Modeling of Electrochemical Cells: Proton Exchange Membrane Fuel Cells

HYD7007 – 01

Lecture 04. Overview of transport processes in PEMs

Dept. of Chemical & Biomolecular Engineering
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Lecture Outline

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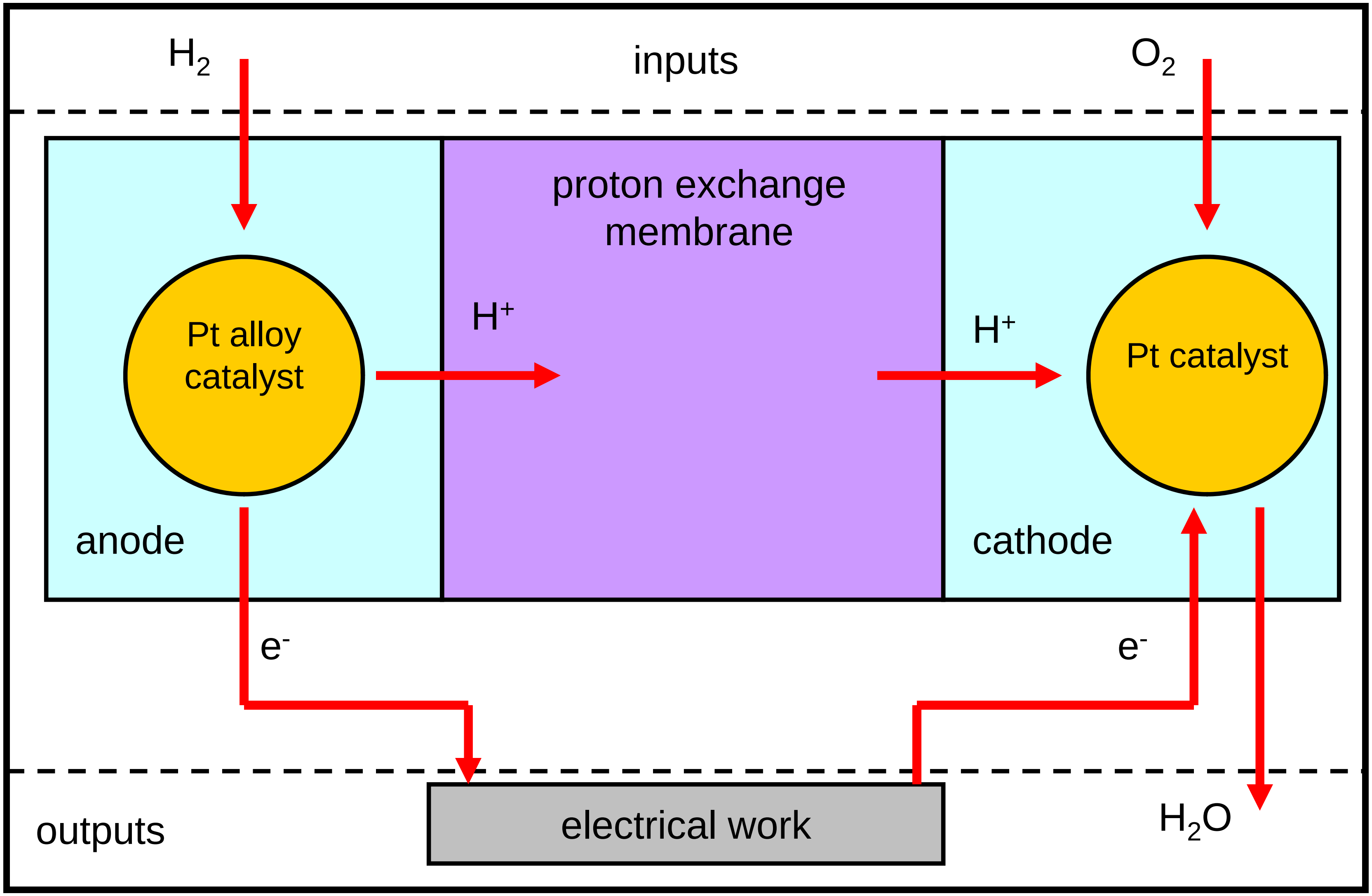
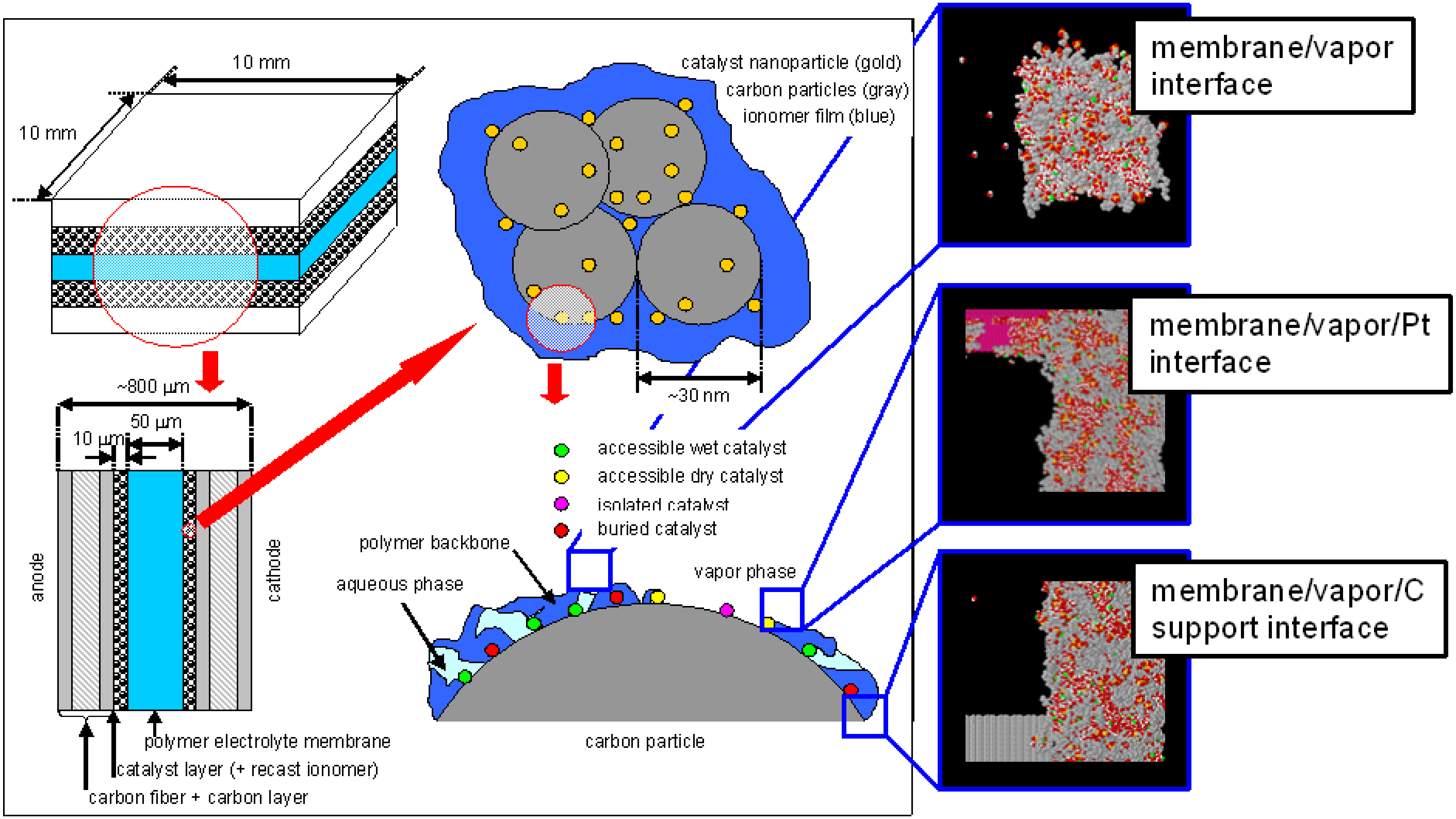
- Review of Macroscopic Structure
- Water Management
- Elementary Steps in Proton Transport
- Relationship between diffusivity and conductivity

