties to carry out the reactions involved in these electrochemical devices is needed.

Platinum is considered in such a traditional catalyst for reactions involved in PEM fuel cells. However, their high costs keep us researching on new approaches to reduce the platinum load on the electrocatalytic material, and, therefore, Pt loading catalyst is still the main issue. Some methodologies for the preparation of disperse transition of metal nanoparticles and carbon nanostructures (CNS) have been developed and are described here.

Catalysis with transition metal sulfides (TMS) also play a crucial role in petroleum industry, owing to their exceptional resistance to poisons. TMS are unique catalysts for the removal of heteroatoms (S, N, O) in the presence of a large amount of hydrogen [1]. In particular, they are the optimal materials to carry out the numerous reactions [2–5]. Through effective synthesis procedures, new non-noble catalysts have been discovered. TMS synthesized by carbonyl route using sulfides and selenides are promising. Besides platinum and noble metal nanoparticles and its alloys, other kinds of materials have shown important electrocatalytic activity in PEM fuel cells. Alonso-Vante and coworkers have proposed semiconducting TMS (sulfides and selenides) as efficient catalysts for cathode fuel cell reactions with significant oxygen reduction activity and high stability in acidic environment. A strategy to synthetize these materials in nanodivided way, is using carbonyl-based molecular clusters as precursors [6]; this route of synthesis offers the possibility to produce well-shaped nanoparticles with right stoichiometries. Ruthenium carbonyl $(Ru_2(CO)_{1,2})$ is extensively employed as feedstock to obtain diverse types of compounds and metallic clusters for new electrocatalysts; the main objective in the catalyst design is to replace and overcome the platinum properties [6-10].

However, platinum metal and its alloys with other transition metals are important catalysts for low-temperature fuel cells. The catalysts are typically developed in a form of nanoparticles for a better dispersion and/or minimum loading of platinum. Since they have the best activities and chemical stability, the problem is the high costs of Pt loadings in operating cathodes. ORR has been examined in the presence of Pt and Pt alloy nanoparticles on carbon-supported, CoN_4 catalysts, Chevrel-type chalcogenide materials, and Ru_xSe_y clusters [7, 11]. The ability to fabricate new model systems in which one can control the number of particles, size, and shape would be of tremendous fundamental importance in catalysis and electrocatalysis, as well as in other technologically important areas that use nanoparticles. On the other hand, chalcogenides are synthesized under mild conditions in the nano-length scale by simple and fast methods. In the final form of the catalyst, chalcogenide atoms interact with surface metal atoms in a chemical way to avoid poisoning. Evident effects were observed in the presence of organic molecules as CH₃OH or HCOOH. Synthesized catalysts have been compared with commercial Pt/C [7, 11]. Further, the ORR kinetics was not perturbed, assessing this phenomenon wherein the sulfur atoms and organic molecules showed a little effect against the molecular oxygen adsorption. Some results demonstrated that the fuel crossover is no longer a major concern; however, the nature of the active sites on the chalcogenides and more investigations on dispersion and synthesis methods will follow for the development of very small and low-cost fuel cells, such as microsystems [12]. Therefore, results suggest the development of novel systems that is not size restricted, and its operation is mainly based on the selectivity and nature of its electrodes.

1.1. Sulfides and selenides: catalysts based on chalcogenides

The challenges of scale-up and commercialization of fuel cells depend on the optimal choice of fuel as well as on the development of cost-effective catalysts. One approach for the ORR is the use of transition metal chalcogenides (TMCs) or dichalcogenides (TMDs), which also have the great advantage of being selective in the presence of methanol. However, the target is to develop materials based essentially on non-noble metals and reduction of the Pt loading [5, 13]. These results promise new opportunities to design cathodic catalysts.

On the other hand, $W_6S_8(PEt_3)_6$ was reported as the first soluble model clusters of the molybdenum Chevrel phases and their (unknown) tungsten analogs [14]. However, according to the literature reviewed, until 2003 tungsten, Chevrel phases had not been reported, despite many years of effort. As reported in many studies, chalcogenides are markedly less sensitive than platinum catalysts to methanol. In accordance with this idea, we endeavored to explore the nature of chalcogenides based on sulfur and thiosalts. These results described a significant tolerance toward some carbonaceous species like monoxide and methanol. Likewise, we called "the decorative nanoexfoliation of platinum model" to explain the effect of sulfur species on the surface of platinum, and further studies demonstrated how the WS₂ planes are highly exfoliated around platinum nanoparticle to avoid the poisoning (see **Figure 1**).

This idea is to design selective catalysts with high activity for PEM fuel cells based on sulfur. We reported novel platinum chalcogenides as cathodic catalysts from platinum with tungsten and molybdenum thiosalts, as well as platinum and sulfide in acid media, and in other studies, we also analyzed the promising results for anodic electrode [15, 16]. In addition, we have studied the interaction with the supported TMS on Vulcan carbon. **Figure 1(a)** and **(b)** shows HRTEM images of the unsupported $Pt_xW_yS_z$. In concordance, **Figure 1(c)** shows a significant effect of the chalcogenide on the platinum surface and the catalytic activity is better in comparison with the commercial platinum at 20 wt.% metal loading [16].

Carbon-supported PtW nanoparticles are usually prepared by impregnation or chemical coreduction of chloroplatinic acid and ammonium tungstate. However, these methods are not suitable for preparing carbon-supported PtW nanoparticles with well-controlled particle size



Figure 1. (a) HRTEM image of the unsupported catalyst $Pt_xW_yS_{z'}$ (b) HRTEM image at high magnification of one platinum nanoparticle decorated by WS₂ nanostructures, and (c) current-potential curves for oxygen reduction for $Pt_xM_yS_z/C$, $Pt_xW_yS_z/C$, $Pt_xW_yS_z/C$, Pt_xC commercial, and Pt_xS_y/C . All samples were immobilized on a glassy carbon RDE, and the measurements were carried out in O₂-saturated 0.5 M H_2SO_4 solution at 5 mV s⁻¹ at 1600 rpm rotation speed and 25°C. The current densities were normalized to the geometric surface area.

and homogeneous composition [17]. In **Figure 1(c)**, we report the ORR polarization curves for three synthesized catalysts and compared it to commercial Pt/C Vulcan at 20 wt.% of metal load. As shown, in all samples, the current density values are higher than the Pt/C. Furthermore, it was noticeable that cathodic current due to the reduction of O_2 commences at much more positive potential for PtWS/C catalyst than the synthesized samples and similar than commercial sample but increases upon further cathodic scan, and overall it shows a significant enhancement versus the Pt/C.

TMCs are a group of materials that show activity toward ORR. It is worthwhile to mention that TMS are the optimal catalysts to carry out the numerous reactions of hydrogenation and hydrogenolysis on different processes for the refining industry. We have reported catalytic materials sulfided by DMDS, and their activities are similar than H₂S. It is an advantage, in order to determine the effect of sulfur on trimetallic catalysts and explore other sulfiding agents. This experimental procedure is also on research by our group [18].

Ruthenium (Ru)-based chalcogenide catalysts synthesized by Alonso-Vante et al. [8, 10, 11] have been among the most promising, due to their high activity and stability toward the ORR in acidic media [19]. Particularly, RuS_2 also has been extensively employed as catalyst for hydrodesulfurization (HDS) reactions. It has been shown that semiconducting transition metal sulfides, such as PdS, PtS, Rh_2S_3 , Ir_2S_3 , and RuS_2 , have higher catalytic activity than the metallic sulfides [20]. However, the electronic environments of the surface of Ru atoms are also compared to the electronic environments and reactivities of metal centers found in d⁶ transition metal complexes that incorporate thiophenic ligands [20, 21].

Cluster compounds of the Chevrel type (MosXs) contain molybdenum octahedral and form metals with the Fermi level clearly below the energy gap. It clearly shows the molybdenum cluster octahedron (accommodating 20 electrons) surrounded by a cube of chalcogen atoms. It is also possible to distinguish the crystal channels between the clusters into which guest atoms can be inserted.

Alonso-Vante and Tributsch were the first that communicated that semiconducting ruthenium-molybdenum chalcogenides having the general formula $Mo_x Ru_y XO_2$ (with X = chalcogen: essentially, one of the elements O, S, Se, and Te) and forming Chevrel phases exhibit good catalytic activity for ORR in acidic solutions and catalyze the four-electron reduction to H_2O over the H_2O_2 route [22]. It was soon found that the catalytic activity is not restricted to Chevrel phases, but other varieties of such chalcogenides are active as well. Many other studies go on; using similar compounds are synthesized in different ways, and this is the purpose of this contribution, in order to enhance the catalytic activity, selectivity, and stability; thus, new modifications on active phases and carbon supports have been explored.

1.2. Carbon nanostructures

1.2.1. Carbon nanotubes and graphene

The morphology, structure, and composition of the support material significantly affect the catalytic activity of the fuel cell catalyst [23]. Carbon is most often used as catalyst support in cathodes because it is inexpensive; it can be prepared in a pure form as high-surface area powders, and it is electrically conductive. However, the atomic arrangement of carbon atoms on the network is the key to determine well-defined properties and therefore specific applications. In order to improve the electrocatalytic efficiency, various carbon support materials such as carbon nanotubes and graphene have been applied recently by our group. Some requirements for these supports are electrical conductivity, good metal-carbon interaction, high surface area, and high inertness in harsh chemical and electrochemical conditions.

Since Iijima's landmark paper in 1991 [24], carbon nanotubes (CNTs) have been studied by many researchers all over the world. Their large length (up to several microns) and small diameter (a few nanometers) give them a large aspect ratio. CNTs are mainly produced by three techniques: arc discharge, laser ablation, and chemical vapor deposition. Research has been targeted toward finding more cost-efficient ways to produce these structures.

According to theoretical models, all of these structures may appear due to non-hexagonal carbon rings that are incorporated in the hexagonal network of the graphene sheet. In particular, coiled carbon nanotubes were first predicted to exist in the early 1990s by Ihara [25] and Dunlap [26], but they were experimentally observed until 1994 by Zhang [27]. On a microscale, periodic incorporation of pentagon and heptagon pairs into the predominantly hexagonal carbon framework in order to create positively and negatively curved surfaces, respectively, can generate a carbon nanotube with regular coiled structure [28].

A large variety of tubule morphologies as straight, coiled, waved, branched, beaded, and regularly bent have been synthesized and observed; however, there are no studies about the growth time which affects CNT morphology. Herein, the growth time promotes the arrangement by hexagonal lattices to produce different shapes [26]. Hence, to prepare high-quality metal catalyst supports, it is necessary to deposit dispersed metal particles onto nanotubes, ideally particles that have diameters within the nanometric range. It is worthwhile to mention

that a combination of catalytic metals, chiefly transition metals such as iron, cobalt, or nickel, leads to the growth of extremely forms of CNTs such as helically wound graphite spirals. Under catalytic conditions, a wide variety of carbon nanotubes, which may not be linear but resemble spaghetti piles, are possible and may not be recognized as carbon.

Recently, aligned and coiled multiwalled carbon nanotubes were successfully obtained inside of quartz tubing by our group using the modified spray pyrolysis method. In **Figure 2**, two types of morphology of multiwalled carbon nanotubes (MWCNTs) are shown. In concordance to these results, variable control is essential to produce CNTs [25, 29].

On the other hand, preparative methods of synthesis of CNS such as graphene are also currently a heavily researched and important issue. The search for a methodology that can reproducibly generate high-quality monolayer graphene sheets with large surface areas and large production volumes is greatly sought after. A popular aqueous-based synthetic route for the production of graphene utilizes GO. It is produced via graphite oxide by various different routes. Hummer's method, for example, involves soaking graphite in a solution of sulfuric acid and potassium permanganate to produce graphite oxide. In this method, we have done some modifications on the variables of synthesis. Our focus to take advantage of the TMD catalytic activity is on the development of different pathways of synthesis to accelerate the electron transport. Therefore, carbon support is another factor that affects the catalysis. Some studies have Wilkinson reported the effect of carbon support on catalytic activity and found the relation between the kinetic and the specific surface areas, pore size distribution, and the N or O content of the carbon support [7].

Here, it is worth to mention that various syntheses and preparations of catalyst routes have been reviewed, with emphasis on the problems and prospects associated with the different methods. However, we reported a simpler synthesis method to prepare Pt-WS₂ nanoparticles supported on Vulcan carbon [30] and later on MWCNT synthesized by modified spray pyrolysis. These results were used to compare the catalytic electroactivity toward the ORR in acid media, in order to carry out studies about the influence of the exfoliated sulfides on Pt nanoparticles to modify its catalytic properties and to enhance the activity of pure Pt. In **Figure 3**, the result of chalcogenides versus Pt on carbon supports is shown. It is clear to



Figure 2. (a) TEM image of straight MWCNT and (b) TEM image of coiled MWCNT synthesized by modified spray pyrolysis method.



Figure 3. ORR polarization curves in oxygen-saturated 0.5 M H_2SO_4 as a function of potential for different platinum electrocatalysts. Pt/C commercial and electrocatalysts synthesized from sulfur (PtxSy/C), tungsten thiosalt, and Pt/MWCNT. All samples have 20 wt.% of active phase. Measurements were carried out in O_2 -saturated 0.5 M H_2SO_4 solution at 5 mV s⁻¹ at 1600 rpm rotation speed and 25°C.

observe the effect of the arrangement of carbon atoms on the kinetic response to increase the current density. The overview of several studies has also suggested that a strong coupling (synergistic effect) interaction between catalysts and substrates is a promising approach for promoting electrocatalytic performance [7, 11, 15, 30].

It should be noted that the constituent atoms of graphite, fullerenes, and graphene share the same basic structural arrangement in what structure begins with six carbon atoms which are tightly bound together (chemically, with a separation of approx. 0.142 nm) in the shape of a regular hexagonal lattice. Moreover, at the next level of organization, graphene is widely considered as the "mother of all graphitic forms." In this sense, compared to black carbon, CNTs show much higher catalyst loading efficiency, electrical conductivity, better durability, and lower impurities. However, due to their high aspect ratio and strong π - π interactions, the dispersion and difficulty to achieve uniform deposition of metal nanoparticles are some challenges in this field. In contrast, the graphene displays better electrical, mechanical, and physical properties and much larger surface area than MWCNTs, which are highly desirable for the catalyst support [31].

1.2.2. Nanostructured hybrids

In PEM fuel cells, platinum-based electrocatalysts are still widely utilized as anode and cathode electrocatalysis. However, carbon nanostructures (nanotubes and graphene), supported on Fe

or Co nanoparticles, show promise for fuel cells, and these nanostructured metal chalcogenides (NMCs), CNS, or even NMC-CNS could also be applied for other energy devices. Some recent reports about utilized GNSs and nitrogen-doped GNS as catalyst supports for Pt nanoparticles toward the ORR, where the constructed fuel cells exhibited the power densities of 440 and 390 Mw cm⁻² for nitrogen-doped GNS-Pt and GNS-Pt, respectively. It is clear that the nitrogen-doped device exhibited an enhanced performance, with improvements attributed to the process of nitrogen doping which created pyrrolic nitrogen defects that acted as anchoring sites for the deposition of Pt nanoparticles and is also likely due to increased electrical conductivity and/or improved carbon-catalyst binding. On the other hand, Pt nanoparticles deposited on graphene submicroparticles (GSP) in addition to carbon black and CNT via reduction method. Results demonstrated that the Pt/GSP was two to three times more durable than the CNT and carbon black alternatives [30].

The main issues about graphene-based materials are focused on structural characteristics, interaction between nanoparticles or functional groups, and their electrochemical performance as catalysts, and a wide variety of graphene-based hybrid nanocomposites are grouped into the next categories: doped/modified graphene, noble metal/graphene hybrids, and graphene/nonmetal composites.

Figure 4 shows catalyst prepared from nitrogen-doped graphene-carbon nanotube hybrids (NGSHs) and their electrochemical behavior toward ORR for graphene-SWCNT hybrids (GSHs), NGSHs, and Pt/C supported on GC electrodes [32]. Those edge planes of GNS also provide defects for the uniform dispersion of Pt nanoparticles, subsequently increasing catalytic activity by increasing the surface area of an electrode as well. However, nitrogen dopants increase the number of defects on the CNT surface, subsequently improving the distribution of a catalyst. Since nitrogen is introduced into the growth process of GNS-CNT hybrid nano-structure, these substituted nitrogen sites prevent the Pt nanoparticles from aggregation [33].

The fast development of nanocarbon materials like graphene enables them to play an increasingly important role in the improvement of non-precious metal-based catalyst (NPMC) performance. ORR activity of Co_9S_8 -N-C catalysts, for instance, was much higher than that of the state-of-the-art Pt/C 0.1 M NaOH solution. Dai et al. synthesized a Co_xS -reduced graphene oxide (RGO) hybrid material by a mild solution-phase reaction followed by a solid-state annealing step. Strong electrochemical coupling of the RGO support with the Co_xS nanoparticles and the desirable morphology, size, and phase of the Co_xS nanoparticles mediated by the RGO template rendered the hybrid with a high ORR catalytic performance in acid media [5, 33]. **Figure 5** shows an illustration of carbon nanostructures and nanoparticles, synthesis, and functionalization methods commonly used by our group.

1.3. Synthesis methods of carbon nanostructures and nanoparticles

Nowadays, the nanoscience has reached the status of a leading science with basics and applied implications in all physics, life, earth sciences, as well as in engineering and materials sciences. **Figure 6** shows the schematic illustration of the focus on research from the synthesis methods of carbon support materials, such as carbon nanotubes and graphene, and metallic nanoparticles that also can be obtained by different methodologies, until the surface modification of these nanomaterials. It could be on TMS or non-noble metals as the active phase of the catalysts for PEM fuel cells.

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Figure 4. (a) Schematic illustration of the preparation of the nitrogen-doped graphene-carbon nanotube hybrids (NGSHs). (b) TEM image of the NGSHs. (c) ORR polarization for graphene-SWCNT hybrids (GSHs), NGSHs, and Pt/C supported on GC electrodes at a rotating rate of 1225 rpm.



Figure 5. Schematic illustration of carbon nanostructures and nanoparticles, synthesis, and functionalization methods reported by our group. Potential applications could be reached with these preparation routes in terms of catalytic activity, time, and cost-effectiveness.

In this regard, our strategy is to generate nanomaterials that could be fabricated by simple methods with the purpose of controlling and understanding at nanoscale the properties of the catalysts based on NMCS and CNS through the atomic behavior at specific conditions, in order to enhance the catalytic activity. This concept focuses on the design and the creation of novel morphology and structure to probe, tune, and optimize the properties to develop functional materials for multiple applications. Nevertheless, significant electrochemical effects



Figure 6. ORR polarization curves in oxygen-saturated $0.5 \text{ M H}_2\text{SO}_4$ as a function of potential for different Pt catalysts at the rotation speed of 1600 rpm. (Reprinted with permission from Royal Society of Chemistry. Lic. No. 4171470897994).

have been observed in different samples of platinum. Morphology and structure dependence can be shown in **Figure 6**. It displays the ORR polarization curves in oxygen-saturated $0.5 \text{ M H}_2\text{SO}_4$ as a function of potential for different geometries of Pt at the rotation speed of 1600 rpm. The response of the kinetic behavior on the atomic structure is clear to observe [5].

On the other hand, it is worth to mention some synthesis methods that are well known and developed by our group. **Table 1** shows some catalysts based on TMC and their method to obtain materials with high catalytic activity on specific reactions [34]. However, a recent development in the field of organometallic chemistry has been the use of organometallic complexes for the high-yield catalytic synthesis of CNT [35–37].

Table 1 An overview of synthesis reports using platinum, sulfur, or selenium.

Some results reported about the ORR activity of the thiospinel compounds were directly related to the type of metal utilized, with an order of Co > Ni > Fe. Moreover, decreased performance was also observed when sulfur was partially replaced with O, Se, or Te. **Table 1** shows an overview of catalyst synthesized for PEM fuel cells. The main methods that we have used to obtain catalysts are spray pyrolysis and Hummer's method, electrochemical methods, ultrasonic techniques, and green synthesis.

