A Review on Bioinspired Proton Exchange Membrane Fuel Cell: Design and Materials

Sara Pedram, Mariah Batool, Kirsten Yapp, Leonard Bonville, and Jasna Jankovic*

With the climate crisis gathering recognition, there has been significant interest in clean energy. As a reliable and clean energy solution, markets transitioning toward sustainable energy have identified polymer electrolyte membrane fuel cells (PEMFCs) as a critical technology. The increasing interest in PEMFCs is primarily due to their high energy density, high efficiency and zero greenhouse gas emission. However, additional development is required to overcome the current barriers associated with fuel cell component design, high manufacturing cost, and insufficient stability. Bioinspired designs have the potential to provide new and valuable insights using novel techniques for extracting design inspirations from biological structures. Applying these design concepts to develop materials and structures for various fuel cell components can be transformative. The well-adapted structures and functional features of biological systems have been proven to greatly enhance the performance of current designs through novel and optimized pathways. Bioinspired designs have indeed lived up to performance expectations and even exceed them. Herein, the potential and value of using these bioinspired designs are discussed. Recent studies and advancements based on nature-inspired structures for components of PEMFCs and how these design considerations substantiate their claim as an attractive alternative to conventional designs are discussed.

1. Introduction

The increasing demands for energy and global concerns associated with conventional power sources have highlighted the necessity for cleaner and more efficient power generation methods. As an electrochemical energy device with high efficiency and no carbon dioxide (CO₂) emission, fuel cells (FCs) have emerged as promising candidates. FCs with an energy efficiency of 40–70% are among the most efficient energy generators due to the elimination of the thermal energy intermediate. The FC system converts the chemical energy of hydrogen and oxygen as the reactants directly into electricity and water, making it the most environmentally friendly and quiet energy system.[1–8]

The primary categorization of FCs depends on the electrolyte layer. Polymer electrolyte membrane fuel cells (PEMFCs), with their high-power density and high efficiency, are the predominant choice for transport applications among the five major types of FCs.[9–15] Components of a PEMFC include a solid polymer membrane, two catalyst layers (CLs), gas-diffusion layers (GDLs) with microporous layers (MPLs), and flow field plates (FFP). The combination of the membrane, CLs, the two GDLs, and the gaskets makes up the membrane electrode assembly (MEA). The MEA is sandwiched between two FFPs that have flow channels built into them. They supply fuel and air as well as eliminate the byproducts of the reactions.[16–20] A schematic of the cell is shown in Figure 1. A single PEMFC composed of an MEA and two FFPs produces less than 1 V, which is very low for most applications. Therefore, to increase the potential to a practical level, the individual cells are connected in series, i.e., the cathode of one cell is electrically connected to the adjoining cell’s anode to form a FC stack.[21,22]

PEMFCs utilize redox reactions to generate electricity. Hydrogen gas is pumped into the anode, where a hydrogen oxidation reaction (HOR) occurs. The hydrogen ions travel through the polymer electrolyte membrane (PEM) from the anode to the cathode while the electrons travel externally to the cathode. Air or oxygen gas is pumped into the cathode and combined with the

S. Pedram, Dr. J. Jankovic
Department of Materials Science and Engineering (MSE)
University of Connecticut
44 Weaver Rd. U-5233, Storrs, CT 06269, USA
E-mail: jasna.jankovic@uconn.edu

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aesr.202000092.

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S. Pedram, M. Batool, K. Yapp, L. Bonville, Dr. J. Jankovic
Center for Clean Energy Engineering
University of Connecticut
44 Weaver Rd. U-5233, Storrs, CT 06269, USA

M. Batool, Dr. J. Jankovic
Institute of Materials Science (IMS)
University of Connecticut
97 N Eagleville Rd Unit 3137, Storrs, CT 06269, USA
other components to go through an oxygen reduction reaction (ORR).

Two predominant mechanisms are possible for the ORR process in the cathode of the PEMFC (i.e., in the acidic environment), and they involve multielectron reactions. In general, electrocatalysts that boost a direct $4e^-$ ORR are preferred for high-performance $\text{H}_2/O_2$ FC development over $2e^-$. The $4e^-$ and $2e^-$ ORR are as follows:

i) Direct four-electron ($4e^-$) oxygen reduction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1)$$

ii) The two-electron ($2e^-$) oxygen reduction

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (3)$$

The overall HOR in the acidic medium, the so-called anode half-cell reaction, involves oxidation of an $H_2$ molecule on the electrode surface (Equation (4)). Electron and proton transfer from the electrode surface and the electrolyte, respectively,

$$\rightarrow 2H^+ + 2e^- \quad (4)$$

Thus, the overall reaction of the PEMFC is

$$2H_2 + O_2 \rightarrow 2H_2O \quad (5)$$

PEMFCs are actively fabricated and commercialized, but research has to be continued to optimize the cells and their components. An approach that has gained popularity in recent years uses inspiration from biological structures to develop alternative materials and structures. Nature with fully hierarchical scaling structures has been a source of design inspiration for different parts of the FC. As manifested and reinforced by substantial data in the specified area of study, bioinspired designs have indeed lived up to the performance expectations or, in some cases, exceeded them. Bioinspired designs focusing on specific components of the FCs have been enumerated and discussed to a great extent in the available literature. However, to the authors’ knowledge, a comprehensive summary reviewing all facets of PEMFCs, where a nature-inspired design can be successfully implemented or have favorable potential to be used, has not been compiled. The objective of this article is to summarize and discuss the different approaches, where researchers have taken inspiration from biological systems for implementation in PEMFCs, including designs and materials for flow fields, catalysts, and membranes, as schematically shown in Figure 2. Bioinspiration can be used to optimize PEMFCs and have an environmental impact by repurposing materials previously determined to be waste as viable materials.

2. Flow Field Design

An optimized FFP design has been proven to improve the electrochemical performance and efficiency of PEMFCs. The FFP is composed of flow channel patterns engraved on the bipolar plates of the PEMFC that assist the delivery of hydrogen to the anode and oxygen to the cathode. As the operation of the flow field requires, its design is essential to ensure effective mass transport, water management, electrical and thermal transport, and mechanical stability for the cell stack. The design parameters that closely impact the operation of the flow field include configuration, dimension, structure, and flow channel pattern. Some of the conventional flow field designs widely used in PEMFCs include pin type, spiral, interdigitated, straight parallel, single-channel, or multiple-channel serpentine, as shown in Figure 3.

An essential function of flow fields in PEMFCs is mass transport, which is analogous to some of the naturally existing mass transport systems such as the network of veins in leaves and the human body. The intricate design of these biological mass transport systems, and their superb functionality, lead the researchers to believe that imitating nature for designing flow fields for PEMFCs could improve their overall operation. To date, numerous bioinspired designs have been introduced and investigated for their impact on the performance of PEMFCs. These designs include various fractal structures, leaves, lungs, porous media, wave-like designs, and bionic designs following Murray’s law. Researchers have enumerated multiple advantages of using...
bioinspired flow fields and compared their performance characteristics with other conventional flow field designs.\textsuperscript{[43–50]}

The flow field design is an intricate process that has to keep different factors and parameters in consideration to achieve optimal performance, such as the minimization of material requirement, uniform distribution of gases, effective water transport, and manufacturability.\textsuperscript{[51,52]} Mathematical models are extensively used to predict the functionality of different components in a similarly simulated environment or operating conditions using computational fluid dynamics (CFD). Thus, this

Figure 2. Bioinspired approach for various components of PEMFCs.