how fuel cells work: conceptual level



Overview of Structure

A membrane electrode assembly from the macroscale to the molecular scale



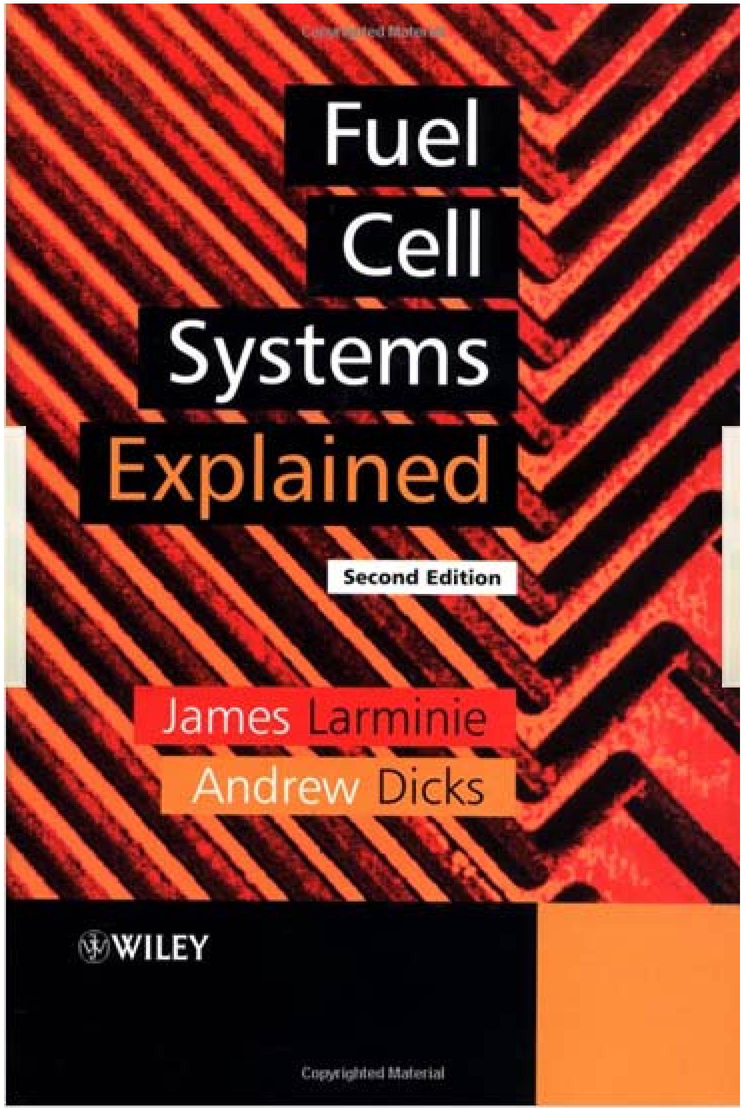
Water management

A good source for a more detailed discussion is

Fuel Cell Systems Explained

By
James Larminie & Andrew Dicks

Wiley, 2nd Edition, 2003



Water management

Water is required in order for the membrane to conduct protons. However, if there is too much water, the electrode will be flooded. The catalyst particles will be submerged beneath a layer of water. Since the diffusivity of molecular hydrogen through water is much lower than the diffusivity of molecular hydrogen through a gaseous phase, the presence of too much water in the electrode represents a significant mass transfer barrier to molecular hydrogen getting to the catalyst surface.

Water management

Sources of water.

Figure 4.10
page 77,
Larminie and Dicks.

