

Improved PEM fuel cell electrodes by controlled self-assembly

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PEM fuel cell electrodes are complex nanostructures containing catalyst, proton and electron conductors, and pores. Their properties are strongly influenced by the materials used, the ratio of proton to electron conductors, and the pore characteristics. Furthermore, the sizes and orientations of these nanoseparated phases control the transport properties. This article describes work that investigates the self-organized nature of electrode nanostructures, and methods to improve electrode properties by controlled self-ordering. It also discusses the significant benefits this seems to offer in terms of greatly reduced platinum use and hence cost of fuel cells.

The main limitation for large-scale application of proton-exchange membrane (PEM) fuel cells and direct liquid fuel cells are costs. The price of fuel cell generated electrical power is still too high for a variety of applications. Cost reduction is, therefore, an important task for the emerging fuel cell industry. Cost reduction can be realized by economy of scale effects in production, and by more efficient use of material. In particular, cost savings can be realized in the electrodes of PEM fuel cells and the electrodes of direct liquid fuel cells by more efficient material use.

Investigation by high-resolution scanning electron microscopy (HR-SEM) of electrodes has disclosed that oriented nanostructures could be created from randomly packed electrodes. If this orientation is in the right direction, it can be highly beneficial to the performance of the fuel cell. A substantial power increase was measured. The mechanism of self-ordering will be discussed here, as well as methods to improve electrode properties by controlled self-ordering.

If we analyze transport of gases, water, electrons and protons in a PEM fuel cell, we find that transport takes place in different directions depending on species, and the part of the fuel cell observed.

- *Electrons:* Electrons are conducted through the fuel cell plates, mainly in the through-plane direction (perpendicular to the

surface). In the gas diffusion layer (GDL) electron transport is in-plane (parallel to the surface) as well as through-plane, while in the electrodes the electrons mainly move in a direction perpendicular to the membrane.

- *Protons:* Proton transport can only be observed in the membrane, and in the electrodes. Transport direction is in both materials through-plane, perpendicular to the membrane surface.
- *Fuel and oxidant:* The fuel (hydrogen) and oxygen flow through the gas distribution channels in the plates. This transport is mainly in-plane, parallel to the membrane. From these channels the gases flow or diffuse in the GDL. Transport of these gases is in-plane as well as through-plane. In the electrodes the gases diffuse through the pores mainly in a direction perpendicular to the membrane. From these pores the gas molecules diffuse through the proton conductor to the catalyst.

Transport of electrons, protons and gases is shown schematically in Figure 1.

Although improvements and cost reductions are required in all parts of the PEM fuel cell, the most important can be realized in the electrodes by improving transport properties. However, improving the transport properties in a PEM electrode is not an easy task. Improving one

property normally leads to degradation of other transport properties. If, for example, we increase the porosity to improve gas transport, the proton and electron resistances will increase because less material is available for conduction.

State-of-the-art electrodes

Before we try to improve the transport properties in PEM electrodes, we need to know the microstructure of these electrodes.

PEM electrodes typically contain catalyst, electron conductor, proton conductor and pores. The catalyst, in general platinum or platinum-containing alloys, is finely dispersed on a suitable electron conductor. Typically this electron conductor is some kind of carbon black. Proton conduction is realized by incorporating a proton-conducting polymer like Nafion™. Pores are obtained by formulating an 'ink' with a volatile (solvent) part and a very high solid content. Pores form during drying such an ink, after the solid particles have reached their maximum packing density.

Figure 2 shows schematically how a typical electrode is prepared.

