Modeling and Simulation in Fuel Cell Development

By **ED FONTES** and **HENRIK EKSTRÖM**

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INTRODUCTION

One possible way to reduce greenhouse gas emissions and slow down climate change is to replace internal combustion engine vehicles with electric vehicles powered by batteries and fuel cells. Electric vehicles also offer the advantage of reducing emissions of pollutants in densely populated areas, improving air quality for their inhabitants. For vehicles driven by electricity from renewable energy sources, the greenhouse gas emissions are very small.

Electric vehicles that operate with fuel cells offer several advantages compared to electric vehicles that use batteries. They can reach a higher energy density (especially for heavy vehicles); exhibit greater efficiency when the electricity used to charge batteries comes from hydrogen; and, compared to battery recharging, can be refueled without requiring very high power from the electric grid.

The main limitations of fuel cells for electric vehicles are their manufacturing cost, limited service life, and relatively low power density compared to that of battery powered electrical vehicles. (Ref. 1).

LIMITATIONS

The three abovementioned limitations all boil down to the microscopic design of the active layer in the oxygen-reducing, gas-diffusion electrodes: the cathode in the fuel cell. While there are other aspects of the design that are important, the design of the active layer is a key aspect of the fuel cell's performance.

Minimizing the manufacturing cost of fuel cells is hindered by the cost of the catalyst used in the active layer: platinum. While the manufacturing cost of almost everything else in the fuel cell can be reduced, it is hard to lower the cost of platinum. Thus, in order to minimize the manufacturing cost, it is crucial to develop active layers that require a very low catalyst load — without reduced performance.

Service life is limited by different degradation mechanisms, such as proton reduction, platinum dissolution, carbon corrosion, formation of radicals that attack the pore electrolyte in the active layer, adsorption of impurities on the catalyst sites, and accumulation of impurities in the pore electrolyte (Ref. 2).

The limitation in power density is mainly caused by the limited catalytic activity of the cathode: the oxygen electrode. This activity can be increased by higher catalyst loading. However, this also means a higher cost and a shorter service life, since a higher load requires a higher current density. (Part of this limitation can be worked around by using several fuel cell stacks in parallel.)
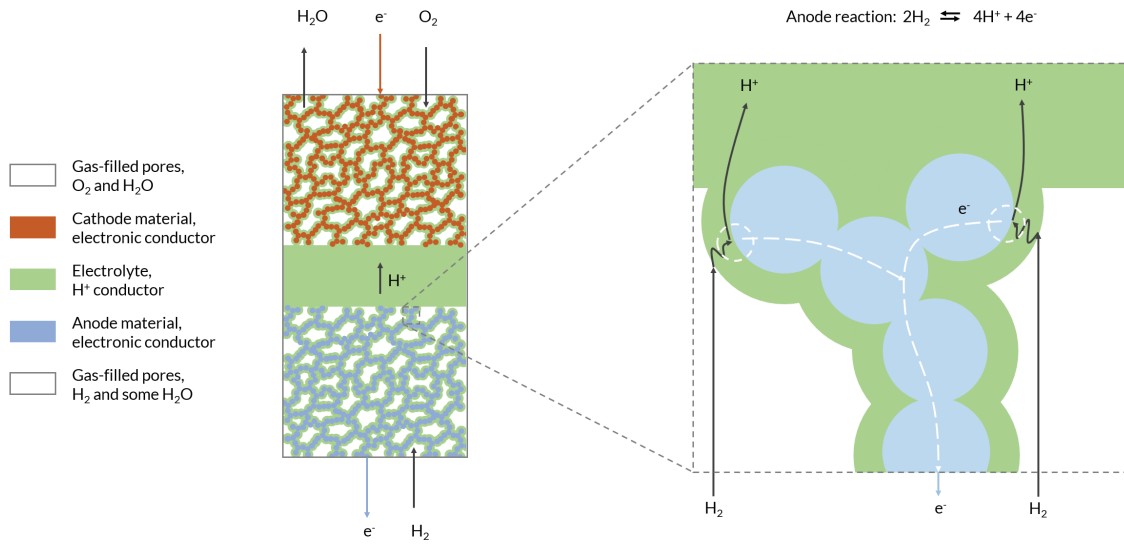
THE ACTIVE LAYER