Figure 3. Different types of conventional flow field designs: a) pin type, b) straight parallel, c) interdigitated, d) single-channel serpentine, e) spiral, and f) multiple-channel serpentine.
approach can serve as a practical way of testing, validating designs, and predicting their functional behavior, saving extra effort and material and time.

For example, the entropy generation of a leaf-based flow field design with channels fabricated per Murray’s law is analyzed using numerical modeling by Cesar et al.\textsuperscript{[53]} The model indicates that thermal and viscous effects account for only \(\approx 10–20\%\) of the net entropy production, whereas mass transport and flow effects account for \(\approx 90\%\). A reduction in entropy generation and pressure drop is achievable by increasing bifurcation levels and using less acute bifurcation angles.

One of the primary aims of using bioinspiration to flow field designs is to enhance thermal and water management capabilities, which is vital for the optimal performance of a PEMFC. Numerous studies have discussed the effects, leading to severe cases of thermal and water management issues in PEMFCs in greater detail. One such effect is the two-phase flow of liquid and gas inside the FC’s flow channels, which is especially evident under high-current-density conditions. Several researchers used 2D and 3D models to predict the factors leading to the two-phase flow and its consequence on FC stability and performance. Two-phase flow occurs due to water production as a result of an electrochemical reaction in the liquid phase under lower operating temperatures and high humidification levels in PEMFCs.\textsuperscript{[44–57]} It is suggested that both capillary and viscous forces govern the two-phase flow. The liquid water tends to interact with the gas flow inside the flow channel, forming distinct droplets that attach themselves to the surface of the GDL, resulting in clogging of pores and inhibition of reactant flow. The parameters which affect the droplet dynamics are the surface tension, contact angle, flow channel geometry, liquid saturation, permeability, and porosity.\textsuperscript{[58–61]} Typically, during the FC operation, the individual droplets subsequently coalesce and increase in size under high gas flow velocities, eventually causing the droplets to detach, leading to slug flow. This type of slug flow is associated with water accumulation and flooding of the flow channels. During the dynamic process of droplet detachment, the liquid pressure increases, leading to the formation and rearrangement of interconnected water pathways, which interfere with/impede the flow of reactant gas within the GDL layer, followed by pressure drop.\textsuperscript{[62–64]} All the effects mentioned earlier collectively degrade the FC’s electrochemical performance.\textsuperscript{[55,65–69]} More extended length flow channels have been reported as a significant cause for water build-up, resolvable by bioinspired flow field structures with shorter, consecutive, and increased branching channels, whereas bioinspired flow field designs based on Murray’s law supporting under-rib convection have also been linked to lower pressure drop.\textsuperscript{[16,70–72]} Porous flow fields also provide the appropriate structure for efficient removal of water, facilitating the transport of oxygen in the GDL layer and helping with the FC’s overall water management, thus minimizing the two-phase flow effect.\textsuperscript{[46,72–74]}

Furthermore, another challenge in the thermal management of FCs is the uneven temperature distribution due to inefficient cooling of the GDL layer, causing a difference in local vapor partial pressures. This effect leads to evaporation of water at hotter sites, releasing the latent heat of evaporation and water condensation at colder sites collectively termed “heat pipe effect.”\textsuperscript{[73–77]} Bioinspired flow field patterns due to their branching networks or porous structures provide large surface areas functioning as heat sinks to avoid localized hotspot formations.\textsuperscript{[78–80]}

Several researchers studied the bioinspired-based flow field design, including leaf vein and lung-based structures, through CFD simulations for PEMFCs. These studies report an overall improvement in performance, uniformity in gas flow distribution, as well as easy removal of excess products for the biomimetic designs compared with the conventional FFPs. The use of the most common approaches for designing and analyzing bioinspired structures and comparison against different conventional flow fields for PEMFCs is shown in Table 1.

Several researchers have reported their findings based on numerical simulations from CFD models compared with results validated with experimentation or available data.\textsuperscript{[65,81–85]} For instance, the work by Guo et al.\textsuperscript{[86]} where different leaf-based flow field designs with reticulate venation, as shown in Figure 4, are fabricated using a selective laser-sintering method, reports a more uniform oxygen distribution but higher pressure drop compared with conventional interdigitated and parallel-in-series designs. The study also discovers a 20–25% enhancement in peak power density achieved by implementing Murray’s law to the biomimetic design for optimizing flow channels and their subchannel diameter. This study also reports close conformance (=less than 10%) of the developed model with experimental results. In a similar study, conducted by Saripella et al.\textsuperscript{[88]} a 30% increase in peak power, better water management function, better uniformity in reactant distribution, pressure, and velocity fields are attained for bioinspired flow field design versus the state-of-the-art (SOA) conventional single-serpentine design in PEMFCs.

In another study, Kloess et al.\textsuperscript{[87]} compare the lung- and parallel venation leaf-based bioinspired flow field designs with conventional serpentine and interdigitated designs, as shown in Figure 5. The research results exhibit a reduced pressure loss in the range of 28–37% and up to \(\approx 30%\) increase in peak power density in both bioinspired designs. The study suggests that further improvement in performance, minimization of contact resistance, and pressure loss is achievable by surface treatment, rounding of corners, and tapering of ends of bipolar plates. The experimental results collected by the authors of this article agree with the numerical model results of the same study.

In a similar study by Badduri et al.,\textsuperscript{[88]} the performance of an interdigitated and noninterdigitated leaf with reticulate venation and lung-based flow field design compared with the triple-serpentine flow for PEMFCs is investigated. The study reports peak power densities of 0.49, 0.47, and 0.39 W cm\(^{-2}\) for lung, noninterdigitated leaf, and triple-serpentine FFP designs, respectively. A summarized graphical representation of gross and net power densities for triple-serpentine, noninterdigitated, and interdigitated leaf-based flow field designs is also shown in Figure 6.