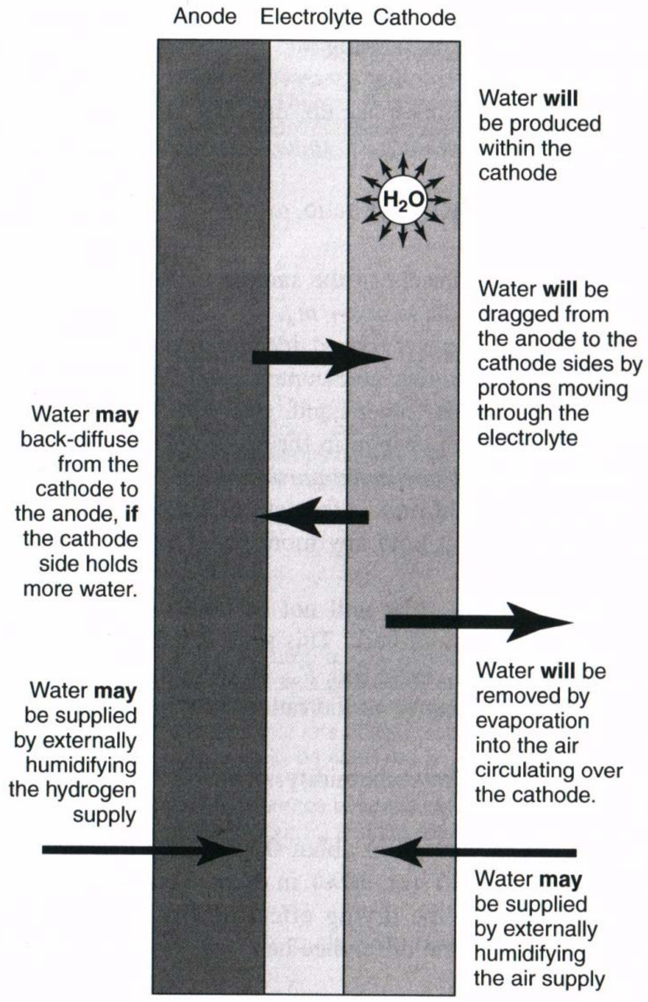


Figure 4.10 The different water movements to, within, and from the electrolyte of a PEM fuel cell.

Water management

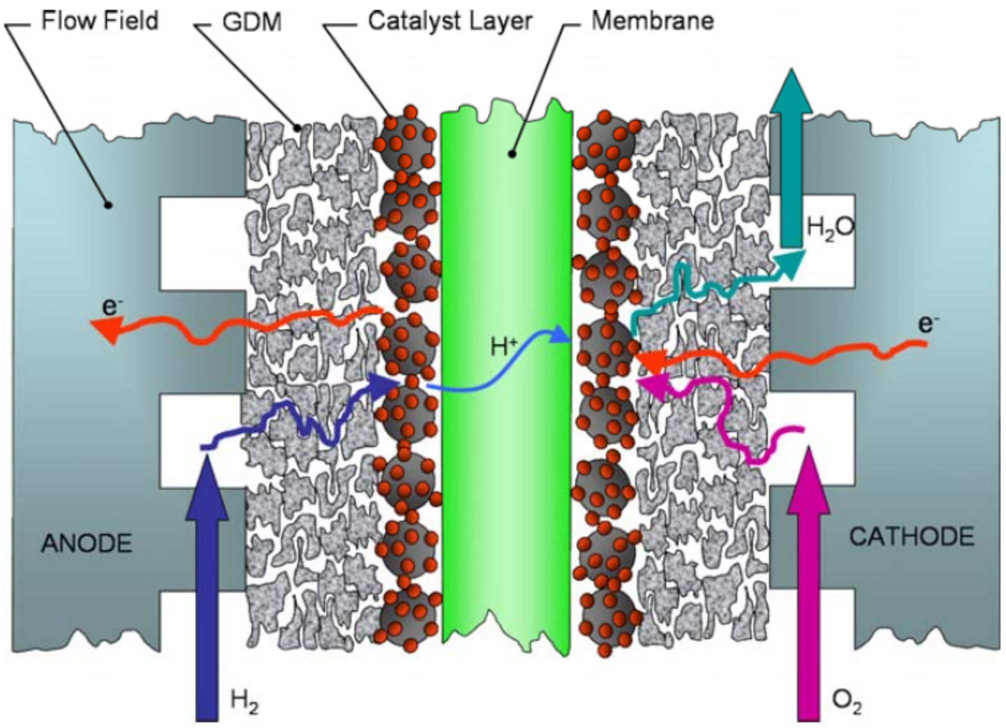
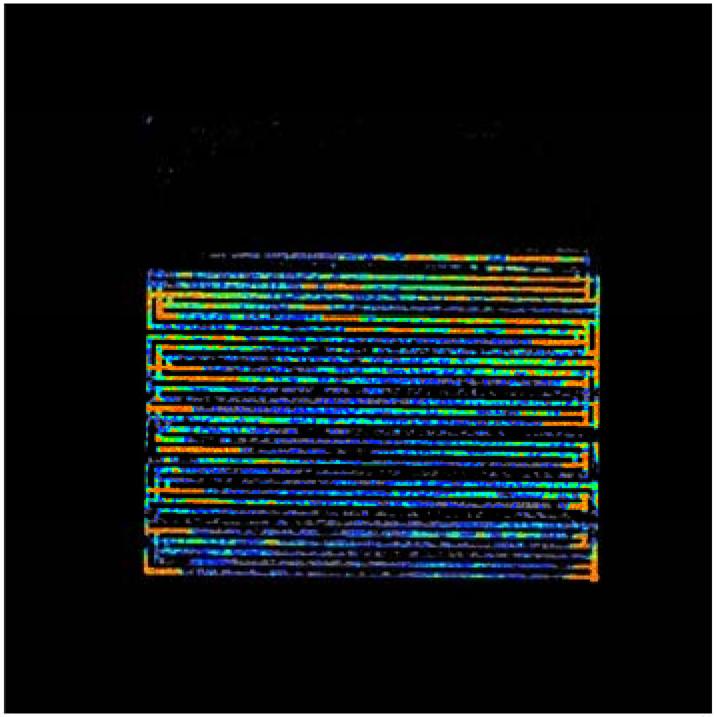