The structure (morphology) of the membrane-electrode assembly (MEA) can be

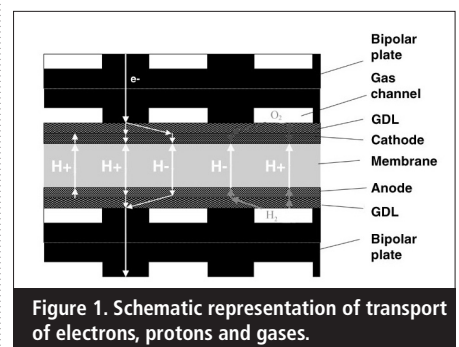
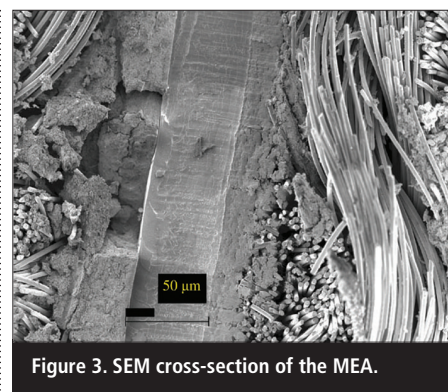
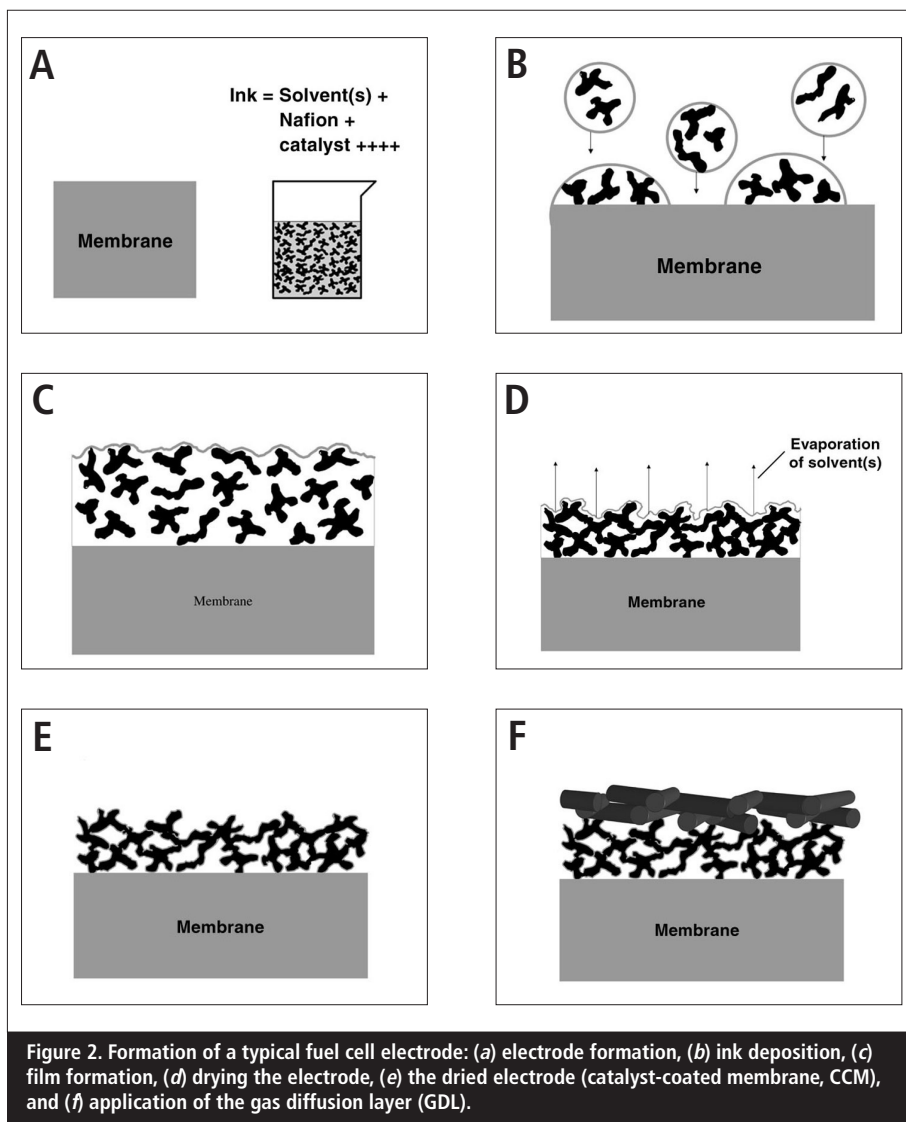


Figure 1. Schematic representation of transport of electrons, protons and gases.



increased we can see through the Nafion coating, and see that the agglomerates are built up from basic carbon particles with a size of approximately 30 nm, and that these particles are coated with finely dispersed platinum (EDX analysis). The size of the platinum particles is 2–5 nm, while the size of the carbon crystals in the 30 nm particles was measured by X-ray diffraction (XRD) to be 2 nm (Figure 7).

It can be concluded from these images that a large part of the platinum catalyst is located deep inside the agglomerates, and is therefore hardly accessible for hydrogen or oxygen.

Based on the HR-SEM photographs, we expect that improvements in catalyst utilization are possible by improving the access of reactants to the buried catalyst in the agglomerates. From the analyses of the transport directions of protons, electrons and gases, and the random morphology seen in the HR-SEM images, we assume that it must be possible to reduce the impedance in the transport direction by orientation of the proton conductor, electron conductor and pores in the main transport direction.