First, the experimental procedure of modified spray pyrolysis is simple and is one of the most commonly used; this methodology represents advantages among others due to its characteristics of using non-sophisticated equipments as well as easiness of scalability. To start, an aqueous solution containing the metal precursor is nebulized into a carrier inert gas that is passed through a furnace. Second, the nebulized precursor solution deposits onto Vycor tube as a substrate, where it reacts and forms the final product. To form nanoparticles, the aerosol is pyrolyzed under inert atmosphere and a set temperature [17, 29].

Recently, we are also producing graphene for PEM fuel cells and other specific applications. In accordance with Hummer's method, we modify some steps in the original method. However, it is worth to mention about a specific application, for instance, about the storage energy, the combination of carbon nanostructures as support, and the functionalization with a pseudocapacitive

Catalyst	Synthesis method conditions	Reference
NEBH ₂ S NEB DMDS NEBDMS	Two aqueous solutions were prepared (A and B). Solution A consisted of ammonium heptamolybdate and ammonium metatungstate dissolved in water at 363 K under stirring. The pH of this solution was maintained at about 9.8 by adding NH ₄ OH. Solution B consisted of nickel nitrate dissolved in water at 363 K while stirring; solution B was slowly added to solution A at 363 K; a precipitate was formed; and then the solid was filtered, washed with hot water, and dried at 393 K. The molar ratio Mo:W:Ni of precipitate was 1:1:2 and was represented as NH ₄ -Ni-Mo _{9.5} W _{0.5} -O. Sulfidation was carried out in a tubular furnace at 673 K for 2 h using H ₂ S, DMDS, or DMS (10 vol. % in hydrogen).	Gochi Y et al., 2005 [2]
Pt _x S _y /C	First, the synthesis of catalytic precursor is from molecular sulfur, and ammonium hexachloroplatinate ($(NH_4)_2PtCl_{e'}$ Alfa Aesar) was reacted under a constant agitation for 12 h at room temperature. The solution was mixed with carbon Vulcan (E-TEK) and stirred continuously for 24 h at room temperature. The precipitates were filtered, washed with distilled water, and dried for 12 h at room temperature on a drier. Finally, the precursor was treated thermally at 350°C under (75% v/v) N ₂ /H ² atmosphere for 2 h.	Gochi-Ponce Y et al., 2006 [15]
Pt _x Mo _y S _z /C, Pt _x W _y S _z /C, or MWCNT	Tungsten or molybdenum thiosalts, as appropriate, and ammonium hexachloroplatinate were reacted under constant agitation for 12 h at room temperature. The solution was mixed with the carbon support and is stirred for 24 h at room temperature. The precipitates were filtered, washed with distilled water, and dried for 12 h at room temperature. The supported precursor was treated at 400°C under N_2/H_2 atmosphere for 2 h.	Gochi-Ponce Y et al. 2006 [16]
Pt/ MWCNT-Fe PtFe/ MWCNT Pt/MWCNT	The coordination complex salt of Pt was synthesized by Burst-Schiffrin method. Ammonium hexachloroplatinate was dissolved into 10 ml triply distillated water. This solution was added to 15 ml of a TOAB in 2-propanol solution at room temperature (25°C). The Pt precursor was filtered under vacuum, washed with deionized water, and dried at 70°C for 8 h. MWCNTs (raw, treated, or cleaned and synthesized by spray pyrolysis) are added to 2-propanol and dispersed in an ultrasonic bath for 1 h. The Pt precursor dissolved in 5 ml 2-propanol solution was added to the MWCNT-Fe suspension and stirred for 1 hr. Finally, 10 mL aqueous solution of NaBH ₄ in excess, 1:10 was added by drip during 5 min to the suspension, which was stirred at room temperature for 12 h to reduce Pt ⁴⁺ to Pt ⁰ . The obtained mixture was then filtered and washed with acetone and water, to be finally dried at 70°C for 4 h.	Rodriguez JR et al. 2014 [35]
Pt-Ni/ MWCNT	MWCNTs were synthesized in a spray pyrolysis. For the MWCNT-Ni, it was necessary to use a thin film (manganese oxide) as substrate previously deposited in the inner walls of the Vycor tubing. The temperatures of MWCNT synthesis were 900 and 800°C for ferrocene and nickelocene, respectively. After the process, once the substrate was completely cold, the MWCNTs were removed (scratched) from the Vycor tubing.	Valenzuela- Muñiz AM et al. 2013 [36]
Ru _x Se _y	Carbon-supported Ru Se _y (20 wt.%) nanoclusters were prepared in aqueous media using RuCl ₃ _xH ₂ O and SeO ₂ . Typically, 0.124 g carbon (Vulcan XC-72) was dispersed in 100 mL of water under nitrogen under vigorous stirring. The resulting suspension was heated to 80°C, mixed at this temperature for 30 min to remove oxygen in water, and then cooled down to room temperature.	Saul Gago A et al., 2012 [12]
	Subsequently, 4 mmol RuCl ₃ _xH ₂ O and 1 mmol SeO ₂ were added to the above suspension and then mixed for another 1 h. Thereafter, 100 mL of a mixture solution containing 0.1 M NaBH ₄ and 0.2 M NaOH was added dropwise (1.25 mL min ⁻¹) to the suspension to reduce the metal ions. The suspension was kept for further reaction for another 10 min and then heated to 80°C for 10 min. The final black powder was collected on the Millipore filter membrane washed with water and dried under vacuum at room temperature.	

Table 1. An overview of synthesis reports using platinum, sulfur, or selenium.

material which generates a synergistic effect in capacitance, thus, in the energy density with an excellent electrochemical performance throughout the system. The main determining factor on this material is the surface area of each electrode that makes up the supercapacitor. Through the synthesis methods of carbon nanostructured materials such as graphene and nanotubes, the size and morphology of the compounds are tunable. This approach favors some specific properties for applications on fuel cell systems such as high surface area, stability, electroconductivity and catalytic activity.

1.3.1. Galvanic displacement

Some progress has been made in catalytic materials and supports preparation techniques, although none of these catalysts has reached the level of a Pt- or Ru-based catalyst in terms of catalytic activity, durability, and chemical/electrochemical stability. In order to make non-noble catalysts commercially feasible, cost-effective, and innovative, synthesis methods are needed for new catalyst discovery and catalyst performance optimization. The use of electrochemical methods, such as galvanic displacement and ultrasonic techniques, for instance, was chosen to describe here.

Figure 7 shows the preparation of core-shell nanoparticle catalysts. We also report here the electrochemical response obtained by PtPd/MWCNT. The parameters investigated were Pt concentration and sonication by a simple and fast galvanic displacement (GD) method, finding that both play a key role in the physicochemical features and, thereby, modifying the performance of the catalysts toward the oxygen reduction reaction (ORR) activity and according to results highly dispersed Pt₁₀Pd₉₀/MWCNT was produced [13, 36, 38].

1.3.2. Ultrasonic-assisted strategy

In addition, it is of great significance to explore different methods to obtain efficient catalysts for the PEM fuel cells. Ultrasonic-assisted strategy is known as a unique synthesis method in materials chemistry. Sonochemical reaction techniques have been introduced in the 1980s by Suslick's group. However, most of the literature works on electrocatalysis published until 2010 are cited by Eunjik Lee (2016) [39]. A number of alloy and core-shell NPs are well discussed. During the past years, a number of new alloy and core-shell NPs based on Pt and Pd have been synthesized by sonochemistry and studied for their electrocatalytic properties [40]. Therefore, in light of the importance of finding more dependable catalysts in the present status of FC researches. Some works cited here are the syntheses of Pt-Pd/MWCNT for enhanced ORR of Pt/MWCNT and PtNi/MWCNT catalysts with high electroactivity, and further ultrasound treatment is used because carbon nanotubes are uniform in size and well dispersed by this via [32]. We also reported about Pt/CNT/TiO₂ catalyst, and here we note the effect of the amount of MWCNT with the current density. In addition, the CO tolerance performance increases in the next sequence of Pt/CNT < Pt/TiO₂ < Pt/CNT/TiO₂ [41].

1.3.3. Green chemistry

According to the principle of green chemistry, the feed stock of any industrial process must be renewable rather than depleting a natural resource. Moreover, the process must be designed to achieve maximum incorporation of the constituent atoms (of the feed stock) in to the final product [39].

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Figure 7. Illustration of basic synthesis approaches for the preparation of core-shell nanoparticle catalysts. Electrochemical (acid) dealloying/leaching results in (a) dealloyed Pt bimetallic core-shell nanoparticles, and (b) Pt-skeleton core- shell nanoparticles, respectively. Reaction process routes generate segregated Pt skin core-shell nanoparticles induced by either (c) strong binding to adsorbates or (d) thermal annealing. The preparation of (e) heterogeneous colloidal core-shell nanoparticles and (f) Pt monolayer core-shell nanoparticles is via heterogeneous nucleation and UPD followed by galvanic displacement, respectively. (Reprinted with permission from Royal Society of Chemistry. Lic. No. 4171470897994).

A great advantage is the use of aqueous solutions instead of any surfactants, additive reagent, or posttreatment in the nanoparticles and CNS synthesis. The preparation of sulfide chalcogenides as reference Pt_xS_y , $Pt_xW_yS_{z'}$ and $Pt_xMo_yS_z$ catalysts were carried out only with water and at room temperature [19, 20] as well as other synthesis methods to produce CNS such as graphene or MWCNTs and nanoparticles, recently cupper nanoparticles, for instance [42].

1.4. Surface modification methods

The functionalization of carbon materials is essential processes for the utilization of these materials. Functional groups or molecules can be directly attached on the periphery of the surfaces of the carbons through various treatments with acids, etc. A large number of oxygen functional groups are created during the activation process by saturation of dangling bonds with oxygen. This creates a rich surface chemistry which is used for selective adsorption. In addition, it determines the ion exchange properties that are relevant for catalyst loading with active components. In **Figure 8**, an illustration of multiple routes of the chemistry of carbon nanotubes in biomedical applications is shown [43, 44]. Although the applications of



Figure 8. Illustration of the chemistry of carbon nanotubes in biomedical applications. Reprinted with permission from (Royal Society of Chemistry, Lic. No. 4171820715591).

functionalized carbon nanotubes are numerous, the modification surface of the individual carbon nanotubes by decorating the surface with OH, COOH, NH_2 , F, or other groups promotes dispersion in a wide variety of solvents and polymers enabling the use of nanotubes in many more applications and different fields of studio. The image above details only one specific application enabled the functionalized carbon nanotubes.

Another example of the modification of carbon nanostructures for different applications is on the design of ultrasensitive biosensors with advantages in the detection of organic molecule. The preparation of the CNT-graphene hybrid, with regard to the complex molecules and nanoparticles that can be anchored to the surface of these nanostructured materials after the oxidation. These results are a significant contribution to the properties that have the nanomaterials mentioned here. Recently, carbon-supported highly dispersed Ru_xSe_y chalcogenide

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Figure 9. Maximum power density achieved with (A) Pt-based and (B) $CoSe_2$ cathodes of a H_2/O_2 PEM fuel cell, an LFFC, a Y-type MRFC, and a multichannel mMRFC (this work). The dashed bar in (B) corresponds to the use of 10 mgcm⁻² Pd at the anode, 10 m HCOOH, and pure O_2 . Preparation of MEAs for the H_2/O_2 systems was done under the same conditions as those used for Pt and CoSe₂ systems. (Reprinted with permission from John Wiley and Sons. Lic. No. 4166570806290).

nanoparticles (1.7 nm) were synthesized; here, Ru and Se precursors in a simple microwaveassisted polyol process. In other studies, $Ir_{85}Se_{15}/C$ was synthesized with an average particle size less than 2 nm by the same method [13].



Figure 10. Schematic illustration of a PEM fuel cell and the use of chalcogenides and carbon nanostructures as anodic and cathodic electrodes.

Different routes of modification of CNS have been used by our group. Some synthesis and modification methods by microwave-assisted are used, the oxidizing agents are acids or even, hydrogen peroxide. On the other hand, the heat treatment is also a key factor of the nanostructures obtained [2, 15, 16, 44–46]. Traditionally, acids have been widely used for attaching to CNT. However, the microwave-assisted polyol is a versatile method for synthesis, dispersion, and surface modification of chalcogenides and CNS. Other important aspects of CNT and graphene are on chemistry, the level of purity and functionalization degree of the starting materials. Actually, our interests are on this direction, and the focus is the search of new catalysts for PEM fuel cell based on chalcogenides and CNS synthesized by rapid and efficient methods.

1.5. Applications for PEM fuel cell systems

To date, microscale system research has focused mostly on miniaturization of functional components, for instance, specialized devices such as clinical and diagnostic test, microanalytical systems for field tests, and various portable devices. Thus, here we mention about chalcogenide such as Ru_xSe_y , $CoSe_{2'}$ Pt_xSe_y and Pt_xS_y that have showed a remarkable selectivity toward the oxygen reduction reaction (ORR) for membraneless microlaminar-flow fuel cell. **Figure 9** shows a significant comparison between Pt, Pt_xS_y, and $CoSe_2$. The maximum power density for fuel cells are achieved with (A) Pt-based and (B) $CoSe_2$ cathodes of a H_2/O_2 for the PEM fuel cell, an LFFC, a Y-type MRFC, and a multichannel mMRFC [12].

This work is inspired by the excellent electrocatalytic activity of chalcogenides and carbon nanostructures which open the door for the development of a novel type of micro- or even nano-fuel cell. **Figure 10** displays a schematic illustration of an application for a PEM fuel cell. Some basic concepts about advantages and disadvantages of these devices were reported by Taner [47, 48]. It is a challenge to develop an active cathode catalyst for the ORR that is tolerant at the same time. One strategy proposed is the use of chalcogenides as anodic catalyst and CNS as cathodic catalyst. On the one hand, this type of chalcogenides can be used as anode, because are tolerant to CO molecules and by other sides of carbon nanostructures can be placed as cathode because of the atomic arrangement of the carbons can behaviors as metal and also can be modified on the surface, it means, doped or well-functionalized to support non-platinum metals, $N_{2'}$ B, P, S, etc. Either as cathode or anode, chalcogenides based on sulfur are promising. The target is to generate a maximum power density, and the key is on the methods of synthesis such as here we described. Moreover, many other studies about these materials are furthered from here. Nevertheless, in addition we report on micro-fabricated membraneless fuel cells with $Pt_x S_y$ - and $CoSe_2$ -tolerant cathodes and show how such materials can be used for developing smaller, simpler, and cheaper for PEM fuel cells.

Acknowledgements

The authors are grateful to Dr. F. Paraguay Delgado for TEM analysis and to Marco Ovalle, student of Nanotechnology Engineering, for their technical support and design of figures and to the National Institute of Technology of México/Technological Institute of Tijuana and Technological Institute of Oaxaca, Mexico, for the collaboration.

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Fundamentals of Electrochemistry with Application to Direct Alcohol Fuel Cell Modeling

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71635

Abstract

Fuel cell modeling is an inherently multiphysics problem. As a result, scientists and engineers trained in different areas are required to work together in this field to address the complex physicochemical phenomena involved in the design and optimization of fuel cell systems. This multidisciplinary approach forces researchers to become accustomed to new concepts. Electrochemical processes, for example, constitute the heart of a fuel cell. Accurate modeling of electrochemical reactions is therefore essential to successfully predict the performance of these devices. However, becoming familiar with the complex concepts of electrochemistry can be an arduous task for those who approach the study of fuel cells from fields other than chemical engineering. This process can extend over time and requires careful reading of many textbooks and papers, the most illuminating ones being hidden to the newcomer in a plethora of recent publications on the subject. The authors, who engaged in the study of fuel cells coming from the field of mechanical engineering, had to travel this road once and, with this contribution, would like to make the journey easier for those who come behind. As an illustrative example, the thermodynamic and electrochemical principles reviewed in this chapter are applied to a complex electrochemical system, the direct ethanol fuel cell (DEFC), reviewing recent work on this problem and suggesting future research directions.

Keywords: PEM fuel cells, direct alcohol fuel cells, fuel cell modeling, electrochemistry, reaction mechanisms

1. Introduction

A fuel cell is an electrochemical device that converts the chemical energy stored in a fuel and an oxidant directly into electricity, heat, and reaction products. The electric current is generated by a pair of *redox* reactions that occur separated by an *electrolyte*. At the anode, the fuel is oxidized,

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generating electrons and ions, while at the cathode the oxidant is reduced, consuming the electrons and ions generated at the anode. The electrolyte is specifically designed so that it cannot conduct electrons, which flow through an external circuit performing electrical work, while it allows the flow of ions needed to maintain global electrical neutrality. Unlike conventional batteries, fuel cells require that the fuel and the oxidant be supplied continuously to sustain the electrochemical reactions.

The operation of a fuel cell is driven by chemical processes. As a result, these devices circumvent the Carnot cycle limitations of thermal devices and the mechanical limitations of systems with moving parts. In addition, the amount of electrical energy that can be generated by a fuel cell is only limited by the capacity of the fuel and oxidant reservoirs, which eliminates the long recharge times characteristic of conventional batteries.

The discovery of the fuel cell operating principle is commonly attributed to Sir William R. Grove [1], who also invented a practical device based on this principle: the so-called *gaseous voltaic battery* [2]. Recent work, however, attributes the discovery to Christian Friedrich Schöenbein, the famous German-Swiss chemist, better known for his discoveries of guncotton and ozone, a year before Sir William R. Grove [3]. It is well known that both scientists maintained a lively scientific correspondence, which may be the origin of the confusion. Anyway, until the introduction of PTFE (Teflon) in 1950s, fuel cells were rather a scientific curiosity than a practical system.

The first practical application of fuel cells was in space. The National Aeronautics and Space Administration (NASA) used them in the Gemini program during the 1950s and later in the Apollo program. The first mission that used a fuel cell was an unmanned suborbital flight on October 30, 1960. The Gemini module launched in that mission mounted the first alkaline fuel cell developed by General Electric, which generated 1 kW power with 29 kg weight and provided a potable water source for the crew of future manned missions. During the Apollo program, NASA used the alkaline fuel cells developed by Pratt & Whitney based on Sir Francis T. Bacon patents [4, 5]. However, it was not until 1990s when the industry (Ballard, Plug Power, etc.) started the development of commercial fuel cells, mainly for automotive and backup power applications, and the US Department of Energy included fuel cells among its main research interests.

Fuel cells are often classified by the type of electrolyte they use, because the charge transport process that occurs in the electrolyte determines drastically the electrochemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the potential fuels, and other factors. These characteristics, in turn, affect the applications for which the different types of fuel cells are most suitable. According to the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRD&D) Plan [6], the largest markets for fuel cells today are in stationary power, portable power, auxiliary power units, backup power, and material handling equipment. Among fuel cell end users, the automotive sector stands out as one of the most relevant ones [7, 8]. However, there are still some barriers for the development of fuel cells, both technical and economical [6]. The use of catalysts is mandatory to reach competitive power densities, as they significantly accelerate the electrochemical reactions. In low-temperature fuel cells, the catalysts are usually based on

noble metals, such as platinum, which are scarce and very expensive. The electrolyte is also one of the main challenges. It often requires strict working conditions (in terms of temperature, humidity, etc.) to operate properly. As well, fuels and oxidants are not always easy to manage or store, which significantly increases system complexity.

The present volume is devoted to proton exchange membrane (PEM) fuel cells, whose particularities are summarized in Section 2. The specific topics of this chapter are addressed next. A brief summary of the overall performance of PEM fuel cells (PEMFCs) is presented in Section 3. Thermodynamic and electrochemical principles of PEM fuel cells are discussed in Sections 4 and 5. And a particular example of application of these principles to the modeling of multistep electrochemical reactions in direct alcohol PEM fuel cells is given in Section 6. Finally, the main conclusions are drawn in Section 7.

2. Proton exchange membrane fuel cells

PEM fuel cells (PEMFCs) use a polymeric electrolyte membrane to separate the anode from the cathode. As previously discussed, the polymer electrolyte membrane allows the transport of protons, but it is impermeable to electrons. The membrane is made of ionomers (synthetic polymers with ionic properties), the most extended one being Nafion[®], discovered in the late 1960s by Walther Grot of DuPont. It contains perfluorovinyl ethers terminated by sulfonic acids with hydrophobic tetrafluoroethylene (Teflon) flexible structures. So the proton conductivity is achieved because the water into the membrane ionizes the acidic groups [9, 10]. The sulfonic groups $-SO_3H$ (with general formula $R-S(=O)_2-OH$, where R represents the generic chain where the group is attached) are highly hydrophilic and can adsorb large amounts of water, creating hydrated regions. In these regions, the H^+ are weakly attracted by the $SO_3^$ groups, which are rigidly attached to the Teflon structure, and they are able to move easily. The hydrated hydrophilic regions thus behave as dilute acids, explaining why the membrane needs to be well hydrated for the proton conductivity to be appreciable. Both the polymeric nature of the membrane and the requirement of membrane hydration restrict the operational temperature range between 60 and 90° C, although air-breathing or passive systems may operate even at room temperature.