In order to improve the design of the active layer of a fuel cell, engineers and scientists have to understand the fundamental transport phenomena, electrode kinetics, thermodynamics, electrolyte chemistry, and catalytic surface activity involved in this layer's charge transfer reactions. These factors have to be understood at the microscopic level.

Let us look closer at the transport and reaction processes that may occur in the active layer in a fuel cell electrode. We will examine a proton exchange membrane fuel cell (PEMFC), which is the strongest fuel cell candidate for use in electric vehicles. The reactions at the anode and cathode are:

$$2H_2 \rightleftharpoons 4H^+ + 4e^- \quad at\ the\ anode$$

$$4H^+ + O_2 + 4e^- \rightleftharpoons 2H_2O \quad at\ the\ cathode$$
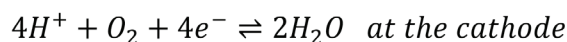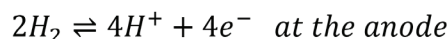
The electrons released at the anode are conducted by the electronic conducting electrode material to the outer circuit. In the outer circuit, the electrons are conducted over a load to the cathode. The protons (hydrogen ions) are transported in the electrolyte and the separator to the cathode. At the cathode, the protons react with oxygen from the cathode gas, electrons are received from the external circuit, and water is formed.

Figure 1 shows a schematic drawing of the processes at the anode's active layer. Note that the active layer contains the anode material with the catalyst (blue), pore electrolyte (green), and gas-filled pores (white). The pore electrolyte consists of a proton-conducting polymer that has been infused into the porous electrodes. Hydrogen from external gas channels is transported in the gas-filled pores, dissolved in the pore electrolyte, and transported through a thin film of pore electrolyte to the active catalyst site (white-dashed circle). Then the hydrogen is oxidized to produce hydrogen ions (protons) at the active site. The electrons released during oxidation are conducted through the anode material to the outer circuit.

FIGURE 1 The processes that occur in the active layer in a PEMFC anode.
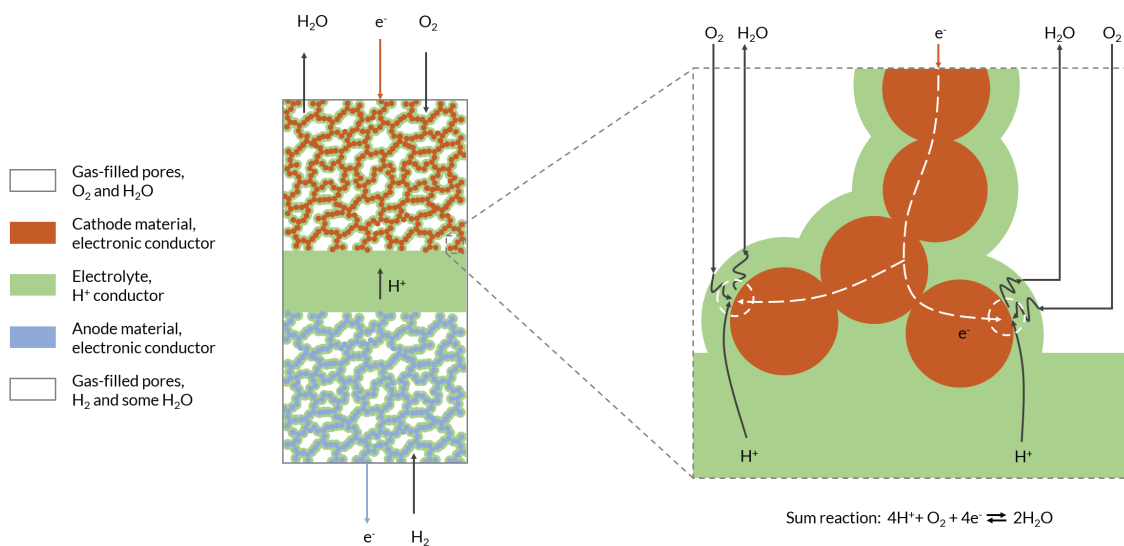
FIGURE 2 The transport and reaction processes that occur at the cathode.