The optimum size of conductors and pores can be calculated/estimated from computer modelling. From calculations we know that the diffusion distance of gases through the proton-conducting polymer should not be more than approximately 10 nm. Based on these assumptions and calculations, the ideal electrode

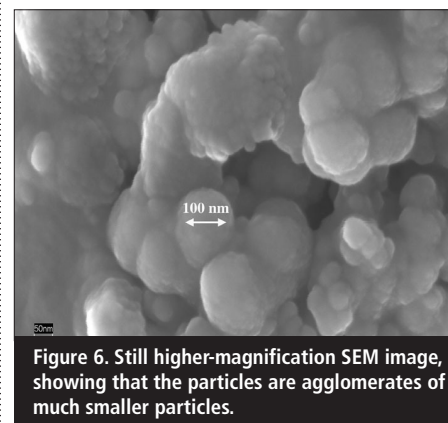
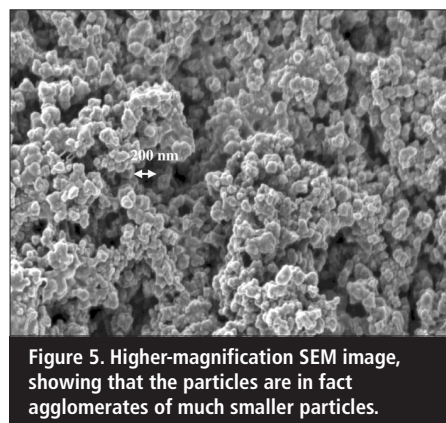
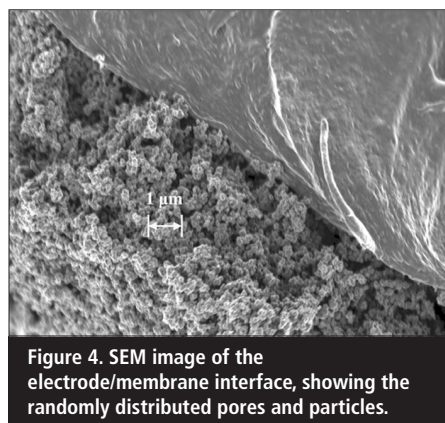
studied by high-resolution scanning electron microscopy (HR-SEM).

Figure 3 shows a cross-section of a PEM fuel cell MEA. The thickness of the membrane (Nafion 112) in this Figure is 50 μm .

If we view the electrode/membrane interface (Figure 4), we see randomly distributed pores and particles.

At higher magnifications it can be seen that the particles are in fact agglomerates of much smaller particles, and that these agglomerates are coated. The composition of this coating was analyzed by energy dispersive X-ray analysis (EDX), and the presence of a Nafion skin was proven (Figures 5 and 6).

If the electron energy in the HR-SEM is



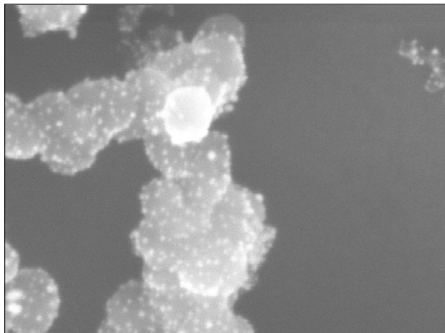


Figure 7. Higher electron energy in the HR-SEM shows that the agglomerates are built up from 30 nm carbon particles, and that these particles are coated with finely dispersed platinum.

can be designed. Figure 8 shows a schematic image of such an ideal electrode structure.

In this ideal electrode the electron conductor is oriented perpendicular to the membrane. At the surface of this electron conductor there is finely dispersed platinum with a particle size of approximately 2 nm. The catalyst-coated, oriented electron conductor is coated with a layer of proton-conducting polymer. The proton conductor is also oriented in a direction perpendicular to the membrane surface.

Because the diameter of the catalyst-coated particles is 30 nm, the optimum diameter of the electron conductor is also 30 nm. A smaller diameter is not possible, because this would damage the carbon support. A larger-diameter, catalyst-coated conductor would lead to poor accessibility of a part of the catalyst. The ideal thickness of the proton-conducting polymer coating on the electron-conducting string is difficult to determine. If the layer is too thin, impedance will be high, while a thick layer of proton-conducting polymer will be a diffusion barrier for the reactants. Based on calculations, a layer thickness of 10 nm seems to be an acceptable compromise.

Realizing the ideal electrode morphology

It was found that under certain conditions the

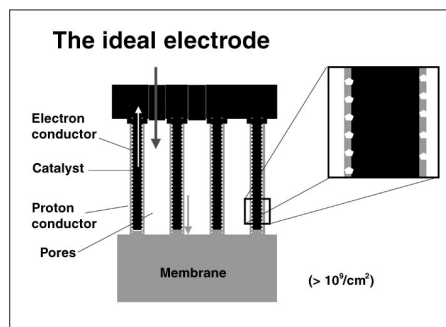


Figure 8. Schematic representation of the ideal electrode.

random morphology in the electrodes could be converted to a morphology that is highly oriented perpendicular to the membrane plane. For this conversion to take place, it is required to have a driving force combined with sufficient mobility in the material. The mobility of polymer structures, such as the PEM electrodes, can be increased by increasing the temperature, by introduction of a low-molecular-weight compound that reduces the glass transition temperature (T_g) of the polymer, or a combination of both.