The transport of protons in the membrane forces the electrochemical reactions to produce or consume protons as charge carriers. At the anode side, the most extended fuel in PEMFCs is hydrogen [7], although alcohols are also used in direct alcohol fuel cells (DAFCs). The use of alcohols generates significantly less power than hydrogen, but they offer safer operation for unattended low-power missions. At the cathode side, oxygen is reduced with the protons and electrons released in the anode to generate water as only reaction product. As previously discussed, the protons reach the cathode crossing the membrane, whereas the electrons are conducted through an external circuit generating current. The oxygen can be supplied as a pure gas or diluted as part of an air stream feed directly to the cell.

To optimize the power output of PEMFCs operated with hydrogen, adequate operating conditions are needed. Most PEMFCs operate between 60 and 80°C to exploit the proton conductivity of the membrane. Proper humidification of the gas feed streams is often used to guarantee an adequate membrane water content. The hydrogen and air streams are usually pressurized (typically at 0.5 bar gauge pressure) to facilitate water management [11]. To provide these cell conditions, additional systems are required. However, other operating conditions have also been investigated to try to eliminate auxiliary systems. Passive fuel cells rely on natural mechanisms, such as capillary forces, diffusion, convection, and evaporation, to achieve cell feeding without extra power consumption. Among the passive systems used, one finds air-breathing systems for the anode electrode [12], pressurized cannisters [13], and capillary liquid systems [14]. There are also passive cells running on different fuels, such as hydrogen [12, 15, 16], methanol [17], and ethanol [18]. In general, passive systems are more suitable for portable power sources [19]. In the last decade, microbial fuel cells (MFCs), which use bacteria as the catalysts to oxidize organic and inorganic matters, have also been developed with application to microdevices [20].

High-temperature polymer exchange membrane fuel cells (HT-PEMFCs) are another variant of PEMFCs. They operate between 100 and 200°C, are able to run in dry conditions, and tolerate impure fuel streams (e.g., hydrogen obtained from reforming gases), and the excess heat can be used for cogeneration. These characteristics can be exploited to simplify the system design, which increases its overall efficiency. Nevertheless, materials other than Nafion must be used for the membrane (PBI, SPEEK, SPI, or SPSV) and the proton carrier (phosphoric acid or ionic liquids) [21, 22]. High-temperature operation has also been considered for DAFCs [23–25] to improve the effectiveness of the C–C bond breaking step in higher alcohols such as ethanol.

2.1. Direct alcohol PEM fuel cells

In addition to hydrogen, several liquid organic and inorganic compounds can be used as fuels in PEMFCs [26]. Common inorganic compounds tested for use are ammonia, hydrazine, borohydrides, and ammonia borane. Among the organic compounds used, there are alcohols, hydrocarbons, acids, and glycol compounds. Most of the organic compounds tested are produced by renewable biomass sources, which makes them a suitable clean option. Besides PEM membranes, also anion exchange membranes (AEMs) are used in alkaline cells [27]. Liquid fuels can be used either pure or diluted for safety reasons. Water is the most used solvent due to its natural properties and because of its importance for the correct operation of the membrane. Alcohols are considered a promising source fuel to fuel cells [28]. Light alcohols, such as methanol or ethanol, are able to electrooxidate at relative low temperatures (less than 90°C). They also have a higher energy density than hydrogen. The electrooxidation of alcohols consumes water, which makes water an optimum solvent for the fuel supply. In addition, aqueous alcohol solutions are typically fed at low concentrations (0.5-2 M), which makes their operation and storage safer. These advantages make DAFCs an alternative option for lowpower applications such as portable devices or unattended remote stations. Furthermore, more complex alcohols (e.g., propanol isomers, 2-methylpropan-2-ol, and butan-2-ol) may be an option at higher temperatures (up to 300°C). Nacef et al. [29] carried out an extensive thermodynamic study about the potential performances of several alcohols used in PEM fuel cells.

Nevertheless, some disadvantages arise when alcohols are used in PEM fuel cells. Contrary to hydrogen, alcohol electrooxidation is a sluggish process that involves many elementary reactions

generating high activation overpotentials. This results in a severe reduction of fuel cell performance. Besides that, since the alcohols are supplied as aqueous dilutions and the membrane is highly permeable to water, a *crossover* flux of fuel is established across the membrane. The fuel that crosses the membrane is electrooxidized at the cathode electrode, generating an undesired parasitic current that also results in larger cathode activation losses [30–37].

The electrooxidation of organic compounds is not straightforward, as it proceeds as a branched, multistep, reaction [38, 39]. Due to the large number of chemical bonds of the compounds, several reactions can be expected. Unfortunately, poisoning species such as carbon monoxide are found among the reaction intermediates that are formed in the reaction path. The CO groups remain adsorbed to the catalyst, blocking the active reaction sites. This produces a sharp reduction of the effective catalyst surface area, which also reduces cell performance [25, 40–42]. To mitigate this effect, binary Pt-based catalysts include a secondary metal, such as Sn or Ru [42–52]; the blockage of active sites is alleviated via a bifunctional mechanism that allows the absorption of hydroxyl groups at lower potentials on the secondary metal, thus favoring further oxidation of Pt-adsorbates blocking the active catalyst sites [53–55]. It is interesting to note that the problem of CO poisoning is not unique to DAFCs; low-temperature PEMFCs running on hydrogen have very low tolerance to impurities (e.g., CO) in the fuel, requiring very high purity hydrogen that is costly to produce. Fuel cells operated with reformate gas also exhibit this problem [56].

DAFCs are suitable for portable power applications (e.g., battery chargers, consumer electronics, handheld terminals, unattended security devices, notebook PCs, emergency response mobile communications, or even auxiliary power units) and material handling equipment. The power requirements for these applications are low, and the cost targets and infrastructure requirements are not as challenging as for transportation applications [6, 57].

Considering all the types of DAFCs currently under development, those running on methanol and ethanol are, in this order, the ones that have reached further progress. Below we describe the particularities of these fuel cells, indicating the main advantages and disadvantages of both.

2.1.1. Direct methanol fuel cells (DMFCs)

Methanol is the simplest alcohol. Due to the lack of the C–C bond present in higher alcohols, methanol is the alcohol with the largest number of hydrogens per carbon [58], which makes it a good hydrogen carrier. However, reforming methanol to H_2 is still under study. By contrast, a DMFC uses methanol as fuel without producing H_2 during the process. The device operates with diluted methanol (1-2 M), and only a fraction of the diluted fuel is used. The device recycles the outlet and replenishes it to keep methanol concentration [59]. Platinum-based catalysts show the best results [60]; additionally, secondary metals are included to reduce the impact of CO poisoning [39, 59, 61, 62]. As previously discussed, the main applications of DMFCs are on small portable devices: battery chargers, consumer electronics, notebook PCs, and portable generators [57, 59, 63]. Actual challenges for DMFCs marked by DOE include reducing Pt loading, reducing methanol crossover to increase efficiency, simplifying the side-on systems to increase energy and power density, improve reliability, and reduce cost [6].

2.1.2. Direct ethanol fuel cells (DEFCs)

Ethanol is a fully renewable alcohol that can be readily obtained from the fermentations of biomass and is much less toxic than methanol [27, 64]. Fuel Cell Technologies Office plans [6] include ethanol tolerance for liquid-feed fuel cells operated with fuel blends. The number of patents in DEFC is steadily growing since 2002, which suggests that DEFC technology is still under development and further progress can be expected [57]. The complete electrooxidation of ethanol to CO₂ would make DEFCs useful even for automotive purposes [27]. But the sluggish kinetics of the ethanol electrooxidation reaction hinders this achievement [27, 65–67]. By way of contrast, due to its larger molecular structure, ethanol has a lower crossover rate than methanol, which together with its slower electrochemical oxidation kinetics produces a lesser effect on the cathode performance [68, 69]. The complexity of ethanol electooxidation is originated by the difficulty of breaking the C–C bond [43, 61, 66, 70–77], a problem that is shared with other higher alcohols.

3. Performance of PEM fuel cells

The overall performance of a fuel cell is usually represented by the current density (i.e., current per unit surface) vs. voltage curve, often referred to as the *polarization curve*. Thermodynamics teaches us that, in an ideal process in which mass and charge transport phenomena occur in a reversible manner, the output voltage should remain constant independently of the current density. Such an ideal reversible voltage, or potential, *E*, is determined by the electrochemical reactions that occur in the cell and therefore is directly related to the redox pair. Operational parameters such as temperature and pressure also influence the ideal reversible potential.

The deviations between the ideal equilibrium potential of the redox pair and the polarization curve provide a measure of the fuel cell efficiency. The actual current density vs. voltage curve for a particular fuel cell (geometry, catalyst/electrode characteristics, and electrolyte properties) and operating conditions (reactant concentrations, flow rates, pressures, temperature, and relative humidity) is dependent on both activation (i.e., kinetic), ohmic, and mass transport losses, to be described below:

- Activation losses are originated by the finite rate of the electrochemical reactions that take place in the cell electrodes.
- Mass transport losses arise when the reactants are not supplied at the same rate than they can be consumed. Mass transport losses are dominated by the porous layers and interfacial phenomena [78]. As previously discussed, one of the main tasks of the porous layers is to smooth the channel-rib pattern of the bipolar plates to provide an as homogeneous as possible supply of reactants to the catalyst layers. However, this task entails a certain mass transfer resistance that produces significant mass transport losses at large current densities.
- Ohmic losses are generated by the irreversible charge transport processes associated with finite charge transport conductivities. Electrons move through the solid phase of the gas diffusion layers and other elements of the cell and their interfaces, while protons are

conducted through the polymeric membrane. Although the charge transport mechanisms are different, both result in finite voltage drops. These losses grow linearly with the current density as stated by Ohm's law.

The actual cell voltage at a given current density can then be expressed as the ideal reversible potential, *E*, minus the so-called activation (act), transport (transp), and ohmic (ohm) overpotentials

$$V = E - \eta_{\rm act} - \eta_{\rm transp} - \eta_{\rm ohm} \tag{1}$$

However, for modeling purposes, the voltage losses are often separated by regions rather than processes

$$V = E - \eta_{\rm a} - \eta_{\rm c} - \eta_{\rm mem} \tag{2}$$

where η_a , $\eta_{c'}$ and η_{mem} denote the voltage losses (including activation, mass transport, and ohmic contributions) at the anode, the cathode, and the membrane.

Electrooxidation reactions arise as a crucial issue in DAFCs, since they largely determine both η_a and η_c . For instance, the incomplete electrooxidation of ethanol hinders the theoretical maximum energy release in direct ethanol fuel cells, while at the same time it generates a variety of partially oxidized products. An accurate DAFC model therefore has to predict current density and overpotentials as well as a detailed description of the residual products. For this purpose, a systematic formulation of the multistep electrochemical reactions that take place in DAFCs is highly desirable.

4. Thermodynamic principles of PEM fuel cells

4.1. Redox pairs

The most important driving processes that take place in a fuel cell are the electrochemical reactions between the fuel and the oxidant. As implied by the prefix *electro*⁻¹, these reactions involve the transfer of electric charges, and this fact is achieved through a pair of *redox* (i.e., *re*duction–*ox*idation) reactions. A *redox* reaction is separated into two half-reactions: the oxidation and the reduction reactions. In the oxidation reaction, the reactant species looses electrons. By contrast, in the reduction reaction, the reactant species gains electrons. The oxidation and reduction reactions take place in the anode and cathode electrodes, respectively.

In a fuel cell, the redox half-reactions are kept separated by an electrolyte, with the electrodes being electrically connected through an external circuit. The electrolyte is an ionic conductor, while the electrodes and the external circuit are made of good electronic conductors. This

¹From Latin electrum, from Ancient Greek élektron, or "amber", a natural resin, which when rubbed produces static electricity.

configuration makes it possible to separate the ionic and electronic currents, the latter being used to perform electrical work through an external circuit.

As discussed above, the reactants used for the oxidation reactions in PEM fuel cells are hydrogen and alcohols, mostly methanol and ethanol. Protons are the ionic charge carrier in these cells, so the oxidation reaction must generate protons for the operation of the system. For instance, the hydrogen oxidation reaction

$$H_2 \rightarrow 2H^+ + 2e^- \tag{3}$$

generates two protons and two electrons per molecule of hydrogen consumed. This reaction occurs in the anode of low-temperature hydrogen PEMFCs, where due to its extreme simplicity the activation losses are very small. In addition to this, the catalyst, typically made of Pt-based particles [39, 79], performs better for simpler reactions such as (3). As implied by the above reaction, hydrogen electrooxidation produces no other products than charge carriers, in this case electrons and protons; hence, it is not necessary to evacuate anything else from the anode electrode, except (maybe) the heat evolved by the reaction.

For low-power portable applications, liquid-feed direct alcohol fuel cells (DAFCs) may also be used. The simplest alcohol is methanol (CH₃OH). The electrooxidation of methanol also produces electrons and protons but generates CO₂ as well and only occurs in the presence of water

$$CH_3OH + H_2O \to CO_2 + 6H^+ + 6e^-$$
 (4)

which requires the supply of water and the evacuation of CO_2 bubbles. This introduces stronger mass transport limitations in the anode of a DMFC than in hydrogen PEMFCs, motivated in particular by the presence of the bubbles.

The methanol oxidation reaction (MOR) takes place in multiple steps [39], and some of them lead to the production of undesirable intermediate products, such as CO [25, 40–42, 56]. Due to the multiple species involved, the reaction is slower and more complex than Reaction (3), which leads to significantly lower current densities in DMFCs than in hydrogen PEMFCs. As a result, complex and expensive catalyst compositions (Pt-Ru nanoparticles supported on high surface area carbon) must be used to minimize activation losses [42–52].

Ethanol is another alcohol used in DAFCs. It is a more complex molecule (CH_3CH_2OH) with a highly stable C–C bond, which makes it even more difficult to react. It is well known that ethanol electrooxidation may proceed through multiple pathways, which includes partial oxidation to acetaldehyde, acetic acid, or methane, as well as complete oxidation to CO_2 , according to the following overall reactions

$$CH_3CH_2OH \rightarrow CH_3COH + 2H^+ + 2e^-$$
 (5a)

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$$
(5b)

$$CH_3CH_2OH + H_2O \rightarrow CO_2 + CH_4 + 4H^+ + 4e^-$$
 (5c)

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$$
 (5d)

While different oxidation reactions occur in PEM fuel cells depending on the fuel type, the reduction reaction is common to all of them, namely the oxygen reduction reaction (ORR)

$$O_2 + 4H^+ + 4e^- \to 2H_2O$$
 (6)

which combines the electrons and protons produced in the anode with a molecule of oxygen to produce water.

When combining Reactions (3), (4), or (5) with Reaction (6), different global reactions can be defined for the cell:

Hydrogen PEM fuel cells (PEMFCs)

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{7}$$

Direct methanol fuel cells (DMFCs)

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \tag{8}$$

• Direct ethanol fuel cells (DEFCs)

$$CH_3CH_2OH + \frac{1}{2}O_2 \rightarrow CH_3COH + H_2O \tag{9}$$

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O$$
(10)

$$CH_3CH_2OH + O_2 \rightarrow CO_2 + CH_4 + H_2O$$
(11)

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \tag{12}$$

4.2. Electrical work and Gibbs free energy

The energy released in a fuel cell comes from the chemical energy stored in the fuel and the oxidant, which is released by the electrochemical reactions that take place in the anode and cathode electrodes. The energy released or consumed by a chemical reaction is represented by its *heat of reaction* or *enthalpy of reaction*. This value is the enthalpy change produced in a chemical reaction, and it is calculated as the difference in *formation enthalpy* between the reaction products (P) and reactants (R) at a given temperature T

$$\Delta h^{0}(T) = \sum_{P} v_{k} h_{k}^{0}(T) - \sum_{R} v_{k} h_{k}^{0}(T)$$
(13)

In the above expression, v_k is the stoichiometric coefficient of species k and $h_k^0(T)$ is the molarspecific formation enthalpy of species k, which can be evaluated at temperature T from its reference value at the standard temperature T_0 as follows

$$h_k^0(T) = \Delta_f h_k^0(T_0) + \left(h_k^0(T) - h_k^0(T_0)\right)$$
(14)

This expression shows that the molar enthalpy of a chemical compound is made up by its molar enthalpy of formation at the reference temperature $\Delta_f h_k^0(T_0)$ plus the enthalpy change associated with the state change at fixed composition $h_k^0(T) - h_k^0(T_0)$ [80]. An extended database for these thermodynamic properties, containing data for over 2000 solid, liquid, and gaseous chemical species, is provided by NASA [81].

During the chemical reactions, entropy also changes. Just like the *enthalpy of reaction* (13), the molar *entropy of reaction* at a given temperature *T* and pressure *p* is defined as

$$\Delta s(T,p) = \sum_{\mathbf{P}} v_k s_k(T,p) - \sum_{\mathbf{R}} v_k s_k(T,p)$$
(15)

Unlike enthalpy, entropy has no formation contribution. As established by the third law of thermodynamics, the *absolute entropy* is defined as the entropy change between the actual estate and the absolute-zero state. For crystalline substances, entropy is zero at the absolute-zero state, whereas noncrystalline substances have a nonzero value of the entropy at the absolute-zero state [80]. The value of the absolute entropy can also be obtained from the NASA library of thermodynamic data [81].

It is well known that not all the energy available in a chemical reaction can be converted to useful work. Therefore, in a fuel cell, not all the energy released by the electrochemical reactions can be converted to electrical work as a result of entropy production. The Gibbs free energy

$$G = H - TS \tag{16}$$

represents the amount of useful energy that can be used as *potential work*. In a given process, the amount of energy that can be released as potential work is the variation of the Gibbs free energy. For an isothermal process, the variation of the molar-specific Gibbs free energy reduces to

$$\Delta \mathbf{g} = \Delta h - T \Delta s \tag{17}$$

The work performed by a fuel cell is completely electrical. In general, electrical work is done when moving a charge Q through a potential difference E. In a fuel cell, the electrical work can be written as

$$W_e = nFE \tag{18}$$

where *n* is the number of moles of electrons transferred in the reaction per mole of fuel consumed and *F* = 96485 C/mole of electrons is Faraday's constant. Since the maximum amount of electrical work that can be obtained is the reduction of the Gibbs free energy ($W_e = -\Delta g$), the electrical reversible potential (or voltage) obtained from the cell is

$$E = \frac{-\Delta g}{nF} \tag{19}$$

The value of the electrical reversible potential at the standard conditions, $T_0 = 298$ K and $p_0 = 100$ kPa, is called the *standard reversible potential of the reaction* E_0 .

As previously discussed, water is commonly produced in PEM fuel cells. Due to the low temperatures of operation ($T < 100^{\circ}$ C), it can be produced in both liquid and gas phases. However, the enthalpy of formation of both phases is different, the difference being the latent heat of vaporization. As a result, the formation of liquid water yields a significantly higher reaction enthalpy than that of water vapor. To decide which phase should be used for determining the potential work, we have to apply the "philosopy" of the *Gibbs free energy* calculation. This accounts for the maximum energy that can be released as work. Since the formation of liquid water releases a larger amount of energy due to the latent heat of vaporization, which is released during condensation, the use of the gas water formation enthalpy implies an incomplete account of the available energy. The value of the reaction enthalpy obtained assuming the formation of liquid water is therefore called the higher heating value (HHV), while that obtained when water vapor is formed is called the lower heating value (LHV).

Another voltage can be defined using the reaction enthalpy (13); the *thermoneutral potential* or *enthapy potential* E_{TH} is

$$E_{TH} = \frac{-\Delta h}{nF} \tag{20}$$

This potential is useful to evaluate all the available energy contained in the fuel.