Once the hydrogen ions have migrated to the cathode, they may react with oxygen at the active sites at the cathode (see Figure 2). Oxygen is transported through the gas-filled pores in the cathode and then through a thin film of pore electrolyte. At the active site, oxygen and protons receive electrons over the active circuit and through conduction in the cathode electrode material to produce water. The reaction at the active site depends on the local electrode potential in relation to the equilibrium, local oxygen concentration, and local water activity. The formed water molecules can be transported out of the cathode as vapor or liquid water. Precipitation of liquid water in the gas-filled pores may occur, depending on the pore structure and local water vapor partial pressure.

The migration of hydrogen ions from the anode to the cathode also depends on the water content of the membrane. Each hydrogen ion drags a few water molecules over the membrane electrolyte from the anode to the cathode.

So, we have transport in the gas phases in both electrodes, in the pore electrolyte, and of water and protons in the membrane. We also have kinetic expressions for the charge transport relations at the active sites. We may also add processes that describe the deterioration of solid particles, for example, through oxidation. The model equations describing these processes are coupled and depend on each other.

The solution of the model equations reveals the losses in the different reaction and transport processes. For example, if water precipitates in the gas-filled pores at the cathode, the transport of oxygen gas through the gas-filled pores slows dramatically. If the model predicts a deterioration of the particles — for example, by oxidation that causes them to detach from the pore electrolyte or from the rest of the electrode material — then the electrons cannot be transported to and from the active sites, causing losses in performance.

The contributions of the different processes to the losses in the cell are difficult to measure experimentally, particularly because they all occur at different time scales. For example, transport in the pore electrolyte is several orders of magnitude slower than transport in the gas-filled pores. Ionic and electronic conduction are extremely fast processes. Charge transfer reactions can be slow (cathode) or relatively fast (hydrogen) — but are relatively fast compared to the transport in the pore electrolyte. Using models in combination with experiments is of great help in describing the contributions of the different processes to the losses in the cell. For example, transient techniques, such as current interrupt and impedance spectroscopy, can be modeled and then compared to and validated by experiments. The contributions of the different losses can be tracked throughout the different operating conditions that occur as the cell ages .

The principle of impedance spectroscopy is quite simple. An average voltage (V_0) is applied with a small sinusoidal perturbation over time. As a consequence, a corresponding sinusoidal current is obtained in response to the voltage perturbations (see Figure 3).

The current response may have a shift in time (δt) compared to the voltage. A shift can be caused by processes that delay the response of the current to the sinusoidal perturbation in voltage. For example, at low frequencies, slow processes like mass transport may be responsible for such a shift, while fast processes may be able to perfectly keep up with the voltage perturbations. At high frequencies, slow processes will only "see" the average voltage; they will not be able to respond to the voltage perturbations. Instead, fast processes, such as the reaction kinetics, will be responsible for the shift in the response at high frequencies. Additionally, the amplitude of the response (δI) may also vary at different frequencies.