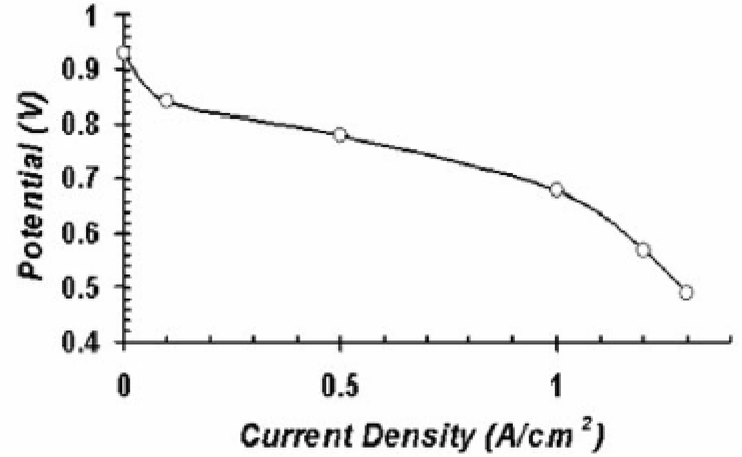
Fig. 1. Key components of a PEM fuel cell (not to scale). Descriptions of individual components are given in the text.



Neutron tomography can be used to image the water distribution within fuel cells. Here we see that water (red) collects in the corners of the manifold in the bipolar plate that is distributing the humidified fuel. (Image is normal to plane of membrane.)

T.A. Trabold et al. / International Journal of Heat and Mass Transfer 49 (2006) 4712–4720

Water management



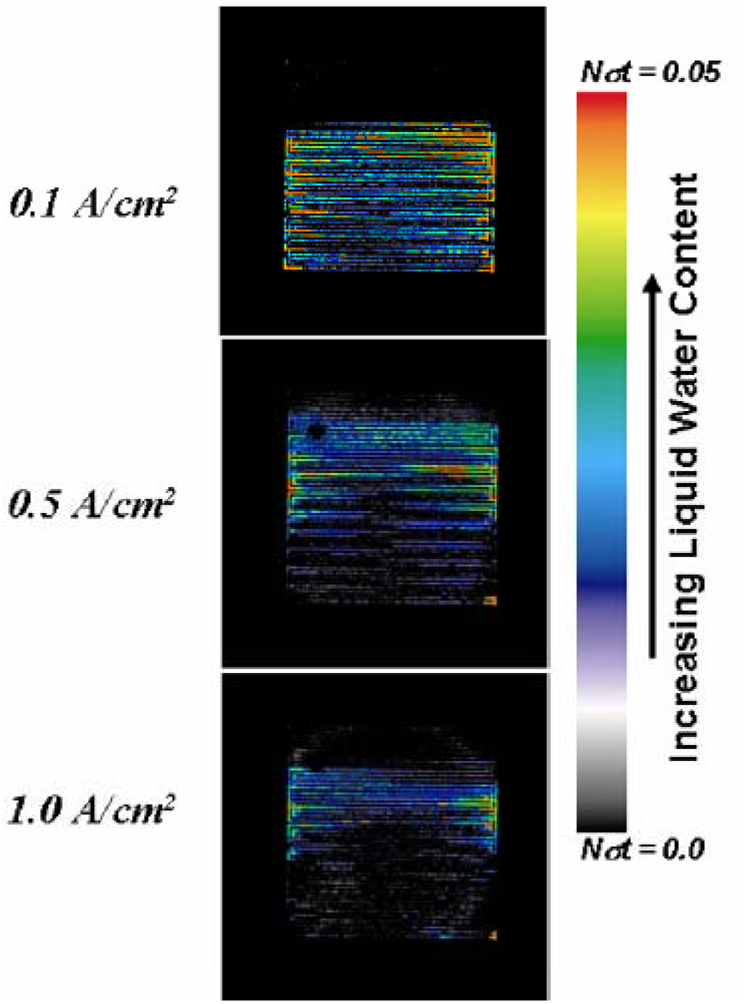


Fig. 10. Fuel cell polarization curve and averaged channel water images at three current densities (80 °C, 270 kPa, 100% inlet relative humidity, anode/cathode stoich = 2/1.3).

T.A. Trabold et al. / International Journal of Heat and Mass Transfer 49 (2006) 4712–4720

Water management

Models provide profiles of water normal to the plane of the membrane.
The anode is drier than the cathode, where the water is produced.