Many studies focus only on implementing the experimental procedure to study the effects of bioinspired flow field designs. Such a study was conducted by Cho et al.\textsuperscript{[90]} focusing on water management aspects for lung-inspired flow field designs using neutron microscopy. Their work on lung-inspired channels shows more susceptibility to flooding at higher current densities of 0.6 A cm\(^{-2}\) and above due to faster gas flow, thereby requiring dynamic water removal. Moreover, this study points out that any defect in branching channels could exacerbate flooding, leading
Table 1. The use of the most common approaches for bioinspired flow field design for PEMFCs.

| Hierarchical transport network and structure of nature | Nature-inspired concept | Results | Ref. |
|-------------------------------------------------------|------------------------|---------|------|
| “Tree-like” fractal anatomic systems                   |                        |         |      |
| [Image 1] Reprinted with permission. Copyright 2013, David Publishing Company. |
| Branch flow channel. Reprinted with permission. Copyright 2012, Springer Nature. |
| Leaf. Reprinted with permission. Copyright 2019, Trans Tech Publications. |
| Cross-emulate venation. Reprinted with permission. Copyright 2015, Springer Nature. |

Fractal parallel flow field plate (FPFFP) versus parallel flow field plate (PFFP) parameters of the FPFFP CFD. Table 1 shows an increase in H₂ flow area, current density, and active area of MEA compared with PFFP. Reproduced with permission. Copyright 2013, David Publishing Company.

| Parameter                        | Minimum | Maximum | Minimum | Maximum |
|----------------------------------|---------|---------|---------|---------|
| Pressure (Pa)                    | 101.324 | 101.347 | 101.324 | 101.347 |
| Temperature (K)                  | 298.15  | 373.15  | 298.15  | 373.15  |
| Density (kg/m³)                  | 0.07    | 0.08    | 0.07    | 0.08    |
| Velocity (m/s)                   | 0       | 10.739  | 0       | 10.739  |
| Temperature (fluid (K))          | 298.15  | 373.15  | 298.15  | 373.15  |
| Mach number                      | 0       | 7.32e-003 | 0       | 7.32e-003 |
| Vorticity (1/s)                  | 0       | 51.038  | 2.198   | 51.038  |
| Shear stress (Pa)                | 0       | 1.62    | 1.62    | 1.62    |
| Heat transfer coefficient (W/m²K) | 7.28e-014 | 2.367 446 | 7.40e-013 | 2.367 448 |
| Surface heat flux (W/m²)         | -56.488 | 188.677 647 | -0.234 | 188.678 372 |
| Heat flux (W/m²)                 | 0       | 146.972 979 | 0       | 146.974 586 |

An increase in H₂ flow area, current density, and active area of MEA is observed for FPFFP compared with PFFP. Reproduced with permission. Copyright 2013, David Publishing Company.

The branch flow channel displays an even current distribution and less pressure drop, improving the cell’s stability and efficiency. Reproduced with permission. Copyright 2012, Springer Nature.

Biomimetic leaf channel shows enhanced reactant/product distribution, less pressure drops, and increased power output, especially at lower voltage reaching a peak at ≈0.65 V. Reproduced with permission. Copyright 2015, Springer Nature.
Table 1. Continued.

| Hierarchical transport network and structure of nature | Nature-inspired concept | Results | Ref. |
|--------------------------------------------------------|-------------------------|---------|------|
| Mesh type parallel venation                             |                         |         | [185,186] |
| ![Mesh type parallel venation](image1)                 |                         |         |      |
| Reproduced with permission [185] Copyright 2012, Elsevier. |

Leaf flow field with more secondary channels (b) shows ≈2.6% higher current density and 3.3% higher power density under the same operating conditions. Reproduced with permission [185] Copyright 2012, Elsevier.

![Parallel venation](image2)  
Parallel venation. Reproduced with permission [187] Copyright 2019, Trans Tech Publications Ltd.

Biochannel flow plate exhibits uniform pressure and reactant distribution, 1.02 A cm\(^{-2}\) current density, and peak power density of 0.49 W cm\(^{-2}\) at 0.6 V, which is 20% more than that for the serpentine channel. Reproduced with permission [187] Copyright 2019, Trans Tech Publications Ltd.
Table 1. Continued.

| Hierarchical transport network and structure of nature | Nature-inspired concept | Results |
|-------------------------------------------------------|-------------------------|---------|
| [Image 1] Parallel venation. Reproduced with permission. Copyright 2012, Elsevier. | [Image 2] The biomimetic flow field demonstrates a peak power density that is 56% and 26% higher than parallel and serpentine flow field design, respectively. Reproduced with permission. Copyright 2012, Elsevier. |
| [Image 3] Pinnate venation with two branching angles. Reproduced with permission. Copyright 2017, Elsevier. | [Image 4] Biomimetic leaf flow channel with two levels of bifurcations at 37° achieves higher power density and lower ohmic losses. Reproduced with permission. Copyright 2017, Elsevier. | [188,189] |
| [Image 5] Biometric flow slab. Reproduced with permission. Copyright 2010, Elsevier. | [Image 6] The biometric flow slab exhibits the lowest pressure drop, efficient water removal, and an increase in current density by 57.13% compared with the parallel flow slab. Reproduced with permission. Copyright 2010, Elsevier. | [181,191] |
### Table 1. Continued.

| Hierarchical transport network and structure of nature | Nature-inspired concept | Results | Ref. |
|------------------------------------------------------|-------------------------|---------|------|
| Lung                                                 | Lung-shaped flow field. Reproduced with permission. Copyright 2017, John Wiley and Sons. | Lung-shaped flow field shows higher efficiency, especially in ohmic and mass transfer regions with uniform fluid velocity and minimum pressure drop. Reduces catalyst material consumption by a factor of 4–8% and improves efficiency by 10–20%. Reproduced with permission. Copyright 2017, John Wiley and Sons. | [182] |
| Murray interdigitated channel                       | Bio-inspired FFP exhibits uniform current distribution and a higher current density of 1.30 A cm\(^{-2}\) at 0.3 V than parallel FFP and higher pressure drops. | | [193] |
Table 1. Continued.

| Hierarchical transport network and structure of nature | Nature-inspired concept | Results | Ref. |
|-------------------------------------------------------|-------------------------|---------|------|
| Cuttlefish fins. Reproduced with permission.[194]     | Bio-inspired wave-like flow channel. Reproduced with permission.[194] | The bioinspired wave-like channel displays a 2.2% increase in power density at 0.45 V with enhanced fuel utilization and reduced flow resistance. Reproduced with permission.[194] | [194] |
| Waveform. Reproduced with permission.[81]            | Reproduced with permission.[81] | Peak power density reduces for an increase in expansion ratio from 1 to 3 for bioinspired waveform channels (case 1–3), with case 1 depicting the best performance and peak power density of 0.55 W cm\(^{-2}\). Reproduced with permission.[81] | [81] |
for serpentine design, whereas the voltage drops
This study reports that the current density of the inter-
which improves
Moreover, this research
for three-level versus one-level bifurcation fractal
design. Aside from the level of bifurcation, there are other impor-
tant parameters to be taken into account for optimal designing of
fractal
and size of the
channel. However, the study suggests that an improved
performance is achievable for a fractal design at higher temper-
water, clogging fractal and parallel channels, reducing the active
area of the cell. However, the study suggests that an improved
performance is achievable for a fractal design at higher temper-
atures, which do not involve removing water in the liquid phase.
Fractal tree-like flow fields are characterized by their branching
structures, and the effects of one, two, and three levels of bifur-
cation in fractal flow channel designs are reported by Lorenzini et al.[45]
The results reveal that an increase in the level of bifurcation sub-
stantially improves the peak power density, exhibiting a 25.25%
crease for three-level versus one-level bifurcation fractal
design. Aside from the level of bifurcation, there are other impor-
tant parameters to be taken into account for optimal designing of
fractal flow fields. Two such parameters are channel-to-rib ratio
channel-to-rib ratio and size of the flow channel, according to a study by Wang.[94]
The results point out that under similar operating conditions, the
power density of the FC increases with a decrease in cross-
sectional area of the channels and channel-to-rib ratio due to
an increase in flow velocity facilitating efficient water removal.
Several novel bionic flow field designs combining the features of nature-inspired and conventional flow channel designs have also been introduced in the past. These types of intersectant flow field designs drawing inspiration from Murray’s law, fractal channels, and other bionic features are introduced in a study by Dong et al.[93] This study reports that the current density of the intersectant design is higher than serpentine design in the lower oper-
tating voltage range of less than 0.4 V. Another innovative 3D
wave flow field is presented by Chen et al.,[96] which improves
fuel distribution by increasing convective mass transfer and con-
firms a 23.8% increase in current density at a voltage of 0.4 V
relative to a conventional straight channel design. This study also
claims that uniformity in distribution of current density and