The reversible potential *E* accounts for the decreasing of the energy due to the entrophy generation of the chemical reactions. In a fuel cell, the actual voltage *V* established between the electrodes is lower than the reversible potential *E* and the enthalpy potential E_{TH} due to the fuel cell irreversibilities. The unused energy is dissipated as heat. Then, the total heat produced by the electrochemical reactions can be simply expressed as

$$Q = I(E_{TH} - V) \tag{21}$$

where *I* represents the amount of current drawn from the cell. It is interesting to note that when using the LHV to evaluate the enthalpy potential E_{TH} one obtains a lower estimation of the residual heat *Q* than when using the HHV. The difference comes from the fact that the HHV includes also the heat released during water condensation. However, the global energy balance should remain the same in both cases as long as the latent heat of vaporization is properly accounted for [78].

4.2.1. Hydrogen potentials

The standard potential of hydrogen PEMFCs is highly dependent on the phase of water produced. The reversible potential at 25°C is 1.229 V for liquid water and 1.185 V for water vapor (**Table 1**). In both cases, the potential decreases with temperature (**Figure 1**). Below 100°C, the production of liquid water releases more energy than that of water vapor, so the

Global reaction	Standard potential @ $T_0 = 298 \text{ K}$
$\overline{H_2 + \frac{1}{2}O_2 \rightarrow H_2O} (l)$	$E_0 = 1.229 \text{ V}$
$\mathrm{H}_2 + \tfrac{1}{2}\mathrm{O}_2 \to \mathrm{H}_2\mathrm{O}~(g)$	$E_0 = 1.185 \text{ V}$
$CH_3OH+\tfrac{3}{2}O_2 \rightarrow CO_2+2H_2O~(l)$	$E_0 = 1.213 \text{ V}$
$CH_3CH_2OH + \tfrac{1}{2}O_2 \rightarrow CH_3COH + H_2O \ (l)$	$E_0 = 1.049 \text{ V}$
$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \ (l)$	$E_0 = 1.151 \text{ V}$
$CH_3CH_2OH+O_2 \rightarrow CO_2+CH_4+H_2O \ (l)$	$E_0 = 0.889 \text{ V}$
$CH_3CH_2OH+3O_2\rightarrow 2CO_2+3H_2O~(l)$	$E_0 = 1.151 \text{ V}$

Table 1. Standard reversible potentials of several global reactions of interest for PEM fuel cell modeling.



Figure 1. Reversible potentials for various global reactions of interest in PEM fuel cells.

potential evaluated using the HHV is higher in that range, whereas the potential obtained using the LHV is higher over 100°C. Low-temperature PEM fuel cells operate assuming the HHV as maximum expected energy.
4.2.2. Methanol potentials

Liquid-feed DMFCs operate at temperatures lower than 100°C, so the HHV is used for calculating their standard potential. At higher temperatures, the phase of methanol also needs to be considered. **Figure 1** shows the evolution of the standard potential for both liquid and gas methanol and water. The potential predicted assuming both species in liquid phase decreases sightly with temperature, while that obtained for gas phase is seen to increase with temperature. This fact is the basis to explore the posibility of using DMFCs at temperatures above 100°C [29].

4.2.3. Ethanol potentials

The ethanol electrooxidation reaction in DEFCs has very complex kinetics with different products [43, 61, 66, 70–77]. **Table 1** shows the global reactions considered in this study (Section 4.1). It is seen that the complete oxidation to CO_2 has the higher reversible potential, which decreases monotonically with temperature as shown in **Figure 1**. Although complete oxidation to CO_2 is difficult to achieve, the reversible potential of this reaction is often used as reference for DEFC models.

4.3. The Nernst equation

So far, the effect of reactant and product concentrations on reversible cell potential has been ignored. To understand this effect, we must introduce the chemical potential. The chemical potential of species k is defined as

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{T, p, n_{l \neq k}}$$
(22)

and represents the change of the Gibbs free energy produced by a change in the number of moles, n_k , of species k. Thermodynamics teaches us that the Gibbs free energy of a mixture can be expressed as the sum of the chemical potentials of all the species composing the mixture

$$G = \sum_{k} n_k \mu_k \tag{23}$$

and that the chemical potential of species k can be expressed as

$$\mu_k = \mu_k^0 + RT \ln a_k \tag{24}$$

in terms of the activity of species *k*, defined as:

$$a_{k} = \begin{cases} p_{k}/p_{0} & \text{ideal gases} \\ C_{k}/C_{0} & \text{for} & \text{ideal dilute solutions} \\ 1 & \text{pure components} \end{cases}$$
(25)

where $C_0 = 1$ M is the reference concentration.

The variation of the molar-specific Gibbs free energy can then be written in terms of the chemical potentials

$$\Delta g = \sum_{\mathbf{P}} v_k \mu_k^0 - \sum_{\mathbf{R}} v_k \mu_k^0 + RT \ln \frac{\prod_{\mathbf{P}} a_k^{v_k}}{\prod_{\mathbf{R}} a_k^{v_k}}$$
(26)

where the variation of the chemical potentials in standard conditions can be written as the standard change in the Gibbs free energy Δg^0 for the reaction

$$\Delta g = \Delta g^0 + RT \ln \frac{\prod_{\rm P} a_k^{\nu_k}}{\prod_{\rm R} a_k^{\nu_k}}$$
⁽²⁷⁾

Using this expression to evaluate the reversible potential of the reaction E using Eq. (19), one obtains the *Nernst equation*

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod_P a_k^{\nu_k}}{\prod_R a_k^{\nu_k}}$$
(28)

which relates the reversible potential *E* of the electrochemical reaction to the standard reversible potential E^0 , temperature, and activities, expressed in terms of concentrations or partial pressures. Eq. (28) owes its name to the German chemist Walther Nernst², who originally obtained it exclusively from experimental work [83, 84], although his equation was later deducted from first thermodynamic principles, as has been shown here.

5. Electrochemical principles of PEM fuel cells

The *key point* to the operation of a fuel cell is that the total reaction is split into two halfreactions that take place separately in the anode and cathode electrodes. The Nernst equation (28) applies to the global reaction and serves to determine the ideal reversible potential, *E*, but a deeper understanding requires to study both half-reactions independently. Obviously, they are electrochemical reactions as they involve electron transfer. In 1905, Julius Tafel proposed an empirical equation that related the current density *j* produced by an electrochemical reaction to the so-called overpotential $\eta = E - E^*$, defined as the difference between the applied potential *E* and the equilibrium potential E^* [85]. This equation is commonly known as the *Tafel equation* and is customarily written in the form

$$\eta = a + b \log j$$
 with $b = \frac{2.3RT}{\alpha F}$ (29)

A detailed review of the historical development of Nernst equation can be found in Ref. [82]

where α is the so-called charge transfer coefficient, whose value must be between 0 and 1, and log indicates decimal logarithm. This equation is widely used in electrochemistry and can be applied in several conditions [86].

Although Tafel obtained its equation purely by experimental methods, in the 1930s Butler and Volmer (and coworkers) derived it from the Arrhenius equation for the rate constant of a chemical reaction, rewriting the activation energy in terms of the Gibbs free energy of activation and the cell overpotential as discussed below.

5.1. From Tafel equation to Butler-Volmer equation

In 1889, Arrhenius [87]³ proposed that the temperature dependence of the rate constant of a chemical reaction could be expressed as

$$\mathfrak{K} = A \exp\left(\frac{-\Delta_A E}{RT}\right) \tag{30}$$

where *T* is the absolute temperature, *A* is the frequency factor, and $\Delta_A E$ is the activation energy. The frequency factor gives the frequency of collisions between reactant molecules. The activation energy can be defined as the change in internal energy from the reactant state to the *activated complex* state, so it is also called the *internal energy of activation*.

Since all the reactions in a fuel cell can be considered as condensed-phase reactions,⁴ the *enthalpy of activation* is approximately equal to the activation energy, so that

$$\mathfrak{K} = A \exp\left(\frac{-\Delta_A H}{RT}\right) \tag{31}$$

Rewriting now the parameter *A* as the product $A' \exp(-\Delta_A S/R)$ allows us to express the reaction constant in terms of the Gibbs free energy of activation $\Delta_A G$

$$\Re = A' \exp\left(\frac{-\Delta_A H - T\Delta_A S}{RT}\right) = A' \exp\left(\frac{-\Delta_A G}{RT}\right)$$
(32)

Advanced kinetic theories (e.g., transition state theory) have tried to estimate the values of *A* and $\Delta_A E$ corresponding to a certain electrochemical reaction and to relate them to molecular properties. However, extending our discussion to such complex descriptions is outside the scope of this work. For the interested reader, a deeper discussion of electron transfer kinetics can be found in Ref. [90].

³A detailed description of the development of Arrhenius equation is presented by [88]. An English translation of the original paper of Arrhenius can be found in Ref. [89], first edited in 1967, pp. 31–35.

⁴In general $\Delta H = \Delta E + \Delta(pV)$ but in condensed-phase reactions $\Delta(pV)$ can be neglected, so that $\Delta E \approx \Delta H$ [90].

5.1.1. Single-step single-electron reactions

To fix ideas, let us consider a generic single-step reversible electrooxidation reaction (similar to the anode half-reaction of a PEMFC) involving the transfer of a single electron

$$\mathbf{R} \rightleftharpoons \mathbf{O} + e^{-} \tag{33}$$

At this point, it is important to note that the Gibbs free energy of activation at a given condition can be written as the Gibbs free energy of activation at a reference state, usually taken as the equilibrium state, hereafter denoted by the subscript 0, plus an additional term that accounts for the deviation of the potential from its value at the reference state. Thus, for the forward (i.e., oxidation) reaction

$$\Delta_A G_{\text{O}x} = \Delta_A G^0 - \alpha_{\text{O}x} F \left(E - E^0 \right) \tag{34}$$

while for the backward (i.e., reduction) reaction

$$\Delta_A G_{\text{Red}} = \Delta_A G^0 + \alpha_{\text{Red}} F(E - E^0)$$
(35)

where α_{Ox} and α_{Red} are the charge transfer coefficients of the oxidation and reduction reactions. The charge transfer coefficients reflect the nature of the electron transfer process in single-step electrochemical reactions [86]. For single electron reactions taking place on metallic surfaces, the value $\alpha_{Ox} \approx 0.5$ is commonly accepted [11, 91]. The value of α_{Ox} is also related to the charge transfer coefficient of the backward reaction, with the symmetry relation $\alpha_{Red} = 1 - \alpha_{Ox}$ being frequently assumed. For a thorough derivation of the above expressions, the reader is referred to Section 3.3.2 of the book of Bard and Faulkner [90].

According to Eqs. (32), (34), and (35), the reaction constants for the forward and backward reactions can be written as

$$\Re_{Ox} = A'_{Ox} \exp\left(\frac{-\Delta_A G_{Ox}}{RT}\right) = A'_{Ox} \exp\left(\frac{-\Delta_A G_{Ox}^0}{RT}\right) \exp\left(\alpha_{Ox} \frac{F(E - E^0)}{RT}\right)$$

$$\Re_{Red} = A'_{Red} \exp\left(\frac{-\Delta_A G_{Red}}{RT}\right) = A'_{Red} \exp\left(\frac{-\Delta_A G_{Red}^0}{RT}\right) \exp\left(-\alpha_{Red} \frac{F(E - E^0)}{RT}\right)$$
(36)

When expressed in moles of species R consumed per unit catalyst surface per unit time, the net reaction rate can be written as follows

$$\Gamma = C_{\rm R} K_{\rm Ox} \exp\left(\alpha_{\rm Ox} \frac{F(E - E^0)}{RT}\right) - C_{\rm O} K_{\rm Red} \exp\left(-\alpha_{\rm Red} \frac{F(E - E^0)}{RT}\right)$$
(37)

where the constants K_{Ox} and K_{Red} incorporate all the terms that are independent of the potential

$$K_r = A'_r \exp\left(\frac{-\Delta_A G_r^0}{RT}\right), \quad r = Ox, \text{ Red}$$
 (38)

In general, the reaction constants K_r appearing in Eq. (37) depend on the temperature T, the reaction being studied, and the type of catalyst where the reaction takes place.

To continue the discussion, it is convenient now to consider the equilibrium condition. At equilibrium, the net reaction rate Γ is zero, since oxidation and reduction occur at the same rate. At this state, the potential reaches an equilibrium value, E^* , and the same happens with the concentrations, C_R^* and C_O^* . From Eq. (37), at equilibrium, the reaction rate of the oxidation and reduction reactions can be written as

$$\Gamma^{\star} = C_{\rm R}^{\star} K_{\rm Ox} \exp\left(\frac{\alpha_{\rm Ox} F(E^{\star} - E^0)}{RT}\right) = C_{\rm O}^{\star} K_{\rm Red} \exp\left(-\frac{\alpha_{\rm Red} F(E^{\star} - E^0)}{RT}\right)$$
(39)

Dividing Eq. (37) by Γ^{\star} and rearranging yields

$$\frac{\Gamma}{\Gamma^{\star}} = \frac{C_{\rm R}}{C_{\rm R}^{\star}} \exp\left(\frac{\alpha_{\rm Ox}F(E-E^{\star})}{RT}\right) - \frac{C_{\rm O}}{C_{\rm O}^{\star}} \exp\left(\frac{-\alpha_{\rm Red}F(E-E^{\star})}{RT}\right)$$
(40)

This expression for Γ circumvents the difficulty of referring the potential to the standard potential, as the overpotential is much simpler to measure experimentally. It was Tafel [85] the first to write the reaction rate in this form, which can also be expressed as

$$\Gamma = \Gamma^{\star} \left[\frac{C_{\rm R}}{C_{\rm R}^{\star}} \exp\left(\frac{\alpha_{\rm Ox} F \eta}{RT}\right) - \frac{C_{\rm O}}{C_{\rm O}^{\star}} \exp\left(\frac{-\alpha_{\rm Red} F \eta}{RT}\right) \right]$$
(41)

in terms of the overpotential, $\eta = E - E^*$. This equation is very often written using the simpler notation

$$\Gamma = C_{\rm R} k_{\rm Ox} \exp\left(\frac{\alpha_{\rm Ox} F \eta}{RT}\right) - C_{\rm O} k_{\rm Red} \exp\left(\frac{-\alpha_{\rm Red} F \eta}{RT}\right)$$
(42)

in terms of the oxidation and reduction rate constants

$$k_{\rm Ox} = \frac{\Gamma^{\star}}{C_{\rm R}^{\star}} \quad \text{and} \quad k_{\rm Red} = \frac{\Gamma^{\star}}{C_{\rm O}^{\star}}$$
(43)

The net current density generated by the electrochemical redox reaction, expressed in amperes per unit catalyst surface area, can be obtained by multiplying the net reaction rate Γ given in (41) by Faraday's constant, resulting in the well-known *Butler-Volmer equation*

$$j = j_0 \left[\frac{C_{\rm R}}{C_{\rm R}^{\star}} \exp\left(\frac{\alpha_{\rm Ox} F \eta}{RT}\right) - \frac{C_{\rm O}}{C_{\rm O}^{\star}} \exp\left(\frac{-\alpha_{\rm Red} F \eta}{RT}\right) \right]$$
(44)

where $j_0 = \Gamma^* F$ is the so-called *exchange current density*, a fundamental electrochemical property that represents the rate of the oxidation and reduction reactions at equilibrium expressed in terms of current density. It is interesting to note that Butler [92] and Volmer [93] found this equation separately, so the name honors both. Under conditions where the backward reaction

can be neglected, for example, for sufficiently high overpotentials, Eq. (44) reduces to the *Tafel equation*, which is written here in exponential form

$$j = FC_{\rm R}k_{\rm Ox} \exp\left(\frac{\alpha_{\rm Ox}F\eta}{RT}\right) \quad \text{or} \quad \eta = \frac{RT}{\alpha_{\rm Ox}F}\ln j - \frac{RT}{\alpha_{\rm Ox}F}\ln\left(FC_{\rm R}k_{\rm Ox}\right) \tag{45}$$

It should be noted that the original *Tafel equation* was written using the decimal logarithm, which yields the factor 2.3 in Eq. (29).⁵

The current density, *j*, appearing in Eqs. (29), (44), and (45) requires further comment. This current density is expressed in amperes per unit catalyst surface area. In order to convert it to amperes per unit volume, as often required for evaluating distributed current sources in threedimensional macro-homogeneous models of fuel cell catalysts layers, the current density *j* has to be multiplied by a geometric factor representing the catalyst surface area per unit volume of catalyst layer. This conversion factor is the so-called *volume-specific catalyst surface area*, often denoted by the letter *a* in the literature. Integrating the volumetric current density *aj* over the thickness of the catalyst layer at a certain location, one obtains the cell current density, hereafter denoted by *i*, which represents the current generated by the cell per unit surface area of catalyst layer and coincides with the protonic current density crossing the membrane.

5.1.2. Multiple-step multiple-electron reactions

Electrochemical reactions in fuel cells usually involve more than a single step and more than a single electron transfer. To deal with multistep reactions involving the transfer of several electrons, it is convenient to assume that there exists an elementary step that is significantly slower than the rest, the so-called *rate-determining step* (RDS) of the global reaction. Some authors [11, 94] propose the relation

$$\alpha_{\rm Ox} + \alpha_{\rm Red} = \frac{n}{v} \tag{46}$$

where n is the total number of electrons transferred and v is the number of times that the RDS must occur for the overall reaction to occur. Other authors [86] propose to write the charge transfer coefficient as a function of the overpotential following *Marcus theory*

$$\alpha_{\rm Ox} = \frac{1}{2} \left(1 + \frac{F\eta}{\lambda} \right) \tag{47}$$

where the parameter λ is referred to as the *reorganization energy*, defined as the energy required to change the nuclear configurations [95]⁶.

 $^{{}^{5}\}ln x = \log x / \log e \approx 2.3 \log x.$

[°]Rudolph A. Markus received the 1992 Nobel Prize in Chemistry "for his contributions to the theory of electron transfer reactions in chemical systems". An extended review of Markus theory is presented in his review [96]. An extension to organic reactions is presented in Ref. [97].