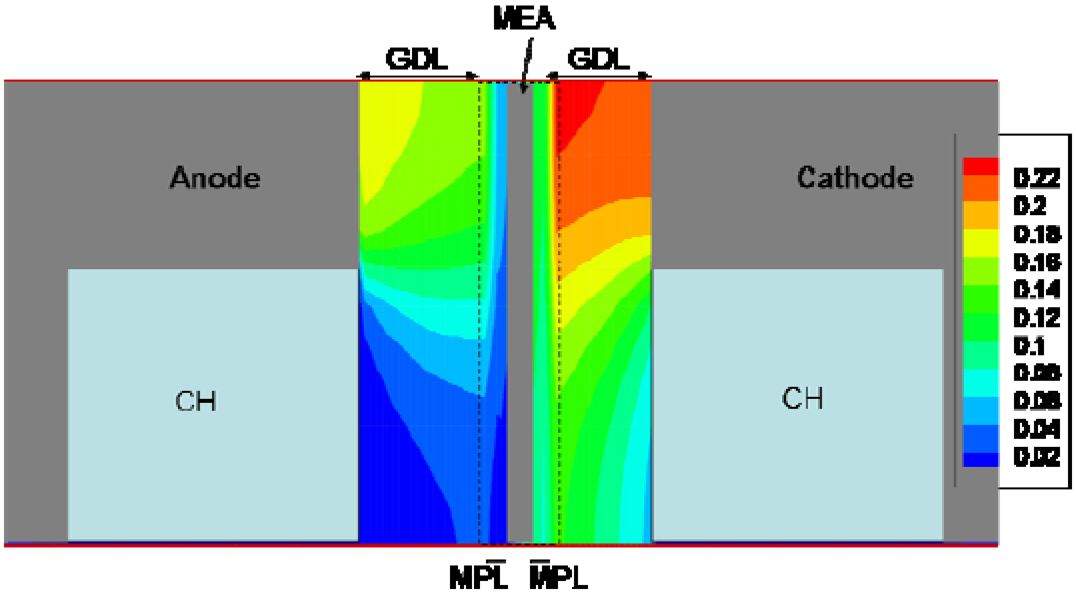
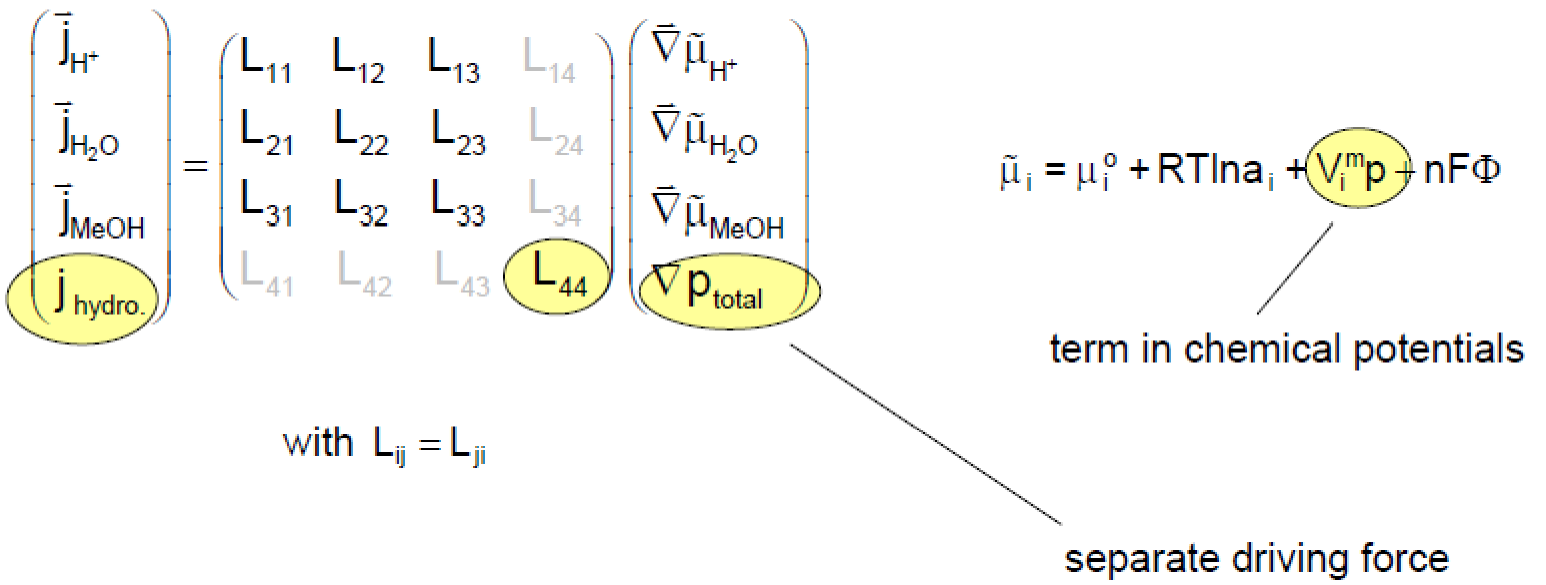


Figure 7. The contours of the liquid water within the MPL and GDL predicted from a 2-D simulation of fuel cell operation at 0.65 V, 1 A/cm^2 and 40 °C.

Wang and Chen, ECS Transaction, 2010.

Water management

diffusion and hydrodynamic flow



$$\begin{pmatrix}\vec{j}_{H^+}\\ \vec{j}_{H_2O}\\ \vec{j}_{MeOH}\\ j_{hydro.}\end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} & L_{14}\\ L_{21} & L_{22} & L_{23} & L_{24}\\ L_{31} & L_{32} & L_{33} & L_{34}\\ L_{41} & L_{42} & L_{43} & L_{44}\end{pmatrix}\begin{pmatrix}\vec{\nabla}\tilde{\mu}_{H^+}\\ \vec{\nabla}\tilde{\mu}_{H_2O}\\ \vec{\nabla}\tilde{\mu}_{MeOH}\\ \nabla p_{total}\end{pmatrix}$$