Another important bioinspired design, the fractal
flow field, was studied by Tuber et al.[91] in comparison with conventional
and serpentine structures. The results reveal that a steady
voltage of 0.7 V is achievable even under a constant load of
128 mA cm$^{-2}$ for serpentine design, whereas the voltage drops
immediately in the case of fractal and parallel flow field designs. The study attributes this voltage drop to the accumulation of
water, clogging fractal and parallel channels, reducing the active
area of the cell. However, the study suggests that an improved
performance is achievable for a fractal design at higher temper-
atures, which do not involve removing water in the liquid phase.
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firms a 23.8% increase in current density at a voltage of 0.4 V
relative to a conventional straight channel design. This study also
claims that uniformity in distribution of current density and
Figure 4. Bioinspired flow field designs with a) interdigitated flow field design with constant channel width; b) noninterdigitated bioinspired design with constant channel width; c) interdigitated design with varying channel widths determined by Murray’s law; and d) comparisons of experimental and computational polarization curves for the bioinspired and parallel-in-series and interdigitated designs. Reproduced with permission. Copyright 2014, Elsevier.

Figure 5. a) Bioinspired leaf flow pattern; b) bioinspired lung flow pattern; c) polarization curve; and d) power density comparison for various flow pattern designs: $P = 2$ atm, $T = 75^\circ$C, RH = 100%. Reproduced with permission. Copyright 2009, Elsevier.
oxygen content reduces with an increase in minimum depth but increases with an increase in wavelength for the 3D wave flow field.

The performance characteristics of a bioinspired porous metal foam design and conventional parallel flow field design are evaluated in a study by Bao. The results indicate that reactant distribution is enhanced in the bioinspired porous structure due to interconnected porous pathways. Still, the pores are also susceptible to retain a small amount of water, and a coating of hydrophobic material can greatly reduce this issue. A similar study by Afshari et al. discusses the implementation of metal foam-based flow field design to provide humidified conditions necessary for PEMFC's membrane for optimal operation. The study emphasizes that the metal foam-based flow channel humidifier is better than a conventional humidifier because of its low cost, easy manufacturability, and better ratio of water recovery.

Significant progress has been achieved by working on new FFP designs that deliver the reactant gases uniformly throughout the MEA and improve water management for efficient power production. CFD modeling has proven to be a helpful tool for evaluating nature-inspired designs. However, these designs have to be supported by experimental studies whenever possible. Most bioinspired FFP designs demonstrate superior FC performance over conventional designs by reducing pressure drop and developing more uniform gas distribution, as evident by the literature.

Further performance optimization in bioinspired flow field design is attainable as validated by various research studies by precise adjustment of parameters and slight design variations in the width of the rib, width and depth of the channel, and length of the channel path. Shallow channels instead of deep channels support under-rib convection, resulting in increased and uniform oxygen distribution and hence better overall performance. An increase in rib-to-channel width increases ohmic losses, whereas a decrease in rib-to-channel width results in a larger pressure drop; therefore, the ratio of 1.0/1.0 has been declared as optimal for achieving high current density. A lower length-to-width ratio of the channel prevents significant pressure drop and aids in effective water removal, increasing active area, whereas a higher length-to-width ratio provides better hydration, mechanical support, and uniform current and temperature distribution. The use of tapered stepped or slanted channels is found to improve performance and mass transport but at the expense of pressure drop and flooding. Moreover, contrary to circular ones, rectangular geometries show reduced pressure loss and better fuel utilization but are prone to retain more water.

The nature-inspired CL, structure, and material are reviewed in the following section for further performance improvement.

3. Catalyst Layer

One of the main issues impeding the PEMFC's domination of the clean energy market is its relatively high price. As shown in Figure 7, the use of precious metal, primarily platinum nanoparticles supported on carbon (Pt/C), for the catalysts in the electrode layer (particularly the cathode) contributes more than 30% of the total cost in a FC stack for high production volumes (500,000 units/year). Membranes, bipolar plates, and GDLs are other costly parts that prevent PEMFCs from being priced competitively.

The research for CL biomimicry in the PEMFCs mostly focuses on the development of nonprecious metal-based electrocatalyst materials or so-called platinum metal group-free
(PGM-free) catalysts. Although continuing improvement in PGM-free catalysts activity and stability has been noted in recent years, they are still inferior compared with the Pt-based catalysts. Another approach is to reduce Pt nanoparticle usage in the CLs using unique catalyst support materials with a high surface area. In this section, the available literature on nature-inspired PEMFC catalysts composition and design is reviewed.

The initial investigation of PGM-free catalysts can be traced back to the 1960s and the feasibility study of phthalocyanine-based catalysts for ORR in the cathode of FCs. However, it became clear that the activity and stability of these compounds are considerably lower than Pt-based catalysts in the acidic FCs. Over the years, researchers showed that heat treatment of the macrocyclic compounds supported on carbon, coupled with the development of more inexpensive synthesis methods, allowed the possibility of nonprecious metal catalysts in PEMFCs. After that, the advancement of high-performance PGM-free catalysts as a replacement for Pt for both ORR and HOR in PEMFCs has attracted more attention. Recently, Ballard Power Systems, in collaboration with Nisshinbo Holdings, produced the world’s first nonprecious metal catalyst-based commercial PEMFC stack in 2017. However, we are still years away from an efficient and competitive PGM-free process; specifically needed are improvements to the activity, stability, and durability of these catalysts.

The world around us affords abundant examples of efficient catalytic processes inspirational for developing these alternative nonprecious metal catalytic materials to conform to the requirement of the targeted technological applications. Herein, a brief history highlighting the development of the bioinspired transition metal oxides and metallic complexes of the nitrogen-containing CL in PEMFCs is presented.