By sweeping over different frequencies, the impedance spectroscopy method is able to separate processes with different time constants. The time shift and the amplitude of the current response to the voltage perturbation are reflected in the complex impedance, where a shift in time is reflected in the imaginary part of the impedance and the absolute value of the impedance reflects the proportionality of the response.
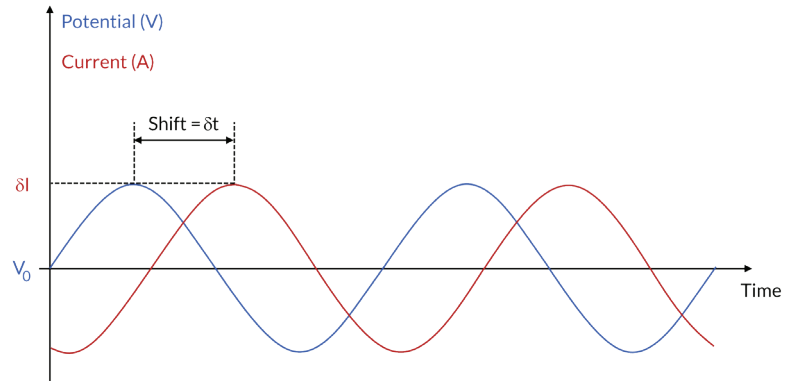

FIGURE 3 A perturbation in electrical potential over the cell results in a current response.
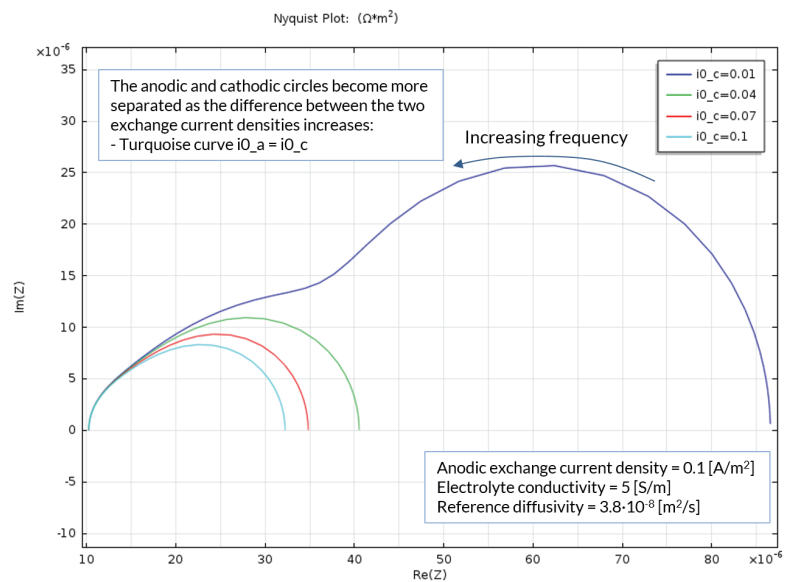
FIGURE 4 Results from an impedance spectroscopy simulation of a fuel cell unit cell. The activity of the cathode catalyst is varied in four different frequency sweeps.