$$\tilde{\mu}_i = \mu_i^o + RT\ln a_i + V_i^m p + nF\Phi$$

term in chemical potentials

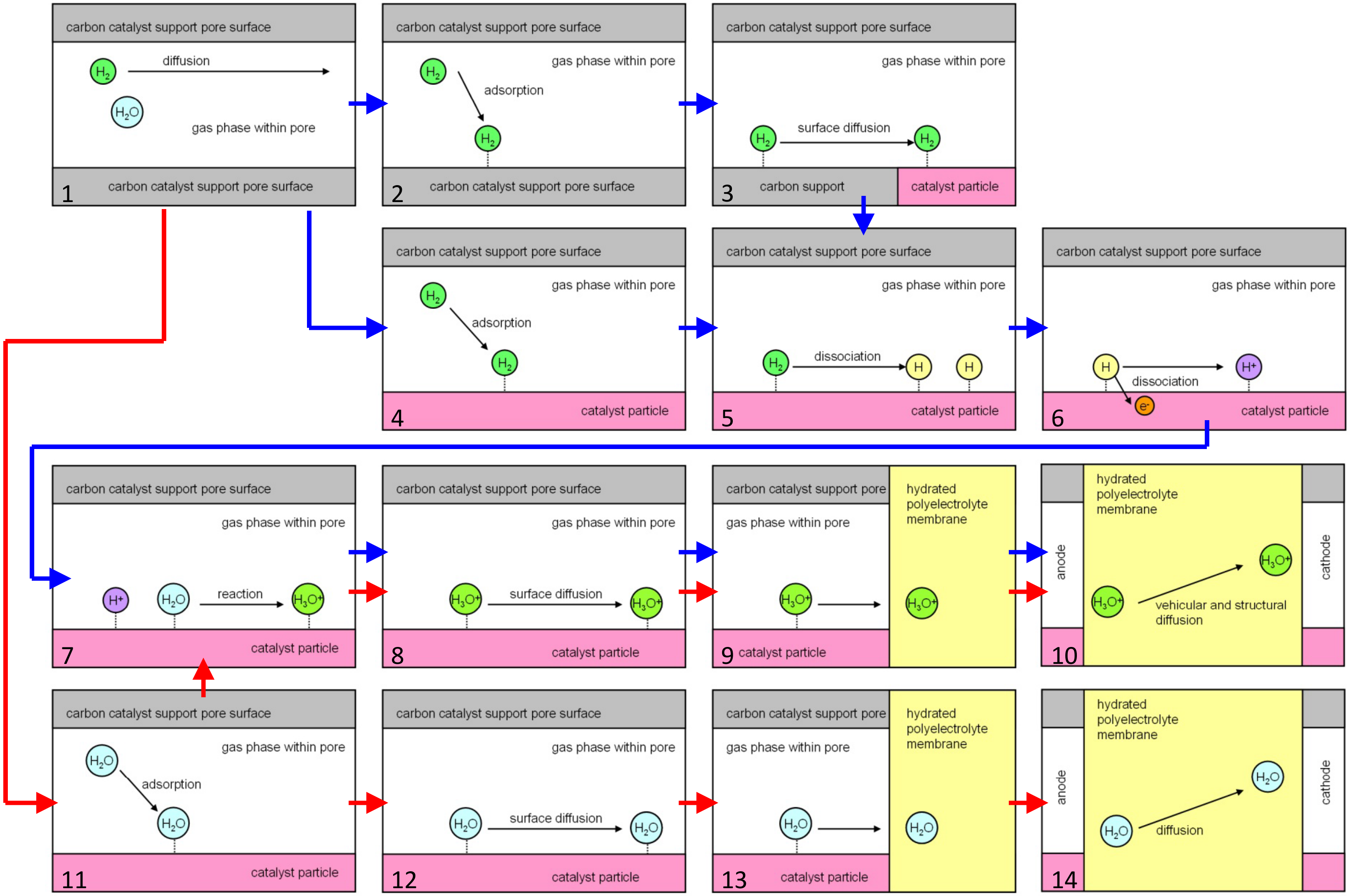
with $L_{ij} = L_{ji}$

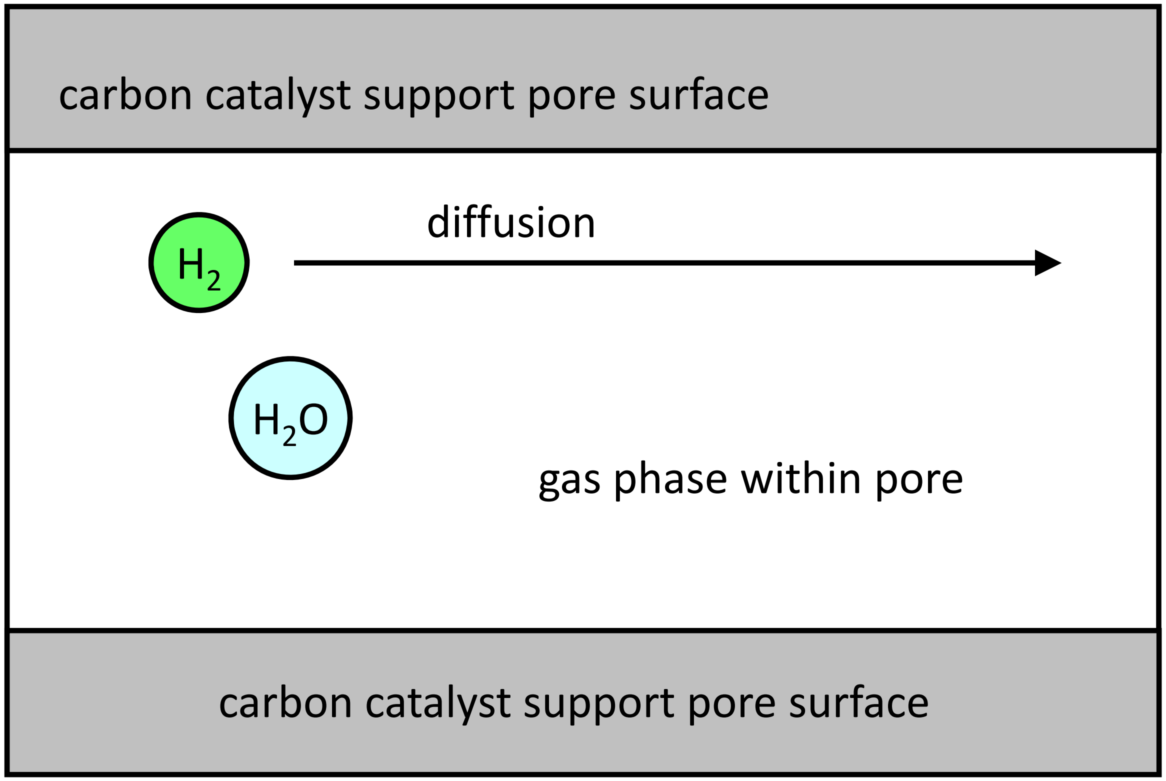
separate driving force

Water transport within a PEM is due to both diffusion and hydrodynamic flow, depending on the state of the membrane. Some operating conditions lead to inhomogeneously hydrated membranes that increase the hydrodynamic driving force.