### 3.1. ORR Catalysts

Oxygen catalytic activation/reduction reaction in biological systems is widely studied as an attractive example of applications in energy-conversion systems. Cytochrome c oxidase (CcS) is the most understood and deeply researched protein in living organisms that catalyzes 4e oxidation of O₂ (ORR at a very low overpotential. CcS is located in the respiratory chain with the active site of iron (II)-porphyrin. This complex structure, also known as heme, consists of iron and porphyrin bonded with distal side copper oxides.

Mimicking these biological redox processes is considered a promising alternative to the PGM-based catalysts in PEMFCs. Most of the bioimitated noble metal-free ORR catalysts rely on transition metal (Fe, Co, Mo, Mn, and Cu) complexes in an appropriate chemical atmosphere such as nitrogen-containing ligands, so-called porphyrin, to replicate the enzyme environment.

One example of molecular structures of metalloporphyrin-based ORR catalysts is shown in Figure 8. Inspired by the exclusive characteristic of its active site, a new catalyst is designed and developed by Cao et al., using iron phthalocyanine (FePc) molecules anchored on pyridine-functionalized carbon nanotubes (Py-CNTs). Although the half-wave potential (E½) value of FePc–Py–CNT composite is lower than that of commercial Pt/C in an acidic environment, the results indicate its potential for practical applications. The FePc–Py–CNT composite structure and its linear sweep voltammogram results are shown in Figure 9.

An overall review of the different aspects of reduced Pt loading and Pt-free catalysts, including the bioinspired CL structure, is provided by Morozan et al. The reader is referred to the study for further information about these metalloenzyme-based cathode layers.

A laccase is a group of multicopper oxidase enzymes that can catalyze O₂ reduction, similar to the process that occurs with the cytochrome oxidase. More detailed information about the similarities and structures of these enzymes can be found in the literature. In this regard, numerous copper complexes as the ORR electrocatalyst have been investigated based on this biological system. This research field presents appealing approaches for synthesizing multinuclear copper-based complexes to imitate the natural rates of ORR for reasonable performance and stability at PEMFC operating conditions.

Thorun’s work on the stability and electrochemical performance of carbon black-supported multinuclear copper complexes over a wide range of pH provides the basis for understanding the efficiency of laccase for ORR. The reduced ORR overpotential for the proposed copper-based catalysts suggests a promising approach for developing ORR catalysts with an FC application.

The ORR performance of the CL regarding the laccase enzyme molecular structure is studied by Wang et al. using a rotating ring-disk electrode (RRDE) technique. This catalyst was synthesized by pyrolysis of the mixture of graphene oxide (as the support of the catalytic sites) and Cu₃₋₁₋₁,₁₀₋₁ phanathroline (Cu(phen)) at different temperatures ranging from 600 to 950 °C. An imperfect coordination configuration of the copper (II) active site surrounded by metal Cu nanoparticle (Cuₙ) and the N ligand embedded in the graphene skeleton results in the optimal atmosphere for the electronic bonding of O₂ to Cuₙ ions, consequently improving the catalytic activity of the catalyst.

In 2015, high stability and catalytic performance of an immobilized multicopper-coordinated complex on the surface of reduced graphene oxide through the biomimetic approach of laccase enzymatic catalytic reaction was reported by Xi et al. A schematic of such a multicopper-centered complex covalently

![Figure 8. Molecular structures of metalloporphyrin-based ORR catalysts. Reproduced with permission. Copyright 2017, Springer Nature.](image-url)
bonded to the surface of reduced graphene oxide is shown in Figure 10. Cyclic voltammetry results show a superior selectivity of the 4e\(^-\) versus 2e\(^-\) oxygen reduction process compared with mononuclear copper complexes. However, this catalyst does not provide the same long-term stability in acidic media as in alkaline media.

In another work, the electrochemical behavior of a \(\pi\)-stacked dinuclear copper complex on a multiwalled CNT (Cu\(_2\)(BPMPPyrene)/MWCNT) electrode over a wide range of pH, mimicking the active site of copper oxidase, is reported by Gentil et al.\(^{[133]}\) The electrode design exhibits ORR electroactivity with an onset potential of +0.57 V at pH 4 and 0.71 V at pH 9 versus reference hydrogen electrode. However, the outcome confirms that the optimal ORR activity of this type of complex appears in basic conditions. A noble metal-free-bioinspired FC is assembled using a bioinspired dinuclear copper complex and the Ni-based complex as cathode and anode, respectively, as shown schematically in Figure 11. The maximum power density of 0.15 mW cm\(^{-2}\) at 0.25 V with an open-circuit voltage of 0.6 V at pH 4 indicates the proficiency of this strategy in designing PGM-free FCs with improved activity.

Although significant progress has been achieved in the development of PGM-free catalysts, these catalysts deal with critical challenges that hinder their commercialization, such as poor stability, low intrinsic catalytic activity, and insufficient active site density.\(^{[134]}\) The reliability of hemes is still a question in the acidic environment of PEMFCs as the stability of these enzymes is limited to neutral alkaline conditions. Cobalt porphyrins, on the other hand, show more stability in an acidic environment. Still, this catalyst promotes the first step of the 2e\(^-\) reduction reaction to produce corrosive hydrogen peroxide rather than the second step to produce water.

In recent decades, studies show that cofacial cobalt porphyrins, "...face-to-face geometry with small lateral displacement between porphyrin subunits..." and overlapping \(\pi\)-orbitals can provide 4e\(^-\) ORR process.\(^{[135–137]}\) From this perspective, templated polymerization of cobalt center bis-porphyrins on the MWCNT is researched via Hay coupling.\(^{[138]}\) These porphyrin structures link together and to the CNTs through multiple \(\pi\)-stacking interactions. Figure 12 shows a schematic representation of the nanotubes coated with the porphyrin polymer. RRDE measurements under acidic conditions display improved catalytic performance and an average value of 4 for transferred electrons.

The natural ascorbate oxidase (AO) and galactose oxidase (GO) are other types of enzymes that conduct the 4e\(^-\) and 2e\(^-\) ORR at the Cu cluster center with an N-heterocyclic-coordinated and an O-coordinated phenoxyl ligand, respectively. The different 2e\(^-\) and 4e\(^-\) ORR activities correspond to the dissimilar electron-donor ability of the two Cu center active site structures in GO and AO. In this respect, adjusting the electron-donor abilities of the Cu-based active centers would benefit a selective 2e\(^-\) / 4e\(^-\) ORR.\(^{[139–141]}\) Coupling Cu to the O- or N-doped carbon for mimicking oxidase-like functions demonstrates maximum selectivity of 84.0% and 97.2% for 2e\(^-\) and 4e\(^-\) electrocatalytic ORR activities, respectively.\(^{[142]}\)

3.2. HOR Catalysts

Hydrogenase enzymes are among the most efficient biocatalysts for the oxidation of molecular hydrogen (H\(_2\)) into protons, an electron, and vice versa. These enzymes containing iron and/
or nickel metal centers as the active sites are potent sources of inspiration to design and fabricate catalysts as an alternative to platinum-based catalysts in energy-related applications.\cite{143-149}

One of the biomimetic approaches to synthesize such CLs was published in 2009 by Goff et al.\cite{144} This work considers the structure of bis-diphosphine nickel complexes. In this process, the electrode is fabricated by covalently bonding the nickel complexes to the MWCNTs to take advantage of their high surface areas and facilitate higher catalyst loading. Experimental results confirm the potential of the biomimetic nanomaterial in PEM technology.