Nevertheless, a closer look at the reactions involved in the whole process will give us a better understanding. For a general electrochemical reaction of the form

$$\mathbf{R} \rightleftharpoons \mathbf{O} + ne^{-} \tag{48}$$

the reaction mechanism could be divided in three parts: the reactions before the RDS

$$\mathbf{R} \rightleftharpoons \mathbf{R}' + n'e^{-} \tag{49}$$

the RDS itself

$$\mathbf{R}' \rightleftharpoons \mathbf{O}' + e^{-} \tag{50}$$

and the reactions after the RDS

$$O' \rightleftharpoons O + n''e^{-} \tag{51}$$

As the RDS acts effectively as a bottleneck for the multistep reaction process, the reaction rate of the global reaction is given in first approximation by that of the RDS. Applying Eq. (42) to the RDS, the following expression is obtained

$$\Gamma = C_{\text{R}'} k_{\text{Ox}}^{\text{RDS}} \exp\left(\frac{\alpha_{\text{Ox}}^{\text{RDS}} F(E - E^{\star \text{RDS}})}{RT}\right) - C_{\text{O}'} k_{\text{Red}}^{\text{RDS}} \exp\left(\frac{-\alpha_{\text{Red}}^{\text{RDS}} F(E - E^{\star \text{RDS}})}{RT}\right)$$
(52)

Pre- and post-RDS reactions take place significantly faster than the RDS. As a result, the concentration of the intermediate compounds (namely R' and O') can be approximated by the equilibrium values obtained from the pre- and post-RDS reactions, respectively. Combining Eq. (42) and the equilibrium condition ($\Gamma = 0$) applied to the pre- and post-RDS reactions, expressions for the concentration of the intermediate compounds in terms of the initial and final products (R and O) can be obtained

$$C_{\mathrm{R}'} = C_{\mathrm{R}} \frac{k'_{\mathrm{Ox}}}{k'_{\mathrm{Red}}} \exp\left(\frac{\left(\alpha'_{\mathrm{Ox}} + \alpha'_{\mathrm{Red}}\right)F\left(E - E'^{\star}\right)}{RT}\right)$$

$$C_{\mathrm{O}'} = C_{\mathrm{O}} \frac{k''_{\mathrm{Red}}}{k''_{\mathrm{Ox}}} \exp\left(\frac{-\left(\alpha''_{\mathrm{Ox}} + \alpha''_{\mathrm{Red}}\right)F\left(E - E''^{\star}\right)}{RT}\right)$$
(53)

Substituting these expressions in Eq. (52) yields the following expression for the reaction rate of the multistep electrochemical reaction

$$\begin{split} \Gamma &= C_{\rm R} \frac{k_{\rm Ox}^{\rm RDS} k'_{\rm Ox}}{k'_{\rm Red}} \exp\left(\left[-\left(\alpha'_{\rm Ox} + \alpha'_{\rm Red}\right) E'^{\star} + \alpha^{\rm RDS} E^{\rm RDS\star}\right] \frac{F}{RT}\right) \\ &\times \exp\left(\left(\alpha'_{\rm Ox} + \alpha'_{\rm Red} + \alpha^{\rm RDS}_{\rm Ox}\right) E \frac{F}{RT}\right) - \end{split}$$

$$C_{O} \frac{k_{\text{Red}}^{\text{RDS}} k'_{\text{Red}}}{k'_{Ox}} \exp\left(\left[\left(\alpha''_{Ox} + \alpha''_{\text{Red}}\right) E''^{\star} - \beta^{\text{RDS}} E^{\text{RDS}\star}\right] \frac{F}{RT}\right) \\ \times \exp\left(-\left(\alpha''_{Ox} + \alpha''_{\text{Red}} + \alpha^{\text{RDS}}_{\text{Red}}\right) E \frac{F}{RT}\right)$$
(54)

The above expression involves absolute potentials, which can not be readily measured. In order to express the overall reaction rate Γ in a more convenient way, the first and second terms can be multiplied by the unit factors

$$\exp\left(\left(\alpha'_{\rm Ox} + \alpha'_{\rm Red} + \alpha^{\rm RDS}_{\rm Ox}\right) \frac{F(E^{\star} - E^{\star})}{RT}\right)$$

and
$$\exp\left(\left(\alpha''_{\rm Ox} + \alpha''_{\rm Red} + \alpha^{\rm RDS}_{\rm Red}\right) \frac{F(E^{\star} - E^{\star})}{RT}\right)$$
(55)

where E^* denotes the equilibrium potential of the complete reaction. This results in the following expression

$$\Gamma = C_{\rm R} \frac{\overline{k_{\rm Red}^{\rm RDS} k_{\rm Ox}'}}{k_{\rm Red}'} \exp\left(\left[-\left(\alpha_{\rm Ox}' + \alpha_{\rm Red}'\right)\left(E'^{\star} - E^{\star}\right) + \alpha_{\rm Ox}^{\rm RDS}\left(E^{\rm RDS\star} - E^{\star}\right)\right] \frac{F}{RT}\right)$$

$$\times \exp\left(\overline{\left(\alpha_{\rm Ox}' + \alpha_{\rm Red}' + \alpha_{\rm Ox}^{\rm RDS}\right)} \frac{F(E - E^{\star})}{RT}\right)$$

$$- C_{\rm O} \frac{k_{\rm Red}^{\rm RDS} k_{\rm Red}''}{k_{\rm Ox}''} \exp\left(\left[\left(\alpha_{\rm Ox}'' + \alpha_{\rm Red}''\right)\left(E''^{\star} - E^{\star}\right) + \alpha_{\rm Red}^{\rm RDS}\left(E^{\rm RDS\star} - E^{\star}\right)\right] \frac{F}{RT}\right)$$

$$k_{\rm Red}$$

$$\times \exp\left(-\underbrace{\left(\alpha_{\rm Ox}'' + \alpha_{\rm Red}'' + \alpha_{\rm Red}^{\rm RDS}\right)}_{\alpha_{\rm Red}} \frac{F(E - E^{\star})}{RT}\right)$$
(56)

which can be rewritten as Eq. (42) by introducing the overpotential η to give

$$\Gamma = C_{\rm R} k_{\rm Ox} \exp\left(\frac{\alpha_{\rm Ox} F \eta}{RT}\right) - C_{\rm O} k_{\rm Red} \exp\left(-\frac{\alpha_{\rm Red} F \eta}{RT}\right)$$
(57)

The above discussion demonstrates how is it possible to define global charge transfer coefficients, α_{Ox} and α_{Red} , and rate constants, k_{Ox} and k_{Red} , for the overall electrochemical reaction from those of the elementary reaction steps. This technique provides a powerful tool for the analysis of complex electrochemical systems, such as the multistep ethanol oxidation reaction (EOR) to be discussed below. As will be seen, the introduction of global kinetic parameters for certain reaction paths is particularly useful when trying to adjust the kinetic constants so as to fit the selectivities of the final products.

5.2. Coverage factors

The electrochemical reactions that take place in a fuel cell need not only to occur but also to have a sufficiently high reaction rate. To provide a favorable environment for the reactions, catalysts are always used in fuel cells. A catalyst is a compound that favors the chemical reaction, but it is not involved in it. The catalyst acts as substrate for the reaction, in that its surface has *places* where the fuel molecules *take place* to proceed with the reaction. In fuel cells, catalysts are pinned up to a porous matrix. The process where the reactive molecules *take place* at the catalyst sites is called adsorption. Once the molecules have been adsorbed, they no longer behave as free molecules; they remain attached to the catalyst site. The so-called adsorbates may undergo electrochemical reaction and later be desorbed as reaction products or, alternatively, be desorbed as unreacted free molecules.

The catalyst acts as an anchor to the adsorbed species. The concentration of these species has no physical meaning because they fill spaces where there are catalyst places; actually, they *cover* the catalyst surface. This behavior is equivalent to the adsorption described by [98] for the atomic deposition over glass surfaces. The amount of absorbed species is thus described by the *surface coverage factor*, Θ , which represents the fraction of the catalyst sites occupied by this species.

The coverage factor of a given species cannot be larger than unity (full coverage of the catalyst places). And if different species can be adsorbed into the same catalyst type, the sum of their coverage factors cannot exceed unity either

$$\sum_{k} \Theta_k \le 1 \tag{58}$$

From the definition of the coverage factors, the fraction of free catalyst sites is given by

$$\Theta_{\rm F} = 1 - \sum_{k} \Theta_k \tag{59}$$

Using these expressions, it is possible to evaluate the net adsorption rate of species k. The adsorption rate is proportional to the available catalyst sites, while the desorption rate is proportional to the fraction of occupied sites, so that

$$q_k = \mathfrak{K}_{ads} \Theta_{\mathrm{F}} - \mathfrak{K}_{des} \Theta_k \tag{60}$$

where the proportionality constants \Re_{ads} and \Re_{des} depend on the kind of absorption mechanism. Langmuir [98] applied this model to the adsorption of a monoatomic layer in a flat surface (e.g., glass); in electrochemical reactions, the absorption/desorption processes often involve reactions with charge transfer. In these cases, the adsorbed species is not the same as the free specie, but Eq. (60) can still be used with the required modifications.

As previously discussed, the reaction rates of the forward and backward reactions are proportional to the molar concentrations of reactants and products, respectively. When an adsorbed species is involved, its concentration is equal to the coverage factor of the adsorbate times the concentration C_c of the catalyst

$$C_k = \Theta_k C_c \tag{61}$$

where C_c remains unchanged during the reaction. As a result, for adsorption/desorption reactions, the catalyst concentration is usually included in the reaction constants, which are thus also strongly affected by the catalysts type. The use of coverage factors in kinetic models of catalytic reactions is widely used in fuel cell modeling [77, 99–104], and will be illustrated in the example presented below.

6. Modeling the ethanol electro-oxidation reaction

Ethanol offers an interesting alternative as a fuel for PEM fuel cells because it can be readily produced by fermentation of biomass, including agricultural raw materials, which makes it currently the major renewable biofuel. On top of that, its mass energy density is about 30% larger than that of methanol, and it is much less toxic [27, 64]. However, the electrooxidation of the complex ethanol molecule is much slower than that of methanol. The ethanol oxidation reaction (EOR) is known to proceed through a multistep reaction process that involves adsorbed species like acetyl (CH₃CO_{ads}) and carbon monoxide (CO_{ads}), leading to a variety of partial oxidation products such as acetaldehyde (CH₃CHO), acetic acid (CH₃COOH), carbon dioxide (CO₂), and methane (CH₄).

6.1. The ethanol oxidation reaction

According to the above discussion, one of the main difficulties encountered in the modeling of DEFCs is the accurate description of the EOR. Different reaction mechanisms have been proposed in the literature [38, 44, 45, 50, 106]. Due to the large amount of intermediate species, both free and adsorbed, and of potential elementary reactions, mathematical models exhibit different levels of complexity [77, 107, 108]. As a particular example, **Figure 2** shows a reaction mechanism for the EOR on binary Pt-based catalysts recently proposed by the authors [105], based on a previous model by Meyer et al. [77] which ignored Reactions I, II, and III. The kinetic model assumes that there are eleven elementary reactions, listed in **Table 2**, involving five adsorbed species, four of them attached to the Pt-sites (CH₃CHOH_{ads}, CH₃CO_{ads}, CO_{ads} and CH_{3ads}), and the fifth (OH_{ads}) to the secondary metal following the bifunctional catalyst assumption [53–55].

The full derivation of the model can be found elsewhere [105]. Here we will only consider Reactions I and III to illustrate the application of the electrochemical rate laws introduced in the previous sections. Reaction I represents the adsorption of ethanol to CH_3CHOH_{ads} . This is an oxidative adsorption reaction, with a net adsorption rate (in moles per unit volume of catalyst layer per unit time) given by

$$q_{\rm I} = \left(1 - \Theta_{\rm CH_3CHOH_{ads}} - \Theta_{\rm CH_3CO_{ads}} - \Theta_{\rm CO_{ads}} - \Theta_{\rm CH_{3ads}}\right) C_{\rm E, \, acl} k_{\rm If} \exp\left(\frac{\alpha_{\rm I}F}{RT}\eta_a\right) -\Theta_{\rm CH_3CHOH_{ads}} k_{\rm Ib} \exp\left(-\frac{(1 - \alpha_{\rm I})F}{RT}\eta_a\right)$$
(62)

The factor between brackets appearing in the forward reaction rate gives the fraction of available Pt-sites, reduced due to the presence of the adsorbates, which act as site-blocker. Note that this term does not account for the presence of adsorbed OH groups, because in the binary catalysts typically used in DEFCs they are preferably attached to the secondary metal. Reaction 3 represents the dissociative adsorption of water to yield adsorbed hydroxyl groups, a reaction that in binary Pt-based catalysts occurs on the secondary metal. The resulting water activation rate is given by

$$q_{3} = k_{3f} \left(1 - \Theta_{\text{OH}_{\text{ads}}} \right) \exp\left(\frac{\alpha_{3}F}{RT}\eta_{a}\right) - k_{3b}\Theta_{\text{OH}_{\text{ads}}} \exp\left(-\frac{(1 - \alpha_{3})F}{RT}\eta_{a}\right)$$
(63)

where now the forward reaction rate is proportional to the fraction of free sites existing on the secondary catalyst, only blocked by the adsorbed hydroxyl groups, while the inverse reaction is proportional to the coverage factor of this adsorbate. In these expressions, α_i are the global charge transfer coefficients and k_i the global reaction constants, which could be related to those of the elementary reaction steps involved in each global reaction as suggested in Eqs. (56) and (57). It



Figure 2. Reaction mechanism for the electron oxidation reaction (EOR) on binary Pt-based catalysts proposed in Ref. [105]. Pt-site adsorbed species are indicated by a dashed box; OH_{ads} is boxed using dotted lines to indicate that it is adsorbed at the secondary metal sites. Reactions 4, 6, and 7 use the adsorbed hydroxyl groups to proceed. The exact stoichiometries are shown in **Table 2**.

should be noted that the volume-specific molar reaction rates, q_r , can be readily obtained from the surface-specific molar reaction rates, Γ_r , discussed in Section 5 by multiplying the latter by the volume-specific catalyst surface area, $q_r = a\Gamma_r$.

Similar rate laws can be written for the remaining reaction steps, leading to a full kinetic model that involves 26 adjustable kinetic parameters: 9 transfer coefficients and 17 reaction constants (see **Table 2**). Using the quasi-steady-state approximation for the adsorbates, that is, assuming that the coverage factors θ_k do not change with time, yields a nonlinear system of equations that can be solved to evaluate the θ_k in terms of the local conditions at the anode catalyst layer. Complementing the kinetic model with appropriate descriptions for mass and charge transport gives rise to a suitable mathematical model for the anode of a DEFC. This model provides, in particular, polarization and power density curves, as well as the variation of the product selectivity and effective electron generation number as a function of the local current density. Using anode polarization and product selectivity data obtained from carefully designed experiments [75], the kinetic parameters can be fitted to reproduce the observed results, leading to a fully predictive model of the anode of a DEFC [105].

6.2. The oxygen reduction reaction

Although the oxygen reduction reaction (ORR) is much simpler than the EOR, it is also known to be a multistep reaction, involving the formation of a number of intermediate

Reaction	_	_	n_{α}
I. $CH_3CH_2OH \rightleftharpoons CH_3CHOH_{ads} + H^+ + e^-$	$k_{\mathrm{I}f}$	$lpha_{ m I}$	1
	$k_{\mathrm Ib}$	_	1
$II. \ CH_3 CHOH_{ads} \rightarrow CH_3 CO_{ads} + 2H^+ + 2e^-$	$k_{\mathrm{II}f}$	$lpha_{\mathrm{II}}$	2
	$k_{\mathrm{II}b}$	_	2
III. $CH_3CHOH_{ads} \rightleftharpoons CH_3CHO + H^+ + e^-$	k_{IIIf}	$lpha_{ m III}$	1
	$k_{\mathrm{III}b}$	_	1
1. $CH_3CH_2OH \rightleftharpoons CH_3CHO + 2H^+ + 2e^-$	k_{1f}	α_1	2
	k_{1b}	_	2
2. CH ₃ CHO \rightleftharpoons CH ₃ CO _{ads} + H ⁺ + e ⁻	k_{2f}	α_2	1
	k_{2b}	_	1
3. $H_2O \rightleftharpoons OH_{ads} + H^+ + e^-$	k_{3f}	α_3	1
	k_{3b}	_	1
4. $CH_3CO_{ads} + OH_{ads} \rightarrow CH_3COOH$	k_4	_	_
5. $CH_3CO_{ads} \rightarrow CO_{ads} + CH_{3ads}$	k_5	_	_
$6.\ CO_{ads} + OH_{ads} \rightarrow CO_2 + H^+ + e^-$	k_6	α_6	1
$7.~CH_{3ads}+2OH_{ads}\rightarrow CO_2+5H^++5e^-$	k_7	α_7	5
8. $CH_{3ads}+H^{+}+e^{-}\rightarrow CH_{4}$	k_8	$lpha_8$	1

Table 2. The 11-step reaction mechanism proposed in [105].

species. The complex nature of the ORR is reflected by the doubling of the Tafel slope at intermediate potentials, which is thought to occur due to a change in the rate determining step of the reaction [78]. This change can be qualitatively described using the double-trap kinetic model [109], which involves four elementary reaction steps: dissociative adsorption of O₂ to O_{ads}, reductive adsorption of O₂ to OH_{ads}, reductive transition of O_{ads} to OH_{ads}, and reductive desorption of OH_{ads} to H₂O. However, reproducing quantitatively the doubling of the Tafel slope requires a more detailed analysis, similar to the one discussed above for the EOR. Complementing the kinetic rate expressions for the four elementary steps with the quasi-steady-state approximation for the two adsorbates, O_{ads} and OH_{ads}, and using appropriate experimental data in order to fit a certain set of adjustable parameters using optimization algorithms, a fully predictive ORR kinetic model is finally obtained [110].

However, the kinetic model of the ORR proposed in Ref. [110] is anticipated to fail when applied to the cathode of a DEFC. In this case, the effect of the parasitic reactions induced by ethanol and acetaldehyde crossover is expected to affect the reaction kinetics in two ways: (1) by introducing mixed potentials required to draw the excess (i.e., parasitic) current density due to crossover and (2) by poisoning the catalyst by adsorbed intermediates of the parasitic reactions, which block a large amount of the available active catalyst sites [111]. Further research is still needed to clarify these complex electrochemical phenomena, which will surely benefit from the systematic approach laid out by the recent investigations discussed in this chapter.

7. Conclusions

In this chapter, the thermodynamic and electrochemical principles of PEM fuel cells have been presented and discussed. These principles have been applied to the study of a complex electrochemical system, the direct ethanol fuel cell, reviewing recent work on this problem and suggesting future research directions.

Nomenclature

Symbols

- a_k Activity of species k
- C_k Molar concentration of species k [mol m⁻³]
- *E* Electric potential [V]
- *F* Faraday constant F = 96480 C
- *h* Molar enthalpy $[J mol^{-1}]$
- H Enthalpy [J]
- g Molar Gibbs free energy [J mol⁻¹]
- *G* Gibbs free energy [J]

- *I* Electric current [A]
- *i* Electric current density [A m⁻²]
- *j* Electric current density per catalyst surface area [A m⁻²]
- *n* Number of electrons transferred
- N_k Molar flux of species $k \text{ [mol m}^{-2} \text{ s}^{-1} \text{]}$
- p_k Pressure of species k [Pa]
- Q Heat [W]
- *q* Volume-specific molar rate of reaction [mol $m^3 s^{-1}$]
- *R* Ideal-gas constant 8.3143 [J mol⁻¹ K⁻¹]
- *s* Molar entropy [J K⁻¹ mol⁻¹]
- S Entropy [J K⁻¹]
- T Temperature [K]
- V Electric voltage [V]
- *W_e* Electrical work [W]

Greek letters

α	Charge transfer coefficient
Г	Surface-specific molar rate of reaction [mol $m^2 \ s^{-1}$]
η	Overpotential $\eta = E - E^*$ [V]
Θ_k	Coverage factor of species <i>k</i>
μ_k	Chemical potential of species <i>k</i>
ρ	Density [kg m ³]
v_k	Stoichiometric coefficient species k [0.35 cm]
ac/agdl	Anode channel/gdl interface
cc/cgdl	Cathode channel/gdl interface
е	Electric
f	Formation
k	Species
Ox	Oxidation reaction

- r Reaction
- Red Reduction reaction

Superscripts

- 0 Reference state conditions
- ★ Equilibrium state conditions

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Chapter 8

PEM-Less Microbial Fuel Cells

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71479

Abstract

Microbial fuel cells (MFCs) are comparatively new technique of simultaneously generating electricity from bio-waste while degrading the organic waste. The use of microbes to generate electricity is an uninterrupted process in MFCs since the bacteria replicate and continue to produce power indefinitely as long as there is enough food source to nurture the bacteria. Besides, MFCs have the potential to produce hydrogen for fuel cells, desalinate sea water, and provide sustainable energy sources for remote areas. Factors like type of electrodes used in the cells, partitioning of cells, oxygen complement and configurations are important factors that affect the performance of MFCs. The fabrication of microbial fuel cells of different configurations and the relationship between the factors affecting the efficiency of single chambered (SC-MFCs) and double chambered (DC-MFCs) will be presented. The experimental data on observations made on the effects of these materials on the MFCs characteristics, electricity generation and wastewater treatment have also been included. The main aim of this study is to find out whether a nonconventional inexpensive clay could be used as an ion-exchange medium alternative to the conventional expensive PEM in the fabrication of MFCs. The results obtained on power generation, current density, open circuit voltage, etc., clearly show that PEM-less MFCs can be used as practical devices for sustainable energy generation.

Keywords: MFC (microbial fuel cell), current density, power density, SC-MFC (single chambered MFC), DC-MFC (double chambered MFC), OCV (open circuit voltage), COD (chemical oxygen demand)

1. Introduction

The production of electricity from waste and renewable biomass using microbes has gained much attention in the recent past [1]. There are three main parts in MFCs [1, 2]. (1) An anode chamber where fuel is oxidized by microorganisms and electron as well as protons are generated. (2) A cathode chamber where electrons and protons are consumed, producing water

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by combining with oxygen. (3) A cation exchange membrane (CEM) which transfers protons from anode chamber to meet with the electrons transferred through external electric circuit from anode chamber to cathode chamber [3–6]. The fuel for the cell is usually domestic or industrial wastewater which contains microorganisms and organic compounds. The reaction for the catabolic activity of the microbes may be summarized as follows:

Microbes

$$C_6 H_{12} O_6 + 6 H_2 O \rightarrow 6 CO_2 + 24 e^- + 24 H^+$$
 (1)

Reduction half reaction:

$$24 \,\mathrm{H}^{+} + 24 \,\mathrm{e}^{-} + 6\mathrm{O}_{2} \rightarrow 12 \,\mathrm{H}_{2}\mathrm{O} \tag{2}$$

Overall oxidation/reduction reaction:

$$C_6 H_{12} O_6 + 6 O_2 \rightarrow 6 C O_2 + 6 H_2 O$$
 (3)

Thus there are two halves of the microbial fuel cell: the aerobic chamber having positively charged electrode with oxygen in abundant, and the anaerobic chamber having negatively charged electrodes. The semi-permeable membrane separate the two chambers allows only hydrogen ions (H^+) and keeps oxygen out of the anaerobic chamber [7].