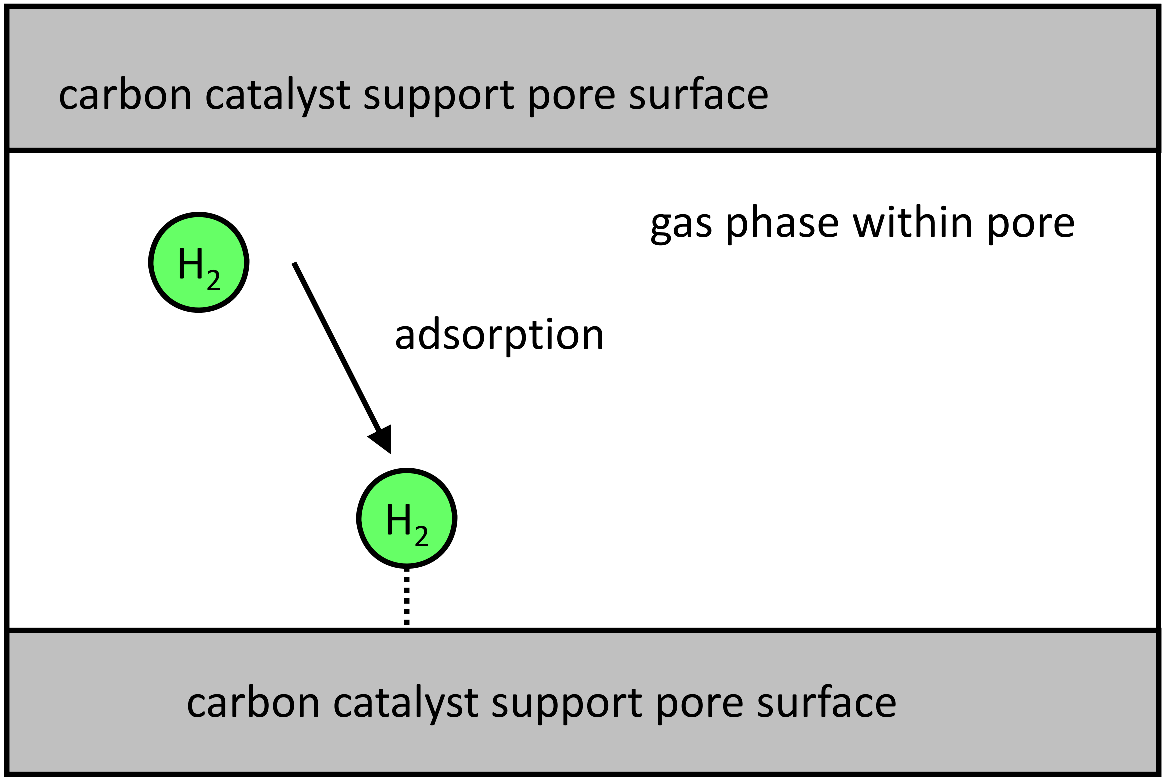
K.D. Kreuer, 2010.