Later, the same group of researchers\cite{150} present a straightforward approach to functionalize MWCNTs by introducing noncovalent \( \pi-\pi \) stacking interactions between CNTs and immobilized metal coordination complexes. The catalytic activity of these new molecular engineered materials for \( \text{H}_2 \) uptake exhibited good stability in the presence of carbon monoxide (CO), as shown in Figure 13, a critical improvement for Nafton-based PEMFCs. Furthermore, specific \( \text{H}_2 \) oxidation current densities (i.e., relative to the mass of immobilized catalyst, including metal and ligands) for the Ni-based materials (250 mA cm\(^{-2}\) mg\(^{-1}\)) are comparable with the commercial Pt-based one (200 mA cm\(^{-2}\) mg\(^{-1}\), 0.5 mgPt cm\(^{-2}\)).

Later on, work by Tran et al.\cite{151} studies the bis-diphosphine nickel complexes, a synthetic material obtained through mimicking the hydrogenase’s active sites, at the anode of a PEMFC. Inferior OVC value (0.85 V) was found compared with the Pt/Pt PEMFC (1.0 V), implying the need for further improvements for ink formulation as well as for the tridimensional structure of the electrodes. Subsequently, the 3D structuring of the nickel bis-diphosphine CL exhibits similar and even a superior surface area and performance results compared with SOA platinum-based electrodes (0.05 mgPt cm\(^{-2}\)).\cite{152}

In 2017, a study by Gentil et al.\cite{153} on the electrocatalytic activity of single-walled CNT-supported nickel bis-diphosphine complexes for the anodic reaction in PEMFCs shows satisfactory stability over a broad pH range and maximum power density of 14 mW cm\(^{-2}\) at 0.47 V.

A comparison of catalytic properties between the bioinspired molecular catalyst (synthetic ligand molecules bonded to a metal) of [Ni\((\text{P}^\text{Cy}_2\text{NArg}_2)\text{C}_2\text{]+}\) complex and [NiFe]-hydrogenases is conducted by Macia et al.\cite{154} for the HOR. The results demonstrate superior overpotential and catalytic performance for Ni catalyst at lower pH, whereas the hydrogenase enzyme outperforms the synthetic Ni catalyst at neutral pH. Moreover, immobilized Ni complex shows appropriate stability in the presence of CO, which empowers the utilization of lower-purity \( \text{H}_2 \) as a fuel.

### 3.3. Conductive Polymer

A hierarchical nanoarray electrode structure is proposed by Xia et al.,\cite{16} inspired by the metalloenzymes molecular structure, an...
active metallic center surrounded by dual-function charge transport media. Vertically aligned nanowire arrays are developed directly on a GDL of FCs through electrochemical polymerization of Nafton and polypyrrole mixture. These nanowires are then decorated with Pt nanoparticles using a wet-chemistry method followed by a reduction step in hydrogen atmosphere. In this copolymer configuration, the sulfonate group of Nafton and polypyrrole functions as the protonic and electronic conductor, respectively. At the same time, interspaces between the nanowires facilitate the continuous transport of reactant and product. A schematic of the fabrication of this electrode is shown in Figure 14. This electrode architecture with simultaneous electron/proton transfer shows comparable PEMFC performance with a conventional Pt–C catalyst with three-times higher Pt loading. The durability test also shows about 37% degradation of the cathode for the novel electrode, whereas 64% for the conventional cathode with Pt–C for 5000 cyclic voltammetry cycles.

Plant hormones are a class of biomolecules with the ability to conduct protons in biological systems. Parthasarathy et al.\cite{155} showed the compatibility of indole-3-acetic acid, a plant hormone of the auxin class, in Nafton matrix without impacting the chemical structure and thermal stability of the polymer membrane. As Nafton/hormone composite suffers from mechanical stability issues, additional studies on the effect of these composite dispersions as the binders in the CL of the PEMFCs produced hormone-modified catalyst layers (both cathode and anode) by adding various proportions of indole-3-acetic acid versus the weight of Pt in the CL. The obtained bioinspired CL demonstrated a higher electroactive Pt area and improved H₂/O₂ PEMFC performance, based on the electrochemical characterization.

3.4. Catalyst Support

The performance and electrochemical activity of a CL depend not only on the catalyst and polymer composition but also on the support material’s structure and properties. Selecting suitable support material with a high surface area delivers more anchoring sites to bind the catalyst nanoparticles. The bioinspired carbon-based support structure with good electrical conductivity, as well as mechanical and chemical stability in the PEMFC operating environment, is reviewed in this section.

Figure 13. a) Schematic representation of bioinspired nickel bis-diphosphine catalyst complex. b) Evolution upon repeated cycling of the H₂ oxidation current density versus normal hydrogen electrode. Reproduced with permission.\cite{150} Copyright 2011, John Wiley and Sons.

Figure 14. Schematic of the fabrication of the electrode arrays. a) Synthetic scheme of the electrode arrays via electrochemical polymerization, b) Pt loading, and c) MEA fabrication. Reproduced under the terms of the CC BY license.\cite{36} Copyright 2015, The Authors, published by Springer Nature.
Work by Wang et al. shows a hierarchical structure design of a PEMFC CL, mimicking the configuration of a pine tree. A carbon nanofiber mat with Pt nanowires is fabricated through annealing electrospun polyvinylpyrrolidone titanium dioxide (PVP-TiO$_2$) film. These Pt nanowires are further embellished by porous bismuth coating to modify the surface atomic structure and catalytic activity. Experimental testing demonstrates higher specific surface area, easier reactant diffusion, and enhanced catalytic activity toward formic acid electro-oxidation compared with a pure Pt surface.

Kong et al. study the mimicry of the marine sponge lattice architectures as carbon–carbon composite support for Pt-based FC catalyst. This mesoscale design configuration is synthesized using two different carbon morphologies consisting of carbon black and MWCNTs at different compositional ratios. The size of the deposited Pt nanocrystal fabricated with wet chemistry is controlled by the carbon matrix pore size and porosity. The correlation between the mesoscale morphology of the carbon support, deposited Pt nanoparticle size, and electrochemical activity results in the optimum Pt size of 5–6 nm for electrochemical performance.

The porous lamellar structure of tunas’ gills produces efficient oxygen exchange due to the large relative surface area, as shown in Figure 15. Yao et al. investigate microporous graphene nanoplatelets (GNPs)-based Fe/N/C electrocatalysts for ORR activity, inspired by this biological structure. The GNP-based Fe/N/C catalysts are fabricated through pyrolysis of highly dispersed polyimide and molten salt mixtures. Scanning and transmission electron microscopy (SEM and TEM) images confirm lamellar morphology and the highly microporous structure of the prepared samples. Good catalytic performance and stability due to increased O$_2$ adsorption and desorption (O$_2$ diffusion) and increased ORR kinetics resulting from improved microporosity of GNP structure are obtained via the RRDE technique. This highlights its potential for PEMFC applications.