For a fuel cell, the impedance response gives insight into several fuel cell properties and processes. At high frequencies, short time scale processes, such as capacitance, electrochemical reactions, and local resistances, affect the impedance. On the other hand, at low frequencies, phenomena such as the diffusion in the pore electrolyte contribute to the impedance. Frequency sweeps can be carried out at different polarizations of the fuel cell to investigate phenomena at different loads. By combining parameter estimation using experimental data with the modeling of impedance spectroscopy, we can then accurately describe transport and reaction properties in fuel cells during operation at different loads. Over time, the models and experiments may reveal the source of deterioration of a cell. This implies that the proper actions in design and material selection can be taken in order to increase performance and slow deterioration.
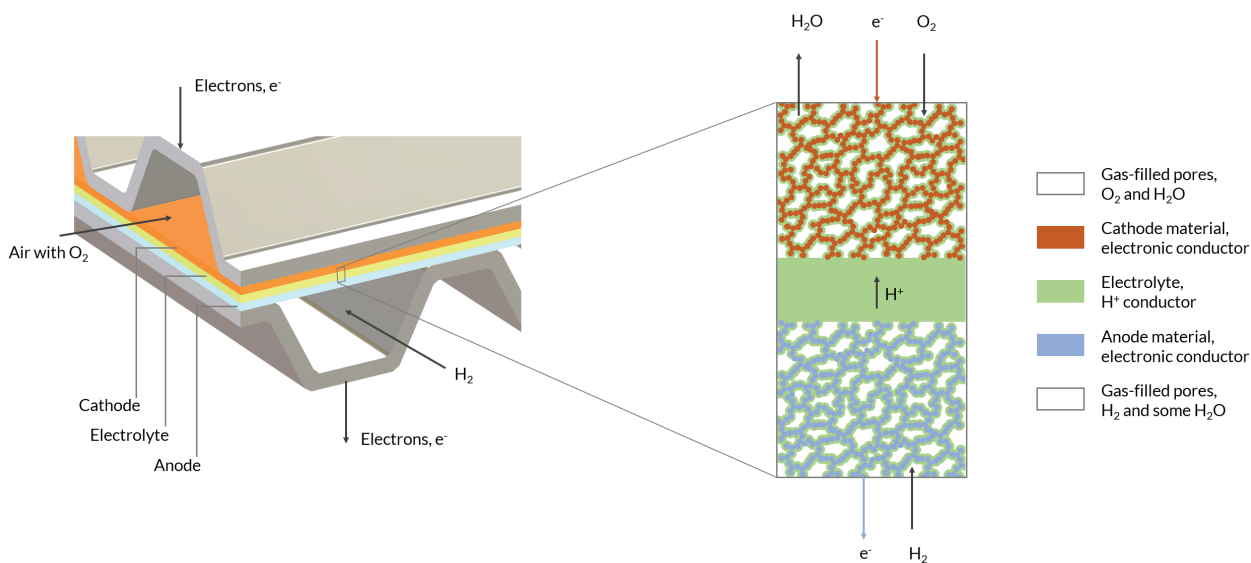
FIGURE 5 A unit cell may interface with a part of the membrane electrode assembly as well as the metallic plates that serve as the current collectors and feeders.

Figure 4 shows a so-called Nyquist plot of the results from a high-fidelity model of a fuel cell unit cell. This is a small experimental cell where the conditions can be controlled very accurately. The model shows the effect of the reaction kinetics at the active sites of the cathode. As the catalyst deteriorates, the cathodic semicircle (the impedance) grows. However, there is no change at very high frequencies, since the kinetics is not able to react to very fast perturbation. The ohmic losses in the cells are constant, making it possible to separate other losses, such as transport losses.

Modeling and simulation offer a very effective, unique way of studying these processes. Although it is very hard to measure the phenomena that occur in the active layer during operation these phenomena can be modeled in detail, and their impacts at the macroscopic level can also be modeled in so-called multiscale models (Ref. 2). Experiments can be designed in order to verify the implications of the microdesign.

One example is the connection of physics-based models for impedance spectroscopy with measurements as shown in Figure 4. This allows scientists and engineers to separate processes in different time scales, such as diffusion (slow) and current conduction (fast). Studying factors that limit the response to perturbations at different time scales may reveal which process that is limiting the performance at the microscale (Refs. 3–5).