The required driving force can be applied by applying a sufficiently strong electric field.

The exact conditions are strongly dependent on materials used, their concentration and ratio, pressure, duration and among other things the employed application and drying conditions of the electrode. The required conditions for electrode orientation have to be determined experimentally for each electrode composition.

If the right conditions are applied, the first stage of orientation takes place as can be seen in Figure 9.

This orientation develops over time (Figure 10), leading eventually to a highly oriented morphology as shown in Figure 11. All catalyst particles are located at the interface of the electron conductor (carbon black) and the proton conductor (Nafion), as shown in Figure 12. The thickness of the Nafion layer on the oriented strings does not exceed 10 nm.

Figure 13 shows in the upper-left corner the oriented electrode, and on the right-hand side the membrane/electrode interface. It is clear that the strings of Nafion-coated carbon black are oriented highly perpendicular to the membrane. The diameter of the strings is approximately 50 nm.

Conclusions

The random morphology in ordinary PEM fuel cell electrodes can be converted to a more oriented morphology, as has been shown by high-resolution SEM. The oriented structure is

composed of long chain-like strings of basic carbon particles that are coated with finely dispersed platinum. On the surface of these oriented strings there is a thin layer of proton conductor.

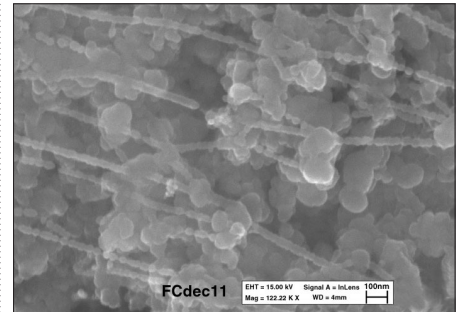


Figure 10. Development of the electrode morphology orientation with time.

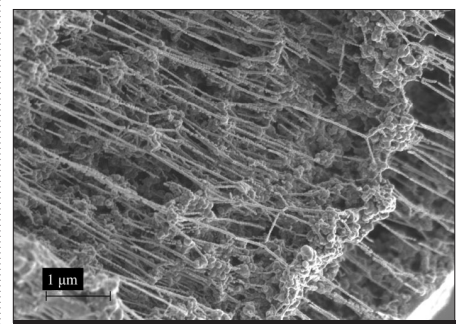


Figure 11. Highly oriented electrode morphology.



Figure 12. All catalyst particles are located at the interface of the electron conductor (carbon black) and the proton conductor (Nafion™).

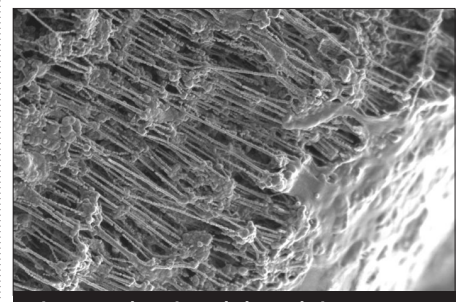


Figure 13. The oriented electrode is at upper-left, and the membrane/electrode interface is on the right-hand side. The 50 nm diameter strings of Nafion-coated carbon black are clearly oriented highly perpendicular to the membrane.

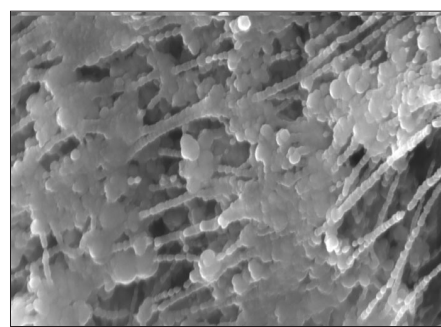


Figure 9. First stage of orientation of the electrode morphology.

On the basis of these photographs it is assumed that all the platinum in these strings is active, or at least can be active. The requirement of direct contact of the catalyst with a proton conductor and an electron conductor, and location of the catalyst within a short distance from a gas-filled pore, seems to be fulfilled.

Platinum utilization in these oriented areas is expected to approach 100%. High catalyst utilization can be used to reduce platinum loading to perhaps 20% of conventional loading levels, without sacrificing performance. Such a reduction in platinum loading would mean a breakthrough in cost reduction for such fuel cells. The proton conductor and the electron conductor are clearly oriented in the transport

direction of both species. This is assumed to result in the minimum resistance.

Cell voltage increases of up to 20% after 'treatment' have been measured.

More research is required to better quantify the effect of orientation on the fuel cell performance.

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