Nature owns many more examples of material properties and structures that can be integrated into the current PEMFC technology to overcome ongoing challenges such as high catalyst cost and poor durability. Extensive research efforts are needed to accomplish this objective. In the following section, a brief review of bioinspired electrolytes for PEMFC applications is presented.

4. Membrane (Electrolyte)

The PEM in the PEMFC conducts hydrogen ions from the anode to the cathode. The PEM material is one of the most important in the operation of the cell. It not only defines the mechanism for ionic transportation, but also determines the materials used for other components and limits the temperature of the FC. Table 2 shows some of the polymers used for PEMFCs along with the chemical structure. Nafion and polymers of similar composition (e.g., Aquivion) are the most common polymers in use. The polymer used determines the mechanism for how the hydrogen ions are conducted as different membranes will have a different medium used to transport ions. The polymer composition and fabrication process defines the membrane backbone and side chains. The proton carrier is the transport medium, such as water, acid, or ionic liquid. The polymer is paired with the transport medium to provide an optimal ionic conductivity and stability of the membrane.

PEMFCs have a broad operating temperature range up to 200 °C. Research has shown that the choice of membrane determines the temperature range in which the cell can operate effectively. This is mainly due to the membrane humidity requirement. Thus, the distinction between low-temperature (LT) and high-temperature (HT) PEMFCs is common. LT-PEMFCs operate at temperatures below 100 °C, and the conduction is dependent upon the presence of water. The operation is optimized for temperatures between 60 and 80 °C. HT-PEMFCs'
operation ranges between 120 and 180 °C, where PEMFCs can cogenerate heat and power and eliminate liquid water that causes mass transport issues while avoiding the extreme degradation present at 200 °C[13,27,160].

Perfluorocarbon sulfonic acid (PFSA) is traditionally the most common membrane for LT-PEMFC. It is almost exclusively paired with a PGM catalyst, Pt. polybenzimidazole (PBI), using H₃PO₄ as the transport medium, and is popular for HT-PEMFCs. Sulfonated polyether ether ketone (SPEEK), sulfonated polyimine (SPI), and sulfonated polysulfone (SPSU) using water as a transport medium are also utilized for HT-PEMFCs[128].

Acid–base composites as anhydrous (low-humidity) proton conductors, having adequate conductivity operating at intermediate (100–200 °C) or subzero temperature, have attracted much interest in FC technologies as well. Connected acid and base groups work as a proton donor and acceptor, respectively, allowing the protons to transport between donor and acceptor through the proton-hopping process (Grotthuss mechanism).[165–169]

Traditional electrolyte membranes for PEMFCs are synthetic. While their properties were thoroughly researched to generate the best efficiency for the cell, synthetic membranes are expensive and can also have negative environmental impacts.[170] In addition, the most commonly implemented synthetic membrane for PEMFCs (Nafion) is toxic to humans.[171,172] The combination of these three negative properties is the driving force behind suitable replacements. Bioinspiration in these membranes takes what was once considered biowaste and repurposes[37] it for use in sustainable energy products.

One of the most researched materials as an alternative for the membrane is chitosan. It is produced as waste from shrimp farms as it is a natural polymer found inside crustaceans’ shells. It is thermally stable below 150 °C and acts as a cation exchange membrane in an acidic solution.[37] The crosslinking reaction of chitosan with sulfuric acid is shown in Figure 16. A study done by Lupatini and Schaffer[37] reports values up to 1.9 × 10⁻² S cm⁻¹ for the ionic conductivity of crosslinked chitosan in sulfuric acid. This ionic conductivity is lower than the conductivity of Nafion, 6.2 × 10⁻² S cm⁻¹ at 100% relative humidity (RH),[173] but is still comparable as they are within the same order of magnitude.

Kalaiselvimary and Prabhu[174] showed a combination of sulfonated chitosan combined with polyethylene oxide (PEO) and graphene oxide. Graphene oxide enhances electrical properties and uses its 2D structure to form the lattice of the composite. An optimum ionic conductivity of 10⁻² S cm⁻¹ at 303 K is reported for this composite membrane, indicating its potential for PEM FC applications.

While the use of chitosan in composite membranes is one way to control the effective parameters, the work of Schaffer et al.[175] characterizes the specific properties within the polymer that controls the proton conductivity. Deacetylation (DD) and molar mass (Mₘ) have a large impact on conductivity but in opposing trends. High DD results in more amine groups that are favorable for proton conduction. The levels of DD and Mₘ present are inversely proportional, so for a high DD, Mₘ is low. This low Mₘ value results in high crystallinity, which limits some of the necessary polymer properties for absorbing water. This study also finds that lower DD and higher Mₘ yielded the best ionic conductivity. The ratio of DD and Mₘ also impacts the thickness of the membrane and water absorption at varying temperatures. If the membrane is too thick, the crystallinity increases and the membrane has

| Name | Structure |
|------|-----------|
| Nafion/PFSA | ![Structure](image1) |
| PBI | ![Structure](image2) |
| SPEEK | ![Structure](image3) |
| SPI | ![Structure](image4) |
| SPSU | ![Structure](image5) |

Table 2. Common PEM polymer structures. Reproduced with permission.[159] Copyright 2013, Elsevier.

Figure 16. Crosslinking reaction between chitosan and sulfuric acid. Reproduced with permission.[37] Copyright 2018, Springer Nature.
lower water absorption. As temperature increases, the membrane can absorb more water due to the increase in pore size.

Another polymer being investigated is agar produced by red seaweed, which makes it both naturally abundant and nontoxic. Agar is of interest to researchers because it has high chain flexibility and possesses multiple cations coordinating oxygen sites. Each unit has both hydroxyl and ether structure, which will enhance ionic conductivity properties. Boopathy's study of a bio-PEM based on agar/NO3 shows a maximum ionic conductivity of 1.44 \times 10^{-7} \text{ S cm}^{-1} at 303 K, which is achieved at a composition of 40:60 agar to the NH4NO3 ratio. This reported ionic conductivity is an order of magnitude lower than Nafion (0.074 S cm\(^{-1}\) at 300 K\(^{176}\)), so likely, more research would be needed to have this biopolymer used commercially.

A publication by Yanbu and Matsui\(^{177}\) discusses the progress on block copolymer thin films. In this study, inspired by muscle fiber, a copolymer of polystyrene (PS) and polyvinyl catechol (PVCa) is saturated with silver ions (Ag). Films with and without Ag are compared to show the differences in geometry, composition, structures, conductivity, etc. The amphiphilic nature of copolymers has an impact on performance in humidified gas, which is an important aspect of function in PEMFCs. Figure 17 shows conductivity testing on membrane samples with and without Ag doping, depicting conductivity increase by a factor of 10 using Ag nanoparticles. However, the highest recorded conductivity was in the order of 10^{-4} \text{ S cm}^{-1}, which is still well below the conductivity of Nafion.