Once these processes are understood, more direct methods may be used. An example is the innovation of using ordered porous structures in the active layer to lower tortuosity. Ordered structures may increase the transport of reactants, improve access to the catalyst surface, and yield a uniform current-density distribution in the active layer (Refs. 1, 6). The results may be
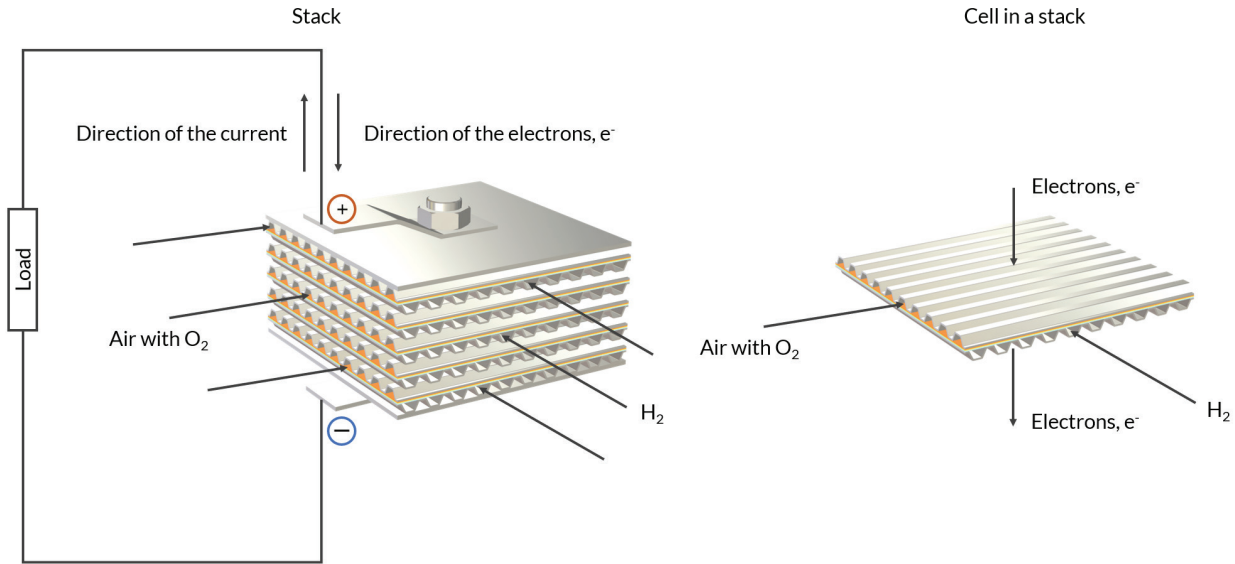
improvements in performance, neither requiring a higher platinum load nor causing the accumulation of water or harmful byproducts that may deteriorate the performance of the active layer over time.

Modeling and simulation can be used for more than exploring new ideas; once a good design has been innovated, mathematical models can be used to further optimize design and operational parameters. This development is iterative and can be made almost automatic by gathering data from operation.

THE FUEL CELL UNIT CELL AND THE FUEL CELL STACK

Each microscopic part of a fuel cell in a fuel cell stack is affected by the configuration of each cell and of the whole stack. This implies that the microscopic details cannot be studied in isolation; they have to couple to the macroscopic factors that may impact a cell. The fuel cell unit cell simulation treats a hydrogen channel and an oxygen channel, with the electrodes and the membrane in between (Figure 5).

Each unit may be part of a stack connected to an external circuit. The units may be equipped with straight parallel channels (Figure 6) or with serpentine channels (Figure 7). Modern fuel cells, like in the Toyota Mirai's (Ref. 7), may also have a more complex structure for the oxygen (air) gas feed. Here, a louver-like structure allows for water to flow down with gravity, away from the cathode, while oxygen can flow upward. In this way, the transport of liquid water in the oxygen electrode is enhanced, which also enhances the transport of oxygen to the active layer. Liquid water in the porous electrode hinders the transport of oxygen. With this design, Toyota has