The main challenges in constructing microbial fuel cells (MFCs) are the identification of materials and architectures that maximize power generation and efficiency, also minimizing the cost of fabrication. Various researchers have tried to use different materials and various architectures for the electrode and membranes. In order to get better performance, a broad range of techniques have also been used [8]; which include "doping" of the anode, varying the electrodes and the use of various types of cathode substrate.

2. Advantages of PEM-less microbial fuel cells over PEM architecture

As we know, the PEM key function is to keep the liquid contents of each chamber separate while still allowing protons to pass between chambers to be utilized in the cathode with the produced electrons. Although proton exchange membranes are often used, Logan [10] has reported that Cation exchange membranes (CEM) work in a similar way but more cost effective than PEM, and sometimes structurally stronger. Both PEM and CEM support in reducing oxygen diffusion in the anode chamber of the cell. However, after using PEM for some of MFCs we have realized that PEM is quite expensive and very delicate to work with. It cannot be reused and also difficult to adapt to desired shapes.

We therefore started searching for other alternatives to replace the most costly and delicate PEM. In the process of this search we came across a local clay mixed with kaolin and bentonite and subsequently fired appropriately achieved the desired results of producing open circuit voltage (OCV) of up to 1.5 volts. This clay system is quite unique, robust, potable, cheap, easy

to acquire locally and can be shaped as desired. It can also be molded to large cells. Even though some cheaper alternatives have been used by many researchers, the use of rigid cation exchange materials such as the clay used in the fabrication of some of MFCs in this research have not been given much attention that is most cost effective and easy to give any desired shape.

3. Section A

This section includes the fabrication, operation and results of three different types of Microbial Fuel Cells (MFCs).

3.1. Single-chambered (SC-MFC) PEM microbial fuel cell

In order to find the effect of chemical oxygen demand (COD) on the open circuit voltage (OCV), Power production and coulombic efficiency single–chambered Microbial Fuel Cells (MFCs) have been fabricated. Three different MFCs of similar design have been fabricated using carbon paper doped with platinum as cathode and graphite as anode separated by Proton Exchange Membrane (PEM) and the effect of COD level on Open Circuit Voltage (OCV), power production and Coulombic efficiency have been studied.

3.2. Double-chambered (DC-MFC) PEM microbial fuel cell

A variety of substrates have been explored relative to the anode substrate which takes the form of any wastewater with some amount of COD. Several modification methods have been developed to improve power generation at the anode level, but the cathode system and configuration have also been a challenge in most researches. The choice of cathode substrate is one of the greatest challenges in fabricating MFCs. A DC-MFC with H_2O_2 cathode has been fabricated and compared with SC-MFC.

3.3. Membrane less microbial fuel cell

In this case, a number of clay mixtures have been used as ion-exchange partition replacing Proton Exchange Membrane (PEM) in designing the MFC and observations have been made on the effects of these materials on the MFCs characteristics; electricity generation and wastewater treatment. The performances of the cells have been then compared in terms of wastewater treatment, power generation and coulombic efficiency.

3.4. Methodology

3.4.1. Single-chambered (SC-MFC) PEM microbial fuel cell

3.4.1.1. Preparation of PEM

Nafion 117 of area 12.6 cm² was taken through the normal cleaning process [distilled water \rightarrow 3% hydrogen peroxide \rightarrow dilute sulfuric acid \rightarrow distilled water].

3.4.1.2. Fabrication of MFCs

Necessary steps for the fabrication of MFCs:

- 2 Perspex slabs were cut, shaped and dilled for each cell.
- Carbon paper doped with platinum was cut and shaped.
- Copper conductor was cut and shaped.
- Preparation of Graphite electrode.
- A plastic container of 2 liters capacity served as the anodic chamber. The anode chamber contains the wastewater and the graphite electrode. The carbon paper tightens onto the PEM served as the cathode.

3.4.1.3. Types of wastewater for MFCs

Following three types of wastewater of different COD and pH from GGBL (Kumasi, Ghana) were used as Fuel for these cells. The characteristics of the wastewater are listed in **Table 1**:

Wastewater	COD(mg/L)	рН
Influent	3790.0	11.18
Anaerobic	748.0	6.80
Balance	4330.0	6.01

Table 1. Type of wastewater used.

3.4.1.4. Operation

The cells were kept at 25°C (±0.5°C). The anode was immersed in the wastewater such that the copper conductor did not touch the water in order to avoid corrosion. The anode chamber was sealed to maintain anaerobic system throughout the experiment. OCV readings were taken for 35 days with the CR10X datalogger which stores the differential voltage every 1 min. A multimeter (Peak Tech 2010DMM) was used in the reading of the load voltage and the current through a resistance box ranging from 0 to 10,000 Ω .

3.4.1.5. Results

The experiment was operational for 35 days. A constant increment of OCV was observed from day one of the operation of MFCs until it got to their peak values of OCV. These values were maintained for about 10 days. Also their pH and COD values at the end experiment are given in **Tables 2** and **3**. The experiments were performed with the wastewater as collected in order to check the viability of the cells without adding inoculants and other chemicals (**Figure 1**).

Wastewater	Starting COD	Ending COD	Starting pH	Ending pH
Influent	3790.0	133	11.18	8.3
Anaerobic	748.0	59	6.8	8.9
Balance	4330.0	267	6.01	8.6

Table 2. pH values obtained.

	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	ΔCOD	
pН	5.9	6.1	6.1	6.2	6.4	6.6	6.7	6.9		
Temp. °C	26	28	26	27	27	28	28	27		
COD (mg/L)	7700	_	-	_	_	_	_	1650	6050	78.6%

Table 3. Change in pH of the wastewater with activities of microbes through the days.

3.4.2. Double-chambered (DC-MFC) PEM microbial fuel cell

3.4.2.1. Architecture

We fabricated the DC-MFC with the porous pot (5 mm thick) containing the anodic substrate immersed into the copper can containing the H_2O_2 catholyte substrate (**Figure 2**), both having working volume of 300 mL in each compartment. The anode electrode is a zinc rod having an outer diameter of 1.2 cm and a geometric surface area of 38.8 cm² and the cathode is the copper can housing the porous pot (this is similar to a Daniel cell). The pot acts as an ion exchange partition. We connected the anode or the zinc rod to the cathode compartment through a copper wire and external resistor of 1000 Ω . The assumption is that the porous pot separation permit only cation transport to the oxidation substrate, as done earlier [9]. The initial pHs in



Figure 1. Power density curve for three different wastewaters from same source, but three different treatment methods.



Figure 2. Simplified schematic diagram of double-chamber MFC with porous pot as anode chamber inserted into copper can as cathode chamber. Porous pot is cationic exchange membrane.

the anode and cathode chambers were 5.9 and 6.8 respectively. The setup was then connected to a Datalogger (Campbell Scientific Datalogger CR10X) to store potential difference across the load at 1 min interval. The cell was place in the laboratory condition of ambient temperature between 26 and 29°C and at 1 atm.

3.4.2.2. Results

Table 4 was experimental calculations in terms of current densities and power densities for comparing the normalization. According to Ref. [10] the above parameters sufficiently describe how efficiently a power is generated by a given system architecture. It can be assumed that protons generated from the bacteria metabolism are conducted through the porous pot to balance the charge in the cathode compartment. In this regard, the operation surface area of the pot may have favor anion-cation coupling and thus accounts for the high OCV observed.

3.4.3. Membrane less microbial fuel cell

3.4.3.1. Materials and methodology

Kaolin and Zeolite were used for the ion exchange media in the earlier experiments which were in the process of publication. In this project we designed two pots or chambers which were custom-made cylinders using Mfensi clay. The capacities of the pots are 1.7 and

	Surface area of rod	Inner surface area of pot	Volume of anode substrate	
	38.8 cm ²	219.44 cm ²	300 mL	
Max. current density	311 mA/m ²	55 mA/m ²	4020 mA/m ³	
Max. power density	375 mW/m ²	6628 mW/m ²	4848 mW/m ³	

Table 4. Densities as normalized by the measured parameters.

1 L. Mfensi clay is commonly used in Ghana for drinking water pots. Its porosity ranging from 5 to 25% satisfies a process that cools the content by seeping and evaporation system. That is, part of the content water soaks the pot to the outer part; the outer part then dries gradually extracting the heat from the inner content. The result is that the inner content becomes cooler than the surrounding depending on the rate of evaporation/drying of the outer part. Mfensi clay is also known to have negative charges. The thickness is 1.0 cm and the apparent porosity as measured is 14.3%. We feel these parameters passed for ion exchange to take place. The cells were fed with 1.40 and 0.80 L wastewater respectively from GGBL (Kumasi, Ghana), with initial COD of 4385 mg/L in the anode pots and 40% H_2O_2 surrounding the pots.

3.4.3.2. Results

There are two aspects this experiment sort to compare; 1) to check whether this type of clay can exchange ions and serves as anodic pot; 2) to verify if the size of pot (or operation surface area) affects the amount of power produced.

3.4.3.3. Effect of pot size

As observed through the polarization measurements, the smaller pot performed better as shown in **Figures 3** and **4**, (Pot 1-1.7 L, Pot 2-1.0 L).

Pot 2 yielded a higher potential difference than the pot 1(which contained more substrate in terms of volume). Same applied to the power densities where the peak occurred at 6429 and 4750 mW/m² respectively.

As shown in **Figure 5** the polarization curves depict the activation region and the ohmic region (actual performance region), but the concentration region not that clear.



Figure 3. Variation of potential drop with external load.



Figure 4. Variation of power density with current density as normalized with the anode graphite electrode (same sizes in both cells).

3.4.4. Determination of internal resistance of an MFC

In **Figure 5** the peaks occurred at 0.828 mW/m² and 1.53 mW/m² for pot 1 and 2 respectively. These values correspond to 330 Ω internal resistance; same for both cells having similar substrate and similar graphite electrodes. The higher OCV value confirms that an MFC that is connected with an external resistance comparable to its internal resistance will produce maximum power [9, 11].



Figure 5. The plotted voltage drop versus current density and power density versus current density curves; normalized with pot operating surface area.

3.4.4.1. Zeolite cells

20% Zeolite was added to Koalin (80%) and molded to a slab of $8 \times 8 \times 1$ cm. This was then fired at the temperature of 3000°C.

3.4.4.2. Results

All the cells were connected to a Datalogger (CR10X) and were observed for 30 days. The open circuit voltage (OCV) for all the cells were recorded every minute and stored for few minutes. Data were then collected via computer interface. **Table 5** shows sample data as collected in excel format.

			Time	Pot 1	Pot 2	Pot-Cu	Pot-Tin	Zeolite
ID	Yr	ProgReg	24 h	OCV/mV	OCV/mV	OCV/mV	OCV/mV	OCV/mV
101	2014	73	1004	-252.7	-123.2	1337.0	980.0	-17.0
101	2014	73	1005	-220.7	-123.2	1337.0	979.0	-12.4
101	2014	73	1006	-179.3	-122.5	1336.0	980.0	-14.4
101	2014	73	1007	-195.3	-122.5	1335.0	1006.0	-19.0
101	2014	73	1008	-202.0	-123.2	1334.0	1024.0	-23.7
101	2014	73	1009	-204.6	-122.5	1335.0	1023.0	-29.0
101	2014	73	1010	-207.3	-123.2	1335.0	1030.0	-32.4
101	2014	73	1011	-210.7	-123.9	1333.0	1029.0	-29.0
101	2014	73	1012	-206.6	-123.9	1331.0	1028.0	-29.0
101	2014	73	1013	-205.3	-118.5	1330.0	1027.0	-31.1
101	2014	73	1014	-206.6	-119.2	1328.0	1025.0	-33.1
101	2014	73	1015	-205.3	-118.5	1326.0	1024.0	-35.1
101	2014	73	1016	-201.3	-117.8	1324.0	1024.0	-35.1
101	2014	73	1017	-196.6	-117.2	1323.0	1025.0	-27.4
101	2014	73	1018	-194.6	-117.2	1322.0	1024.0	-26.4
101	2014	73	1019	-197.3	-116.5	1321.0	1023.0	-26.4
101	2014	73	1020	-193.3	-115.8	1320.0	1023.0	-27.7
101	2014	73	1021	-194.0	-115.2	1320.0	1023.0	-28.7
101	2014	73	1022	-196.0	-115.2	1319.0	1022.0	-29.7
101	2014	73	1023	-194.6	-113.2	1319.0	1023.0	-30.4

Table 5. Sample data as stored by the Datalogger.

Both cells were fed with same wastewater of COD = 4385 mg/L and same diluted H_2O_2 . It was found that the OCVs generated by the Cu-Can/porous-pot cell was higher as compared with the zeolite cell, i.e., 1337 and -17 mV respectively. We suspected the zeolite by its property absorbs the ions and release when it can no longer contain it and thus accounts for the negative OCV from the start. Load of 100 Ω was then connected across the terminals of the zeolite cell and 1000 Ω was connected across the pot cell. The recorded voltages now become the potential drop for both DC-MFCs. The readings per minutes were averaged to hours of reading so as to reduce volume of data that can be handled. The result is plotted in **Figure 6**.

It was observed that at the stationary phase microbial growth rate is balanced by microbial death rate as a result of paucity of food and nutrients, as well as the presence of waste metabolic products. Consequently, a stationary population is achieved, but too early or may be due to the flow of current across the bridge. Death phase stage sees to a greater increase in death rate, as compared to growth rate, resulting in a sharp decrease in the number of microbes over the days.

3.4.5. Polarizations

For similar characterization, each cell was subjected to variable loads ranging from 100 to 15,000 Ω and the voltage drop values recorded as given in **Table 6**. This is required to examine the extent to which the cells could be used to power the devices. Both cells were normalized by their operational surface areas; for porous pot the total surface area containing the anodic substrate was 219.4 cm² and that for zeolite slab was 16.0 cm² (**Figure 7**).



Figure 6. Zeolite and porous pot MFCs: OCV and Pd time variation curves.

	Pot3-Cu: Op-Sf Area = 219.4 cm ²			Pot3-Cu: Op-Sf Area = 219.4 cm ² Zeolite: Op-Sf Area = 16.0 cm ²				
Resistance	Current	Cur-Den	Pd	Pow-Den	Current	Cur-Den	Pd	Pow-Den
Ohms	mA	mA/m ²	mV	mW/m ²	mA	mA/m ²	mV	W/m ²
100	1.610	73.38	161	11.81	0.230	143.75	23	3.31
200	1.425	64.95	285	18.51	0.205	128.13	41	5.25
330	1.155	52.62	381	20.05	0.191	119.32	63	7.52
400	1.060	48.31	424	20.48	0.180	112.50	72	8.10
500	0.934	42.57	467	19.88	0.168	105.00	84	8.82
600	0.842	38.36	505	19.37	0.155	96.88	93	9.01
700	0.774	35.29	542	19.13	0.147	91.96	103	9.47
800	0.710	32.36	568	18.38	0.139	86.72	111	9.63
900	0.660	30.08	594	17.87	0.131	81.94	118	9.67
1000	0.614	27.99	614	17.18	0.124	77.50	124	9.61
2000	0.356	16.23	712	11.55	0.082	51.25	164	8.41
3200	0.235	10.73	753	8.08	0.058	36.33	186	6.76
3900	0.198	9.01	771	6.95	0.050	31.09	194	6.03
4800	0.164	7.47	787	5.88	0.042	26.17	201	5.26
7000	0.115	5.24	805	4.22	0.030	18.84	211	3.98
7900	0.103	4.69	813	3.81	0.027	17.01	215	3.66
9000	0.091	4.15	820	3.41	0.024	15.14	218	3.30
10,000	0.083	3.76	826	3.11	0.022	13.75	220	3.03
10,900	0.076	3.47	831	2.89	0.020	12.79	223	2.85
12,000	0.070	3.17	835	2.65	0.019	11.72	225	2.64
13,000	0.065	2.95	840	2.47	0.017	10.87	226	2.46
14,000	0.060	2.74	843	2.31	0.016	10.18	228	2.32
15,000	0.056	2.57	846	2.17	0.015	9.54	229	2.19

Table 6. Cells characterization data.

It has been found that the *Balance wastewater* produced power most significantly than the other two. It has been observed that the current generation of the cells increased for a higher COD and lower pH. The removal of COD of observed to be highest for the cell which produces higher current. The COD for Balance dropped from 4386 to 267 mg/L for the 36 days of running (**Tables 7** and **8**). Summary of other Generated Parameters:



Figure 7. Polarization power curves for kaolin/bentonite porous pot and clay/zeolite pot.

				~ - •	
Substrate	Max. OCV (mV)	Max Current (mA)	Power Density (mW/cm²)	Current Density (mA/cm ²)	Internal Resistance (Ω)
Balance	782	0.330	246	8.04	3 k
Influent	345	0.021	37.9	0.34	8 k
Anaerobic	66	0.003	10.7	0.028	10 k

Table 7. Observed results in relation with types of wastewater.

Parameters	Pot 1	Pot 2
Initial COD	4385 mg/L	4385 mg/L
Final COD	571 mg/L	522 mg/L
% COD removal	86.98	88.10
Apparent porosity	14.3%	14.3%
OCV (mA)	300	250
R _{int} (Ω)	330	330
Imax (mA/m ²)	11.87	18.62
Pmax (mW/m ²)	4750	6429

Table 8. Measured MFCs characteristics of the two pots.

The factors that affect the cathode and anode potentials were investigated. Compared with other membrane types, cation exchange partition, clay anodic container and aluminum cathode container assembly yielded such performance. This system might be useful in applications of MFC type at a very low cost. Mfensi clay is said to have negative charges which might be responsible for negative OCV. This approach represents a potential solution for simultaneous electricity production and removal of COD and thus offers a technological tool both for sustainable energy generation and for economic viability.

Both, double chamber membrane-less-microbial-fuel-cells (MLMFCs) were found to give COD reduction greater than 88%, with maximum power production 20.48 mW/m² as normalized with the anodic substrate container surface area. It was expected to generate enough power to light a LED through only one cell so as to be able to power low voltage circuits or devices. However, efforts are being made to improve the structures of Zeolite DC-MFC for better performance.

4. Section B

4.1. Effect of COD and H₂O₂ concentration on double chamber MFC (DC-MFC)

In the present section an attempt has been made to investigate the effect of hydrogen peroxide (H_2O_2) and COD on the performance of DC-MFCs. It has been found that 80% H_2O_2 or a mixture of 1:4 exhibited higher power generation while 20–60% concentration have no effect. This shows that H_2O_2 can be used as oxidizing agent between the concentrations of 70–90%. The values of power densities of the order 24.56 W/m² for Balance substrate (7562 mg/L COD) for 80% H_2O_2 confirms the effect of CODs on the performance of DC-MFC.

The results of this study indicate that the efficiency in DC-MFCs can effectively be increased by varying the concentration of H_2O_2 as cathodic substance. Specifically, the investigation shows that this paper supports the earlier result by [9] of the use of hydrogen peroxide as cathode substrate. Upon investigation of different catholyte concentrations, dilution of H_2O_2 at a certain level must be necessary to achieve high efficiency and power generation.

4.2. Fabrication of DC-MFC

The MFC chambers were fabricated using plastic containers of two equal volume of 1.8 L each. These anode and cathode chambers were separated by proton exchange membrane (PEM—Nafion 117) [9] as shown in **Figure 8**.