Studies on the proton transport channels in living organisms such as Halobacterium or cytochrome oxidase complex reveal a rate of 10^5 proton conduction per second along one amino acid-filled channel at the potential drop of 100 mV. Protons exchange and conduct within the amino acid molecule due to the presence of proton donors (a carboxyl group) and acceptor groups (an amino group). In this context, Leem et al.\(^{177}\) investigate the performance of amino acid-modified membranes. The pores of polyethylene terephthalate (PET) and polycarbonate (PC) membranes are filled with SiO2 nanoparticles garnished with amino acid molecules such as L-lysine, as shown in Figure 18. Although the new membranes deliver lower FC power output, improvements in this process are very likely, considering the early-stage development of these types of membranes.

Following the same idea, Wang's study of a hybrid composite membrane using a bifunctional SiO2 nanofiber in Nafion matrix for PEM applications incorporates an amino acid molecule chain onto the surface of SiO2 nanofibers to construct efficient proton-conducting pathways, followed by impregnation with Nafion solution. A schematic diagram of the modified Nafion membrane with biofunctional SiO2 nanofiber (cysteine) is shown in Figure 19. The effects of different polar groups (–SO3H, –OH, and –NH2) on the development of proton-conductive pathways are investigated by applying different types of amino acids (cysteine, serine, lysine, and glycine). These bio-mimicry membranes offer superior thermal and dimensional stability, water uptake, and proton conductivity to the Nafion membrane with the maximum value is 0.2424 S cm\(^{-1}\) at 80 °C.

Finally, in terms of the bioinspired solutions for the anhydrous acid–base composite proton exchange membranes, He et al. reported an artificial acid–base pair inspired by mussel bio-adhesion. Polydopamine-modified graphene oxide (DGO) sheets are fused into a sulfonated poly (ether ketone) (SPEEK) matrix to form the nanocomposite membrane. The interfacial electrostatic attractions between the sulfonic acid groups in SPEEK chains and –NH2/-NH– groups in DGO sheets generate acid–base pairs that provide a long-range low-energy-barrier pathway for proton hopping. The result of a PEMFC single-cell test for such a membrane with SPEEK/DGO wt% of 5 demonstrates an open circuit voltage of 0.96 V, a 47% increase in maximum current density, and a 38% increase in maximum power density than the SPEEK control membrane.

Although significant progress has been achieved to increase the efficiency of the PEMs, further improvement in electrolyte conductivity and thermal and mechanical stabilities of the current PEMs is required. Nature-inspired designs and bio-based membrane materials show great potential to benefit PEMFC development and improve its efficiency and performance.

5. Conclusion

PEMFC technologies are increasing in popularity, especially in portable power sources. As the awareness for sustainable power sources increases globally, green energy research and use will continue to rise. As PEMFCs are already commercialized, there are existing standards for the materials and designs for the primary components. However, the integration of bioinspiration has been demonstrated to enhance the cells in a variety of aspects.
Regarding FFPs, extensive research shows that designs found in nature can optimize mass transport, water management, and the performance of FCs. The designs inspired by veins in leaves, lungs, and fractal structures showed improvements between 5% and 40% depending upon configuration and other cell properties. It can be logically concluded that these patterns in nature have evolved over a long time to optimize their function in mass transport and hence can be used to improve this aspect of FCs.

Bioinspiration is useful in FC CLs and membrane design as well. Focusing on PGM-free catalysts, several options are shown to be promising, for example, mimicking the structure of cytochrome c oxidases and multicopper oxidase enzymes for the cathode and hydrogenase enzyme for the anode of the PEMFC. These approaches offer promise for reducing the use of costly platinum catalysts. While nature-inspired PGM-free materials can reduce cost, these biostructured designs can also increase the performance of the CL. Similar to the CL, the membrane can use bioinspiration in the form of biopolymers (chitosan and agar) and proton transport channels in living organisms such as Halobacterium to replace the current membrane layer used in PEMFCs.

The integration of bioinspiration is further along with flow fields versus other components. Bioinspired CLs and electrolyte membranes require further research before they can adequately compete with the current materials and replace them commercially. These biocomponents can improve performance while decreasing cost and toxicity. All these approaches will help propel PEMFCs as green energy power-generating sources.

Figure 18. Scheme of a) amino acid molecules attached to the silica nanoparticle surface illuminating the transmission of protons through the amino acid network. b) A membrane channel filled with silica nanoparticles (larger spheres) with the surface-attached amino acid network (smaller spheres). Reproduced with permission.[179] Copyright 2008, American Chemical Society.

Figure 19. Schematic diagram of the modified Naion membrane with biofunctional SiO$_2$ nanofiber (cysteine). Reproduced with permission.[180] Copyright 2017, Elsevier.
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Conflict of Interest
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Sara Pedram is currently a Ph.D. student in the Materials Science and Engineering Department at the University of Connecticut. Hitherto, she worked as a researcher at the Chemistry and Chemical Engineering Research Center of Iran (CCERCI) and Pierre and Marie Curie University in France, focusing on plasma surface treatment of polymeric membranes for water treatment. At UConn, she works on the fabrication and characterization of newly designed bioinspired fuel cells as green energy power-generating sources.

Mariah Batool is currently pursuing her Ph.D. in materials science at the University of Connecticut under the Foreign Fulbright Scholarship Program. She worked with Hyundai Engineering Ltd. for an Oil & Gas Refinery up-gradation project, which fueled her interest in clean energy research. She has experience working on the fabrication of solid oxide fuel cells and designing phase-change materials during her M.S. Her current research involves investigating state-of-the-art image-processing methods for materials characterization for use in polymer electrolyte membrane fuel cells.

Kirsten Yapp is a graduate research fellow at the University of Connecticut and works with the National Institute for Undersea Vehicle Technology. Currently, she is working on her M.Sc. in advanced manufacturing for energy systems and was previously a part of the Naval Research Enterprise Internship Program. Her primary research focuses on Li-ion batteries and polymer electrolyte membrane fuel cells.

Leonard Bonville is currently a research specialist for the Center for Clean Energy Engineering at the University of Connecticut, focusing on catalyst fabrication and testing for both performance and stability. Previously, he was Vice President of Engineering at International Fuel Cell (IFC), Division of United Technologies, where he managed more than 120 engineers and scientists in the development and application of the IFC fuel cell database for the manufacture and improvement of IFC fuel cell products.
Jasna Jankovic is an assistant professor in the Materials Science and Engineering Department at the University of Connecticut. Prior to this appointment, she worked as a senior research scientist at the Automotive Fuel Cell Cooperation, Burnaby, a Canada-based joint venture of Daimler AG and Ford Motor Company. At U.Conn., Dr. Jankovic's research is in the areas of advanced characterization of clean energy systems, including fuel cells, electrolyzers, and batteries, fabrication using electrospinning, and application of biomimicry in clean energy systems.