Stack

Cell in a stack

Direction of the current   Direction of the electrons, e⁻

Load

Air with O$_2$

Electrons, e⁻

Air with O$_2$

H$_2$

Electrons, e⁻

H$_2$

FIGURE 6 Left: Stack with cross-flow configuration; i.e., the oxygen and hydrogen channels run in a 90-degree angle relative to each other. Right: One cell in the stack. Figures 1, 2, 5, and 6 progress from the microscale to the stack scale.
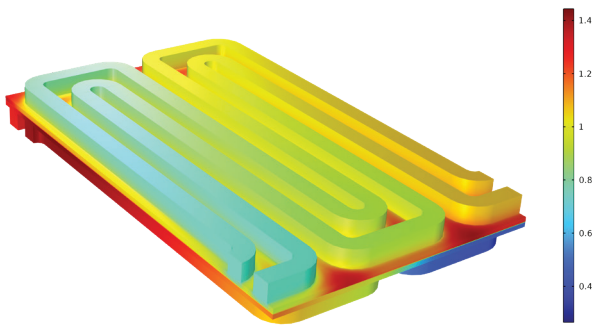
FIGURE 7 Relative humidity in a section of a serpentine channel PEMFC, in contrast to the straight channel configuration in Figure 6. The section is small enough to include all of the relevant transport and reaction processes in the fuel cell in a high-fidelity model.

considerably enhanced the performance of its fuel cell (Ref. 7). Figure 8 shows a schematic of how this louver structure might look.

High-fidelity models can be coupled and incorporated into models of a fuel cell unit cell, stack, or whole system, including the electric drivetrain of the vehicle (the load in Figure 6). This requires reduced and fitted lumped models that are automatically updated using more detailed models when a new range of operation is encountered. In this way, modeling and simulation can also be used to determine the state and remaining service life of a fuel cell system (Ref. 3).

Liquid H$_2$O

Anode

Liquid H$_2$O

Liquid H$_2$O

Electrolyte

Cathode

H$_2$ O$_2$

H$_2$ O$_2$
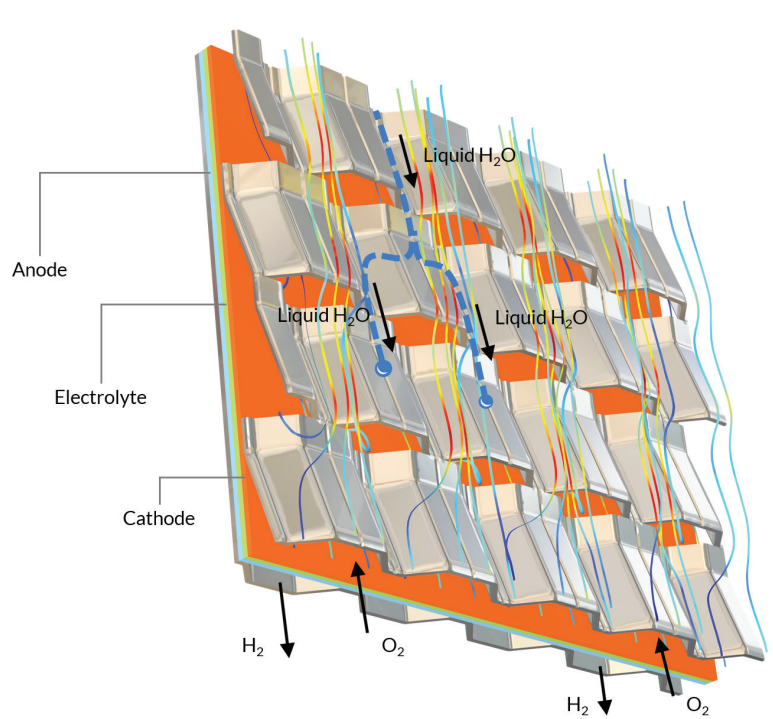
FIGURE 8 A louver-like structure allows for water to flow down and oxygen (air) to flow up. In this way, the transport of liquid water away from the cathode is enhanced and does not obstruct the transport of oxygen in the electrode (Ref. 7).

CONCLUDING REMARKS

The development of fuel cells and the design of the active layer will continue to lead to lower platinum loads, longer service life, and increased power density. To a great extent, this progress is due to the understanding, innovation, and optimization tools offered by modeling and simulation. These tools also allow for an optimal combination of fuel cells, batteries, and supercapacitors in order to deliver energy and power density at a low cost and with maximum service life. Modeling and simulation will continue to be important in the work of reducing greenhouse gas emissions and other pollutants from cars, buses, and trucks.

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