Two different kinds of waste water obtained from the Guinness Ghana Brewery Limited (GGBL—Kumasi) were used in the anode chambers, one with COD—1273 mg/L and the other with COD—7562 mg/L. the cathode chambers were filled with H_2O_2 mixed liquid. Plain graphite rods of surface area 86.7 cm² were used as cathode and anode; as the surface area of anode does not affect power production [10]. The voltage and current were measured with a Digital multimeter (Peak Tech® 2010 DMM).open circuit voltage E was obtained and stored using a data acquisition system (Campbell Scientific Ltd. Datalogger—CR10X).



Figure 8. Double chamber PEM setup.

In systems that contain a membrane separating the two electrode chambers, it is possible to normalize power based on the membrane projected surface area;

Current Density normalized by PEM area = $\frac{E}{A_{PEM}}$

Power density as normalized with PEM area = $\frac{E^2}{R \times A_{env}}$

Power density as normalized with volume of anode chamber = $\frac{E^2}{R \times V}$

Where *E* is load voltage, *R* is load resistance, A_{PEM} is active PEM area and V_{an} is volume of anode chamber.

4.3. Results

The open circuit voltage as against concentration of H_2O_2 at the anode chamber is shown in **Figure 9**. Whereas the open circuit voltage in relation with time has been shown in **Figure 10**. Also the variation of power with current density for various concentrations of H_2O_2 is shown in **Figure 12**.

The drops and the ramps were observed to occur in the nights where the temperature dropped from 28°C to between 27°C and 25°C. This temperature effect may not be for the peroxide, but for the biological substrate.

Polarization curves were obtained by varying external resistances from 100 to 10,000 Ω (Figure 11).

As may be seen in the above **Figure 9**, the 80% concentration at the cathode exhibited a significantly high polarization than expected. It should also be observed that the addition of 20% water showed about 80% increase in voltage over the pure peroxide (100%). The fact that the other concentrations in the cathode chamber performed so poorly in comparison to the 80% concentration is evidence that potential difference may be dependent on the number of ions exchanged between anode and cathode chambers. Non-diluted hydrogen
peroxide (100%) in the experiment washed the surface of the cathode clean. This may be due to the high reactivity of H_2O_2 . This also shows that H_2O_2 is an oxidation agent between 75–90% concentration.



Figure 9. OCV versus hydrogen peroxide concentration.



Figure 10. Performance comparison in relation to open circuit voltages plotted as a function of time for varying concentration.



Figure 11. Performance comparison in relation to hydrogen peroxide (6% w/v with stabilizer) concentration.



Figure 12. Variation of power with current density for various concentrations of H2O2

Similar characteristics were observed for power versus current density relationship. Maximum power density as normalized with PEM area is $24,564 \text{ mW/m}^2$, which is equivalent to 17.2 mW/L as normalized by substrate volume.

4.4. Effect of CODs and H₂O₂ concentration on power density

As H_2O_2 concentration is crucial in this experiment as the CODs of the substrates, though the percentage dilution has significant impact on the performance of the two systems. Moderately, the earlier result indicated that the power density actually depends on the COD of the anodic substrate. As shown in **Figure 12** the OCVs were not far apart and thus compare favorably, but this could not be said about their power densities. From 20 h on more ions may have been released as bio-activity increases. The peaks of their power densities were far apart and would have been dependent on the CODs of the two systems as exhibited in **Figure 13**.

The OCV may be similar, but as current strictly depends on the number of useful electric charges present in the system are responsible of bio-electrochemical reaction; the reason would be probable.



Figure 13. Comparative state of the two similar MFCs.

5. Section C

5.1. Multi-chamber microbial fuel cells (MFCs) with clay as ion exchange partition

This section includes the performance of multi-chambered MFCs. Performance of each micro cell in the system was observed to be significant in terms of their yields as could be in standalone single cell. Each adjacent cell tends to supplement the other so that series configuration is not possible in the same multi-system. In parallel configuration, all anode terminals connected as one and all cathode terminals connected together, resulting in higher current as shown in **Figure 14**. This higher power can therefore perform for longer period when connected to a load. Few experimental uses attested to such performances.

5.1.1. Materials and methodology

The clay material was obtained from Mfensi, a town near Kumasi—Ghana. As in **Table 9** was the constituent of the clay as used in the earth wares sold in the market.

The varying chambers were molded and fired at the Department of Ceramics, KNUST. The chambers were in 2, 4, 6, and 9 sets. As in **Figure 14** a chamber is $3.8 \times 3.8 \times 9$ cm (approx. 130 cm³ in volume) and 0.6 cm thick. Porosity was measured to be 14%. The outer part of each set of pot was coated to prevent the liquid seeping out.

5.1.2. Wastewater used in MFCs

Wastewater from the Guinness Ghana Brewery Limited (GGBL, Kumasi) has being our favorite for anode substrate, primarily because of its known source and safety measures attached to its disposal. Besides, it is suitable for electricity generation in MFCs due to the food-derived nature of the organic matter. Good results were obtained in earlier studies with this wastewa-

Element	%	Element	%
Na ₂ O	6.15	K ₂ O	1.66
MgO	1.28	CaO	0.54
Al ₂ O ₃	13.82	TiO ₂	0.04
SiO ₂	65.26	MnO	0.07
P ₂ O ₅	0.23	FeO ₃	0.83
SO ₃	0.10	LOI	10.00
Cl	0.02	Total	100

Table 9. Composition of Mfensi clay from geological survey department (Ghana) X-ray fluorescence laboratory results.



Figure 14. Comparative power densities versus current densities of the two MFCs.

ter with varying CODs [9, 12, 13]. Each cell was fed with wastewater of COD equals to 6340 gm/L and 80% concentration of H_2O_2 alternatively. 80% concentrated H_2O_2 was done earlier to ascertain the veracity of suitable dilution for higher performance [13].

5.1.3. Choice of electrodes

Most of the publications on suitable electrodes [10, 14] have laid emphasis on carbon and its variance, but these experiments continually use zinc rods and copper plates for good results. In the present work, zinc plates of surface area 24 cm² each were inserted in the wastewater and copper rod of same surface area placed in the H_2O_2 respectively making each adjacent pot forming a cell (**Figure 15**).



Figure 15. Designed and fabricated Mfensi clay chambers; anode/cathode chamber applied to all cells.

5.1.4. Measurements

Each cell was connected to Datalogger (Campbell Sci CR10X), open circuit voltage (OCV) and potential drop across 1 K load were recorded per minute for 35 days. Ambient temperature varied over the period between 24°C and 25°C.

5.2. Parallel connection

4, 6 and 9 combinations were connected in parallel (**Figure 16**) and to the Datalogger. That is, zinc plates in each anode pot were connected together and copper plates were also connected together as one terminal.

5.3. Series connection

Series connection in the multi system appeared isolated and as in **Figure 16b** each cell was connected to a load and thus tend worked independently. Such single cell measurement was plotted in **Figures 17** and **18**.

5.3.1. Results

There were two aspects of these experiments sort to compare; 1) measure the performance of single cell in the multi MFC system; 2) performance of total multi cell as a single cell. Although all the cells were co-joint with each other as the partition between them act as ion-exchange medium. Each adjacent pot combination in the alternative forms a cell. The cells were also taken through the polarization measurements using resistors of 100–15,000 Ω . Voltage drops were recorded through PeakTech 2010DMM Multimeter.

First portion of **Figure 17** (A) on the curves presented OCVs recorded by the Datalogger without load. When the loads were connected there were sharp drops in line with ohm's law of electric circuit calculation [15]. Some of the cells continually dip with hours of operation while others maintain constant voltages (B). 9 and 6 chambered cells configured into parallel cells each respectively, were the top 2 of higher operation voltages, meaning these can be used for longer operation period.



Figure 16. (a) Parallel cell configuration (9 chambered cell); (b): Series cell configuration.



OCV/Pd measured per hour

Figure 17. Voltage recorded for the first 5 days.



Figure 18. Voltage drop across varying resistors against current density.

Current density was calculated based on the surface area of the anode electrode ($I_D = Pd/RA_{an}$), and Power density was then calculated using $P = I_D E$ (where I_D is the current density and E the voltage drop).

It was observed that OCV did not follow a pattern (**Figure 18**). The fourth cell from the 9 chambered cell had the highest OCV of 1414 mV which was probably due to the fact that this particular cell had two anodes and one cathode.

From both polarization and power curves for 4/2Cell show the highest yield, compared to 4/1Cell. Although the OCV for 9/4Cell was highest it was not consistent with ohmic portion of characteristic curves of **Figures 18** and **19**. These curves show how well the cells maintain voltages as a function of the current produced. Resistive effects in fuel cells reduce the



Figure 19. Histogram resulting from Table 10.



Figure 20. Power density verse current density comparing individual cell in multi MFC system.

efficiency of the cell by dispelling power in the partitions and substrate resistances. This effect is also observed due to the insulation of the anode electrode. The voltage generated here is far more complicated to understand or predict, and as usual the inference can be deduced from the total result. Almost all the individual cells have their internal resistance $R_{int} = 330 \ \Omega$, and [10, 15, 16] we see that the maximum power resulted at a point where $R_{int} = R_{ext'}$ then $P_{max} = E_{emt}/4R_{int}$ [17].

The parameter that must have caused the variation in nature of the histogram with regards to 4/2Cell might be due to the partition characteristic between anode/cathode of the cell, with all other factors been the same; i.e. substrates, anode, cathode and ambient conditions.

The maximum power as shown in **Figure 21** was 41.25 mW/cm² for 9 chambered cells. The activation losses and ohmic portions of the polarization curves were more pronounced in both **Figures 17** and **20**. The concentration polarization drops were overcome within the range of load/resistors (100–15,000 Ω) used for the measurements. Concentration losses are most important loss parameters to be overcome for optimum design of the MFC architecture. These losses were said to arise from resistance of ion conduction due to the substrates and the membrane or partition between anode and cathode, the flow of electrons through the electrodes to the contact load points [10]. Our choice of clay partition could have accounted for reduction in concentration losses and also ensuring good contacts in the circuit, and the source of anode substrate that enhanced solution conductivity.



Figure 21. Polarization and power density curves for parallel combination multi MFC system.

	OCV/ mV	Resistance/Ω	Pd: E/ mV	Current/mA	Current Density/mA/ cm ²	Power Density/mW/ cm ²
9 Chambered	1260	1000	633	0.633	0.0264	16.6954
cells	1347	1000	654	0.654	0.0273	17.8215
	1302	1000	771	0.771	0.0321	24.7684
	1414	1000	868	0.868	0.0362	31.3927
6 Chambered Cell	1331	1000	861	0.861	0.0359	30.8884
	1179	1000	819	0.819	0.0341	27.9484
	1215	1000	761	0.761	0.0317	24.1300
4 Chambered Cell	1223	1000	637	0.637	0.0265	16.9070
	1380	1000	894	0.894	0.0373	33.3015
2 Chambered (one cell)	1228	1000	486	0.486	0.0203	9.8415
9 Parallel (as one cell)	1118	1000	903	0.903	0.0125	11.3251
6 Parallel (as one cell)	1380	1000	994	0.994	0.0138	13.7227
4 Parallel (as one cell)	1223	1000	835	0.835	0.0174	14.5255

Table 10. Comparison of individual cells in the multi MFC system.

6. Section D

6.1. Mfensi clay as ion-exchange-partition in double chamber microbial fuel cells (DC-MFCs)

This section includes the development of a low cost double chambered microbial fuel cells (DC-MFCs) for power generation as well as for wastewater treatment simultaneously. These fuel cells were fabricated using a locally available Mfensi clay as an ion-exchange-partition. These cells also used pot-electrode combination that is: (1) pot-graphite/graphite combination and (2) pot-zinc/copper combination. Both MFCs were connected to a Campbell Datalogger CR10X to measure and store initial open circuit voltages (OCV) as well as potential drops across 1000 Ω resistor for 30 days. Experimental results showed maximum power densities of 118 and 79 mW/m² for the Pot-zinc/copper pair electrode and Pot-graphite/graphite pair electrode respectively.

6.2. Materials and architecture of DC-MFCs

The materials used for this work includes Mfensi clay from the Atwima Nwabiagya District in Ashanti Region of Ghana, The clay is known to have negative charges. Two cylindrical chambers (**Figure 22**) of capacities of 1.7 and 1 L and thickness of 1 cm were fabricated



Figure 22. Pot 1 and 2.

from the clay and fired at a temperature of 1050°C in the Department of Ceramics – College of Arts and Social Sciences, KNUST. The apparent porosity of the cylinders as measured was 14.3%. **Figure 23** shows an MFC assembly consisting of an improvised cathode which was an Aluminum cooking utensil housing the cylindrical chamber and also containing 40% diluted hydrogen peroxide (H_2O_2). The ion-exchange partition houses the anodic substrate. The two cells under investigation were fed with 1.40 and 0.80 L wastewater respectively from Guinness Ghana Breweries Ltd. (GGBL- Kumasi, Ghana), which had an initial COD of 4385 mg/L.

6.3. Results and discussion

Figure 24 shows the variation in potential drop (OCV) with time for zinc/copper and graphite/graphite electrode pairs.

Pot-graphite/graphite pair yielded contrary results although same substrates were used. The results obtained for this electrode pair (the lower curve of the plot) shows a gradual rise of the initial OCV of -300 mV to almost 0 V after which a gradual fall was observed over the time period. The negative result of pot-graphite/graphite pair was thought to be the effect of negatively charged of Mfensi clay that tend to neutralize the incoming positively charged ions from the anode.

The polarization curves as well as plots of power densities versus current densities for cells loaded with incremental load of 100–1500 Ω have been depicted in **Figures 25–27**. **Figure 25** shows that pot-zinc/copper pair produced higher values in relation to the applied external



Figure 23. MFC assembly.



Figure 24. Variation in potential drop (OCV) with time.



Figure 25. Variation of potential drop with external load relating to pot-graphite/graphite pair and pot-zinc/copper pair.

loads ranging from 0 to 15,000 Ω and **Figure 26** shows the variation of potential drop with current density relating to pot-graphite/graphite pair and pot-zinc/copper pair.

6.4. Determination of internal resistance of the cells

The internal resistance is one of the major characteristics of a MFC, in accordance with the theorem of maximum power delivered by an electromotive force. An MFC connected with an external resistance equals to its internal resistance will give a maximum power output [10, 11]. From **Figure 27** the peaks occurred at 118 and 79 mW/m² for zinc/copper and graphite/graphite systems respectively. The alternative to finding internal resistance was calculated from the slope of **Figure 26**. The peak value corresponds to 200 Ω internal



Figure 26. Variation of potential drop with current density relating to pot-graphite/graphite pair and pot-zinc/copper pair.



Figure 27. Variation of power density versus current density as normalized with the anode electrodes relating to potgraphite/graphite pair and pot-zinc/copper pair.

resistance for zinc/copper system and 556 Ω graphite/graphite. The internal resistance however seems to be high for graphite/graphite system, as can be anticipated using the polarization curve method (**Table 11**).

The unconventional inexpensive Mfensi clay ion-exchange medium used for the study seems to be a viable alternative to the conventional expensive PEM. It was observed that a porosity of 14.3% may facilitate the flow of liquid in both directions though. We believe it holds the future for improvements in MFC performance. This approach represents a potential solution for simultaneous electricity production and removal of COD and thus offers a technological tool for sustainable energy generation.

Pot-Zn/Cu	Pot-C/C
4385 mg/L	4385 mg/L
571 mg/L	522 mg/L
86.98	88.10
14.3%	14.3%
800	-250
200	556
403	19
118	78
6.8	6.8
7.9	8.4
	Pot-Zn/Cu 4385 mg/L 571 mg/L 86.98 14.3% 800 200 403 118 6.8 7.9

Table 11. Observed characteristics of the two MFCs in this study.

Acknowledgements

I would like to thank Prof. K. Singh, the co-author of most of the research papers on MFCs for assisting in the preparation of this chapter. I would also like to thank the Department of Physics for providing necessary facilities for the work. I sincerely thank the management of Guinness Ghana Breweries Limited (GGBL, Kumasi) and staffs for the supply of wastewater and their help with the analytical measurements of COD for the entire project.

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Advanced Supporting Materials for Polymer Electrolyte Membrane Fuel Cells

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71314

Abstract

Among the various kinds of fuel cell, polymer electrolyte membrane fuel cell (PEMFC) is the most prominent energy conversion device for portable applications. The catalystsupporting materials provi.de active triple phase boundary for electrochemical reactions where the reactant molecules can easily interact with the catalyst surface. Catalysts play a vital role for improving the overall efficiency of the fuel cells through the advancement in the catalyst and their supporting materials for cathodic oxygen reduction reaction (ORR) in PEMFCs. The supporting materials mainly contribute to increase the electrocatalytic activity of the catalysts by providing more active surface area and extended life-time. The major roles of supporting materials are (i) they act as electron source with improved conductivity; (ii) they hold the metal nanoparticles; (iii) they possess higher surface area and (iv) they should have better stability under operating conditions. In this chapter, the various supporting materials were reviewed carefully based on their nature and performance toward the electrochemical reduction of oxygen for PEMFCs. They are classified into three major categories as (i) carbon supports; (ii) carbon-free supports, and (iii) polymer nanocomposites. In summary, the overall view on support materials and their role on electrocatalysis for fuel cell reactions is provided.

Keywords: oxygen reduction reaction, carbon supports, graphene, clay minerals, metal oxides, support-free catalysts

1. Introduction

In order to move toward a sustainable existence in our extreme energy-dependent society, there is a convincing need to adopt environmentally sustainable methods for energy production, storage, and conversion [1]. A significant task is being placed to produce power without damaging our ecological system. The fossil fuels such as coal and petroleum products are

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nonrenewable, and burning of these fuels increases the level of pollution and leads to global warming. Nowadays, many eco-friendly alternatives are explored as possible renewable energy sources such as solar, wind, tidal, and hydrothermal power but can be availed only at a particular climatic season. Till date, the internal combustion engines (ICEs) are used as major energy source to meet the global energy demand in wide range of applications [2]. ICEs are involved in the conversion of heat energy to mechanical energy and further used to generate the electrical energy, and this combustion process emits harmful greenhouse gases such as carbon dioxide (CO₂), carbon monoxide (CO), etc. The limited availability of fossil fuels and emission of pollutant gases propel the search of alternative and sustainable clean energy sources [1–3].

Among the various alternative energy sources, fuel cell is the most reliable choice with efficient energy conversion technology which converts chemical energy into an electrical energy through electrochemical reactions namely anodic oxidation and cathodic reduction reactions. Fuel cells are clean energy conversion device, where the oxidant and reductant are continuously supplied to produce electricity, unlike primary batteries that contain pre-packed chemical components. Fuel cells can provide long-term solutions as sustainable and efficient energy conversion devices with minimum or zero emission of greenhouse gases [4]. Significant environmental benefits are expected on fuel cells, particularly for automobile sector and power generation for stationary and portable applications.

Basically, fuel cell is an electrochemical cell, which continuously converts the chemical energy of a fuel and an oxidant to electrical energy in an electrode-electrolyte system, designed for continuous feeding of reactants at a high temperature in the presence of an electrocatalyst to catalyze the oxidation and reduction reactions [5].

(i) Hydrogen at the anode undergoes oxidation to form protons as shown below.

$$H_2 \to 2H^+ + 2e^ E^o = 0.000 \text{ V vs.RHE}$$
 (1)

(ii) Oxygen at the cathode undergoes reduction to from water as given below [6].

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 $E^o = 1.299 \text{ V vs.RHE}$ (2)

Generally, pure hydrogen, methanol, ethanol, etc., can be taken as a fuel that can be oxidized at the anode, while the oxygen or air is taken as the oxidant and get reduced at the cathode. Here, the oxygen reduction reaction (ORR) has sluggish reaction kinetics due to a complex multistep reaction mechanism, which can be catalyzed by electrocatalysts. Electrocatalysts are mostly the metal nanoparticles embedded or decorated over the supporting materials, which provide uniform dispersion to the metal nanoparticles, stability by physical intact, higher surface area, and good electron/proton conductivity that helps to construct three phase boundary. This chapter deals about the role and importance of advanced supporting materials such as various kind of carbon materials, noncarbonaceous supports like inorganic materials, and conductive polymeric supports for cathodic oxygen reduction in polymer electrolyte membrane fuel cells (PEMFCs).

2. Types of fuel cells

Fuel cells are classified in many ways as direct and indirect fuel cells based on operating temperature, the state of matter of the elements of the fuel cell, and the type of electrolyte used. As shown in **Figure 1**, the fuel cells are classified based on their operating temperature such as low-temperature fuel cells and high-temperature fuel cells. Proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), and alkaline fuel cell (AFC) are placed under the category of low-temperature fuel cells.

Solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), and phosphoric acid fuel cell (PAFC) are placed under the category of high-temperature fuel cells. Among this classification, PEMFCs are more attractive and reliable than other fuel cells due to the wide range of application,



Figure 1. Schematic representation of various types of fuel cells with anodic and cathodic feeds and the corresponding electrolyte charge carriers and byproducts.

high efficiency, and near zero emission of pollutants, and it could be a basic system for DMFC and AFC. The alkaline or acidic solutions are used as electrolytes in fuel cells called *mobile electrolyte system*. If the electrolyte is soaked up in a porous material such as asbestos, it is called as an *immobile electrolyte system or matrix system* [5–8].

3. Proton exchange membrane fuel cell (PEMFC)

The proton exchange membrane fuel cell also known as the polymer electrolyte membrane fuel cell works at typically less than 100°C with special polymer electrolyte membranes. This lower temperature fuel cell is the preferred choice for transportation vehicles, portable applications like hand held devices because of its quick start-up, low operating temperature, and excellent energy efficiency. The electrolyte in this fuel cell is an ion exchange membrane – perfluorinated sulfonic acid polymer – commercially sold as Nafion, a good proton-conducting ionomer [5, 9]. The only byproduct in this fuel cell is water, and the water management in the PEMFC is critical for efficient performance. The fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced, because the membrane should be kept under hydrated conditions.

Figure 2 shows the schematic representation of cross sectional view of PEMFC. The low operation temperature of PEMFC requires active electrocatalysts such as Pt. The hydrogen oxidation reaction (HOR) is relatively facile and requires low Pt loading of ca. 0.05 mg/cm² [10]. However, the oxygen reduction is sluggish, and the rate of ORR is most critical at the



Figure 2. Cross-sectional view of polymer electrolyte membrane fuel cell.

cathode and requires more active element like platinum (Pt). Typically, the carbon-supported Pt nanoparticles (Pt/C) having ~2–3 nm size and high Pt surface area (~100 m²/g) is ideal to enhance the reaction rate. Although the use of Pt/C is preferred compared to other catalysts due to the acid resistant property of Pt, corrosion of carbon support and the loss of expensive electrocatalyst push the research community to find the other alternative solutions in terms of advanced supporting materials to increase the activity by higher surface area and life time of Pt, Pt-M alloy, and non-n Pt catalysts without compromising the fuel cell efficiency [11].

Among the fuel cells, PEMFCs have got huge attention due to

- a. high energy conversion efficiency,
- **b.** low operating temperature (around 100°C),
- c. quick startup,
- d. almost zero emission of pollutants with water as the only byproduct, and
- e. can be used for automobile applications because of its portability and easy to operation.

Although PEMFC has many advantages as stated above, the wide spread usage and commercialization are not realized due to the *kinetically sluggish cathodic reduction of oxygen*. The two major electrochemical reactions occur in PEMFC, whereas hydrogen oxidation at anode is intrinsically faster than cathodic oxygen reduction on catalyst surface, because the O—O bond dissociation energy (494 kJ/mol) in O₂ molecule is higher than H—H (433 kJ/mol) [12, 13]. The ORR is a complex multistep reaction involving many electron transfer process with the formation of different intermediates depending on the pH of the electrolyte. In PEMFC, the ORR mechanism can proceed by two different reaction pathways. They are: (i) direct four electron transfer leading to water formation as the only byproduct and (ii) two electron transfer mechanism leading to the formation of H₂O₂ intermediate which again undergoes reduction in a series of electron transfer steps to form water. The reduction of the molecular oxygen in aqueous acid electrolyte solutions in PEMFC (particularly in sulfuric or perchloric acid medium) is assumed to proceed through either of the two major pathways as shown below [11, 14].

(i) The direct 4-electron transfer reduction reaction to H₂O.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 $E^{\circ} = 1.299 \text{ V vs.RHE}$ (3)

(ii) The parallel 2-electron transfer reduction reaction to form H_2O_2 .

 $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $E^{\circ} = 0.700 \text{ V vs.RHE}$ (4)

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^\circ = 1.760 \text{ V vs.RHE}$$
 (5)

where E° is the thermodynamic standard electrode potential at 298.25 K and 1 atm. In 2-electron transfer pathway, two possible products are formed either the reaction stops with the production of H_2O_2 as an intermediate or it is further reduced by another 2-electron transfer to produce

 H_2O as the final product. The extent of reduction reaction appears to depend on the chosen catalyst material; thus, it confirms the role of the electrocatalyst on overall efficiency of fuel cell, which includes the choice of catalyst and its supporting material. The 4-electron route is the most favored reaction pathway, since it produces a high voltage for a H_2 - O_2 PEM fuel cell. For better performance and efficiency, fuel cell requires the sufficient *three phase boundary* (fuel cell reactions occurs in electrode-electrolyte interface) in membrane electrode assembly, which consists of reactant gas molecule, electron conduction over solid catalyst surface (either metal or nonmetal nanomaterials with supports), and proton conduction through polymer electrolyte (conducting polymeric materials) [15, 16]. It seems that the catalyst, catalyst supports, and the conducting polymers are playing a key role in acceleration of kinetics of fuel cell reaction, peculiarly for cathodic dioxygen reduction.

4. Catalyst supports

Catalysts are supported on high surface area materials which are playing a major role to increase electrochemically active surface area of electrocatalysts by providing uniform dispersion and accessibility of active sites for fuel cell reactions. The electrocatalyst with active surface area must be intact directly with electronic and ionic conducting materials, and hence, it is named as *three phase boundary* [16]. The major role of supporting materials is (i) to act as electron source with improved conductivity; (ii) to hold the metal nanoparticles (physical interaction); (iii) to possess higher surface area; (iv) to provide better stability; (v) to provide porosity; and (vi) to have higher corrosion resistance under fuel cell operating conditions [17, 18]. Many forms of carbonaceous materials are available, which vary based on its structure, conductivity, thermal stability, surface area, etc., which include the preparation procedure with different physiochemical approaches [19]. Even though, some certain number of carbon materials have got huge attention for various applications in wide range of fields such as sensor, medicine, and especially for energy materials.

5. Carbon supports

Carbon materials are widely employed catalyst support for energy applications, and its multidimensional structure provides high electrical conductivity and surface area with greater chemical and electrochemical stability. Carbon supports are the major choice of catalyst support for fuel cell reactions in both anode and cathode electrocatalysts to conduct electrons and heat in [20, 21]. A common choice of carbon support material is Vulcan Carbon XC-72 (VC, BET specific surface area 254 m²/g), due to low cost, high-specific surface area, adhesion properties with catalyst particles and distribution, better interaction with the polymer, and high conductivity [21–23]. It has noticeable disadvantages such as carbon corrosion owing to its surface oxidation to produce CO_2 during fuel cell operation and results in dissolution of Pt nanoparticles from the carbon support leading to low Pt utilization and less performance [24].

Carbon corrosion is one of the key factors inducing cathode electrocatalyst (Pt/C) degradation in PEM fuel cells. It is electrochemical oxidation and thus needs to be investigated *in situ* with potential imposed because the ORR occurs at potentials closer to those where oxidation of carbon can also happen [25]. Carbon is not thermodynamically stable at higher potentials in the fuel cell environment, which is problematic for long-time durability of the electrocatalysts. Carbon corrosion depends on the operating temperature, high potentials (above 0.5 V vs. RHE), low pH, and high humidity. During oxidation, the major product formed is CO_2 with trace amounts of CO [24–26].

Typically, the electrochemical oxidation reaction of carbon takes place as follows [23-25],

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- E^\circ = 0.207 V \text{ vs.RHE}$$
 (6)

$$C + H_2O \rightarrow CO + 2H^+ + 2e^ E^{\circ} = 0.518 \text{ V vs.RHE}$$
 (7)

Carbon monoxide (CO) is thermodynamically unstable and therefore slowly converted to CO₂.

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- E^- = -0.103 \text{ V vs.RHE}$$
 (8)

Pt is also found to catalyze the carbon oxidation [23]. Under fuel cell operating conditions, the corrosion rate is significant, leading to large voltage degradation, and further, the CO formed deactivates the Pt catalysts. Several reports reveal that the corrosion of carbon support reduces the integrity of the catalyst layer and enhances Pt dissolution [25–28]. **Figure 3** shows the TEM images (**Figure 3a** and **b**) of Pt/C captured before and after the durability test, and **Figure 3c** depicts the same as a schematic representation [29]. Wang et al. have reported the effect of carbon support corrosion on the stability of Pt/C using two different carbon support materials such as Vulcan carbon XC-72 (VC) and Black Pearls 2000 (BP-2000). They have concluded that the decrease in ECSA of Pt embedded carbon support materials reveals the loss of Pt nanoparticles during the accelerated durability test due to surface oxidation of carbon supports.

Among these conventional carbon supports, carbon nanotubes and graphene derivatives have got huge attention and employed as major catalyst supports for fuel cell applications due to its excellent physiochemical properties. Carbon nanotubes (CNTs) are the family of carbon allotropes consist of *sp*² hybridized carbons bonded in a hexagonal lattice arrangement [30]. They are described as cylindrical hollow natured materials formed by the rolling of single or multi layers of graphene sheets called single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), respectively. SWCNTs and MWCNTs are typically 0.8–2 nm and 5–20 nm of diameters, respectively, while MWCNT can exceed 100 nm of diameters. The lengths of CNTs range from less than 100 nm to several centimeters and are considered to be one dimensional (1D) structure [31, 32]. CNTs are possessing good electronic conductivity, thermal conductivity, and mechanical stability than conventional carbon supports. In recent days, surface functionalized CNTs [32–35], N, S, B, and halogens-doped CNTs [36, 37] and hybrid CNTs [37, 38] were prepared and employed as catalyst support for ORR in PEMFC.



Figure 3. Carbon support corrosion during potential cycling on Pt/C lead catalyst dissolution and agglomeration observed from same location TEM images (a and b) [34]; (c) schematic representation.

An exceptionally outstanding performance was derived from the new carbon supporting material for ORR namely graphene, an iconic carbon form in the history of material sciences. It is a single-layer sp^2 bonded carbon with 2-dimensional (2D) honeycomb structure. It exhibits high crystalline nature, and electronic conductivity explores a new looks to the carbon chemistry especially for energy applications [37–39]. Generally, the physiochemical properties of the graphene materials are related to its synthesis approach and surface treatment. It is a building block of all graphitic materials when it wrapped into 0-dimensional fullerene, 1-dimensional carbon nanotubes, and 3-dimensional graphite. The physical properties of graphene can be defined through preparation method. Especially, the porosity of graphene may be either mesoporous or microporous, and hence, it is one of the critical properties which contribute to accelerate the kinetics of electrochemical reactions in PEMFC. Usually, the carbon supports are the prime choice as catalyst support for cathodic ORR in PEMFC providing high surface area and conductivity, whereas the surface oxidation of carbon supports suppresses the performance of catalyst through surface masking, leading to poor ORR kinetics. The physical properties such as porosity, specific surface area, and conductivity of various carbon supports are summarized in Table 1.

Name of the material	Nature of porosity	Specific surface area (m²/g)	Electrical conductivity (S/cm)	Ref. no.
Vulcan carbon	Micro porous	254	4.0	[20]
Carbon black	Micro porous	475	1.4	[20]
Carbon nanotube				
Single-walled carbon nanotube	Micro porous	400–900	$10^2 - 10^6$	[34]
Multi-walled carbon nanotube	Mesoporous	200-400	$10^3 - 10^5$	[34]
Graphite	Meso-/microporous	10–20	$2-3 \times 10^4$	[35]
Graphene		1500	~2000	[35]

Table 1. Various carbon materials and their physical properties.

6. Carbon-free catalyst supports

In general, carbon-free supports are mostly inorganic metal oxides, and other mineral oxides possess better corrosion resistance, improved interaction with metal nanoparticles, and stable morphology. However, these materials are poor in electrical conductivity, and low porosity leads to less specific surface area than highly porous supporting materials. The major inorganic additives are metal oxides (SiO₂, TiO₂, CeO₂, etc., [40, 41]), some of the carbides (WC, VC, etc., [42, 43]), and layered silicate materials such as clay minerals [44, 45], which are increasingly used as catalyst supports for PEM fuel cells. Clay minerals belong to a subtype of phyllosilicates with characteristic layered structures. Two basic layered structural units are important in the formation of the clay-structured materials: the tetrahedral structure formed by silicon and oxygen atoms and the octahedral structure formed by aluminum/magnesium and oxygen atoms. The tetrahedral units are linked through their corners, forming a tetrahedral sheet, whereas the octahedral units are edge-linked, resulting in an octahedral sheet. The structural framework of the clay platelets is basically composed of these two kinds of sheets joined together to form layers.

Layered silicates are clay minerals built of two structural units. The simplest form of clay minerals is the 1:1 structure (e.g. *kaolinite*) where a silica tetrahedral sheet is fused to an aluminum octahedron, sharing the oxygen atoms. However, commonly employed layered silicates for the preparation of polymer nanocomposites, such as montmorillonite (MMT), belong to the family of 2:1 phyllosilicates, more specifically *smectites* [46]. Their crystal structure consists of stacked layers made of two silica tetrahedrons fused to an edge-shared octahedral sheet of alumina. The layer thickness is approximately 1 nm, and the adjacent layers are separated by a regular van der Waals gap called the interlayer or gallery. Clay layers carry negative charges due to the replacement of some Si⁴⁺ ions in the tetrahedral sheets or some Al³⁺ or Mg²⁺ ions in the octahedral sheets. To compensate the negative charges created, cations (Na⁺ or Ca²⁺) are usually present in the interlayer domain. When clays are dispersed in aqueous solution, these charge-compensating cations can be exchanged and replaced by others present in the bulk solution. Although smectite types of clays have substantial importance in



Figure 4. Schematic representation of amino propyl functionalized Mg-phyllosilicate clay.

multidisciplinary applications, they require surface modification by covalent functionalization to improve the dispersing ability in aqueous or organic media [46–48].

Like naturally occurring clay minerals, synthetic clay also employed as catalyst support for cathodic oxygen reduction in PEM fuel cells. Amino propyl functionalized Mg-phyllosilicate clay employed as catalyst support for ORR in PEMFC [49, 50]. The amino groups of synthetic clay hold metal nanoparticles by physical interaction and increase the stability of the catalyst than conventional carbon supports. In **Figure 4**, the layered structure of aminoclay is schematically presented. The structure of aminoclay contains 2:1 Mg-phyllosilicate layer with surface functionalized arm-like amino propyl groups. Hence, the amino groups can hold the metal nanoparticles and provides uniform distribution for the preparation of polymer nanocomposite membranes.

7. Polymer nanocomposites

The proton conducting membranes are inserted between the anodic and cathodic compartments to prevent mixing of reactants and to conduct protons formed due to the oxidation of hydrogen at the anodic compartment to cathodic side. The polymer electrolyte membrane should possess high proton conductivity, low fuel permeability, good thermal stability, and better film forming ability, and more importantly, it should be of low cost and should have high durability. Under fuel cell-operating conditions, it should have sufficient water uptake and moderate swelling, excellent electrochemical stability in an aggressive environment like low or high pH solutions, and good mechanical strength, i.e., significant stability in structure and morphology [15]. Nafion is a perfluorinated ionomer containing hydrophobic polytetra-fluoroethylene (PTFE) backbone with pendant-like side chains of perfluorinated vinyl ethers terminated by perfluorosulfonic acid groups as shown in **Figure 5**.

Nafion has many key properties such as thermal, mechanical, and chemical stability and, most importantly, high water-saturated proton conductivities during long-term fuel cell operation. Teflon-like PTFE backbone provides the long-term durability during the oxidative and reductive fuel-cell operating conditions [9]. But the drawbacks of Nafion membrane include low conductivity under low humidification, poor performance at elevated temperatures (above 90°C), and high cost. Therefore, in order to improve the properties of Nafion under fuel cell working conditions, some nanoscale additives are usually added to obtain Nafion nanocomposites [17, 51, 52]. Therefore, an extensive research has been attempted by many researchers to synthesize novel polymer nanocomposite materials by blending with suitable polymers and organic/inorganic additives with improved physicochemical properties. Many conducting polymers were used such as poly (aniline), poly(ethylene oxide), poly(styrene), poly(vinyl alcohol), poly(propylene), poly(vinyl pyrrolidone), and poly(3,4-ethylenedioxythiophene), etc., along with Nafion to form polymer blends. In polymer nanocomposites, inorganic additives such as quaternary ammonium salts, SiO₂, TiO₂, WO₂, etc. [40, 41, 52, 53] and layered silicate minerals such as clay minerals [50] are used as fillers



Figure 5. Chemical structure and pictorial representation of Nafion ionomer with hydrophilic clusters and hydrophobic backbone units.

and used as catalyst supports for energy applications. Aminoclay/Nafion nanocomposite membranes were prepared through sol–gel approach with embedded Pt nanoparticles by simple chemical reduction method. The electrocatalytic performance and durability of Pt nanoparticles– embedded Aminoclay/Nafion toward ORR were studied for PEMFC [49, 50].

In electrochemical processes, the electron transfer between solid-liquid interfaces is the elementary step, and the interfacial properties such as conductivity, surface area, etc. have significant influence on electron transfer [54]. In contact with electrolytic solution, electrodes (catalyst materials) can act as a source or a sink for electrons to change the electroactive species according to classical voltammetry. The nature of the electrode surface can alter the efficiency of the electron-transfer process and mass-transport regime. Therefore, it is extremely important to obtain the desired electrochemical properties at the interface between the electrode and the electrolytic solution by modifying the electrode surface. In conventional electrochemical cells, bulk Pt was employed as electrocatalyst to catalyze the fuel cell reactions and thus have disadvantage of low surface area and poor utilization [54–56]. Later on, the nanosized electrocatalysts got more attention especially in energy applications due to their unique physical and chemical properties. Nanomaterials show size, shape, and composition-dependent properties, and a single material can show a wide range of properties and applications depending on the size [57–59]. As the dimensions of a particle decrease, the surface-area/volume ratio drastically increases. When this ratio is large, the low-coordinate atoms on the particle surface predominate and dominate the particle properties called as surface effects. Surface effects make the properties of nanoparticles different from those of the corresponding bulk materials [56, 60– 62]. Thus, the surface activity can be further enhanced by the proper choice of supporting materials, which meet the requirements to provide three phase boundary for electrochemical reactions in fuel cells.

8. Conclusion

In conclusion, catalyst-supporting materials are playing a crucial role for improving the overall efficiency by enhancing the activity and stability for PEMFCs. The major requirements of promising supporting materials for fuel cell catalysis are high surface area, good electrical conductivity, porosity, and better stability under fuel cell operating conditions. Carbon supports are widely used supporting materials for ORR in PEMFC. Due to the surface oxidation, conventional carbon supports diminish the activity of catalysts under fuel cell operating conditions. In order to overcome these issues without compromising the performance of catalysts, novel carbon materials such as CNT, graphene and its derivatives, noncarbon supports, and conducting polymers are used as catalyst supports for ORR. Hence, the overall efficiency and performance of the fuel cell are laid on nature of the catalysts and their supporting materials, which can provide sufficient *triple phase boundary*, where the reactant gas molecule undergoes electrochemical reaction over the catalysts with hybrid supporting materials is still en route to attain better fuel cell performance and efficiency, which make the technology as commercially viable.

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Edited by Tolga Taner

The main idea of this study is to scrutinize the performance efficiency and enhancement of modelling and simulations of PEM fuel cell. Besides, the research of PEM fuel cell performance can figure out many critical issues for an alternative resource energy. The chapters collected in the book are contributions by invited researchers with a long-standing experience in different research areas. I hope that the material presented here is understandable to a wide audience, not only energy engineers but also scientists from various disciplines. The book contains nine chapters in three sections: (1) "General Information About PEM Fuel Cell", (2) "PEM Fuel Cell Technology" and (3) "Many Different Applications of PEM Fuel Cell". This book presents detailed and up-to-date evaluations in different areas and was written by academics with experience in their field. It is anticipated that this book will make a scientific contribution to PEM fuel cell and other alternative energy resource workers, researchers, academics, PhD students and other scientists both in the present and in the future.

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