Transport Processes in Anode Side of Membrane Electrode Assembly

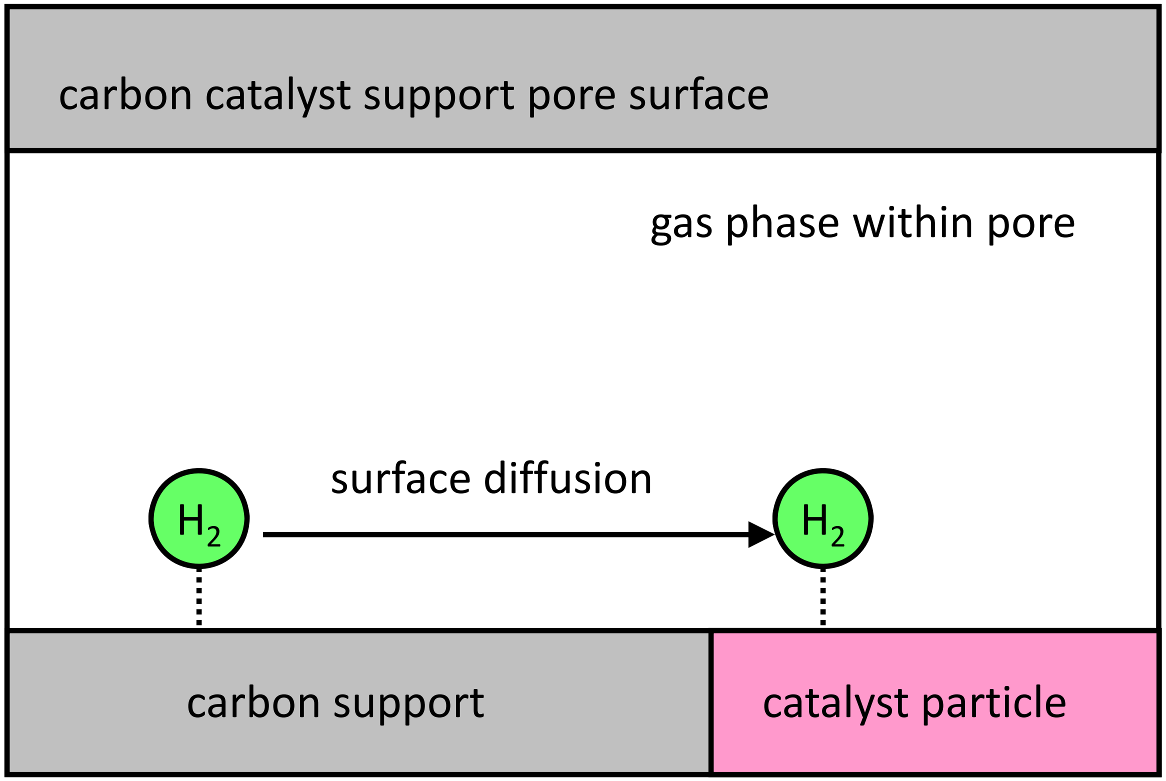




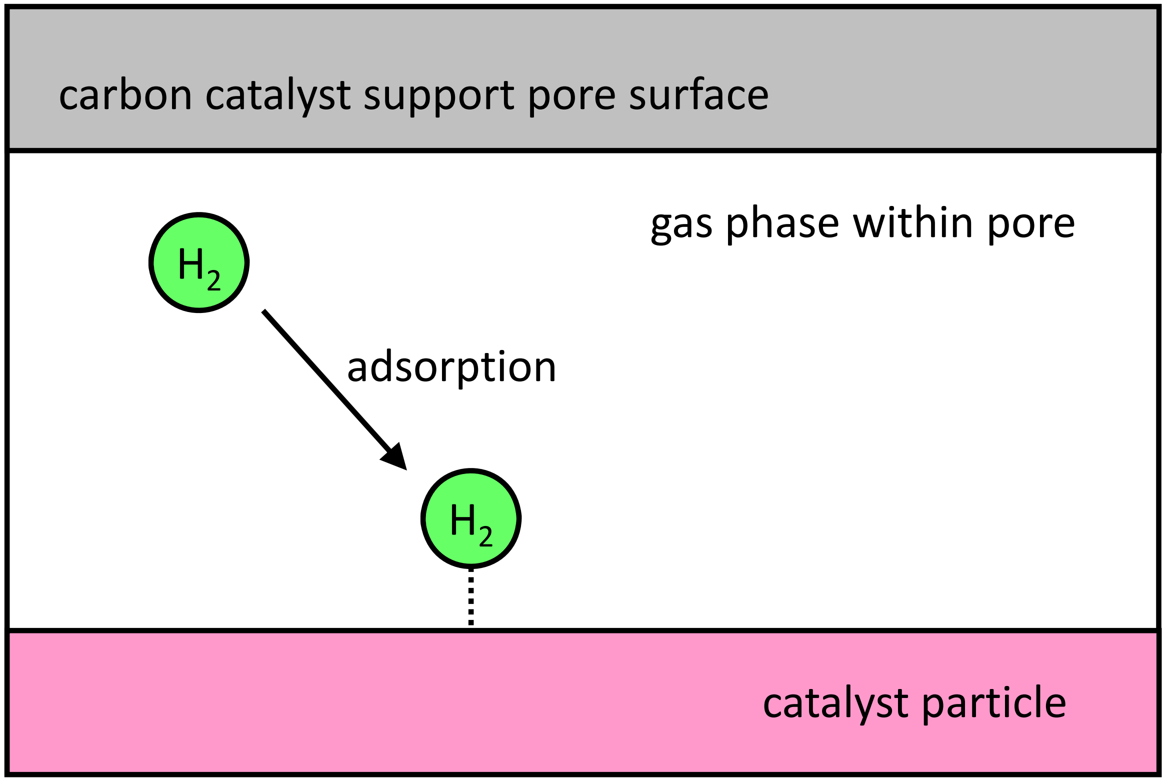
Step 1. H_2 and H_2O diffuse through carbon pores of anode.



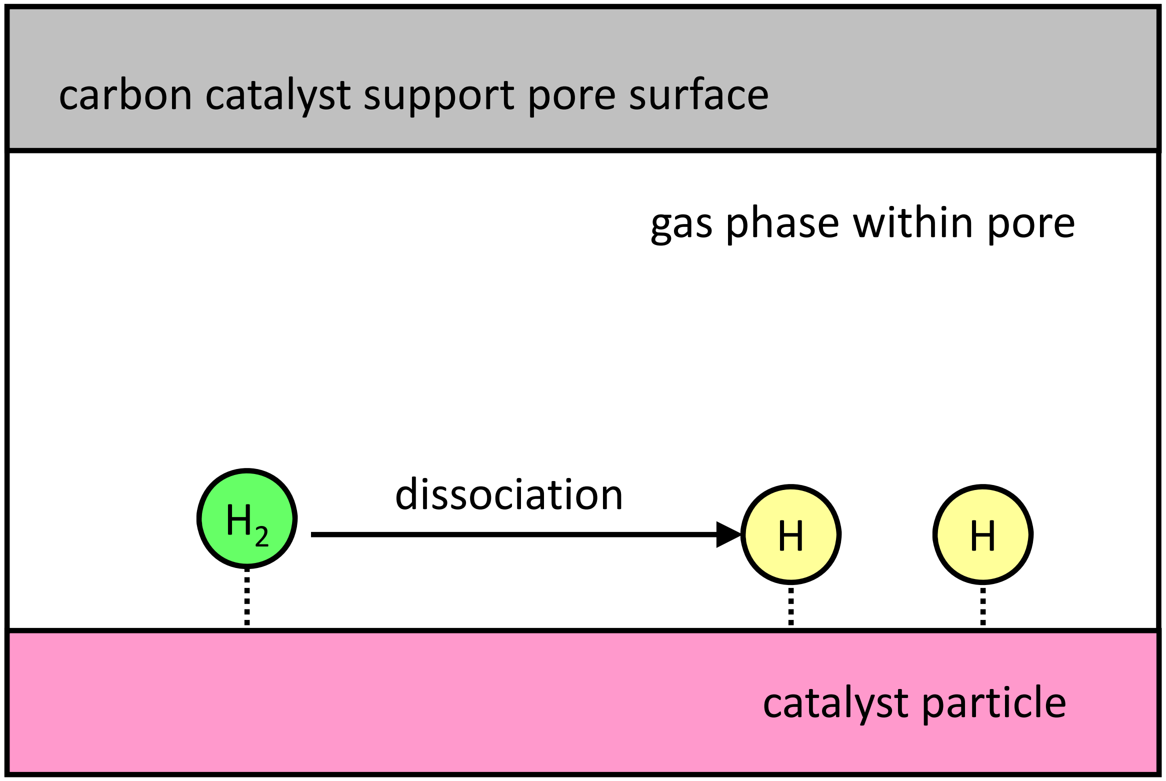
Step 2. H_2 adsorbs on carbon support pore surface.



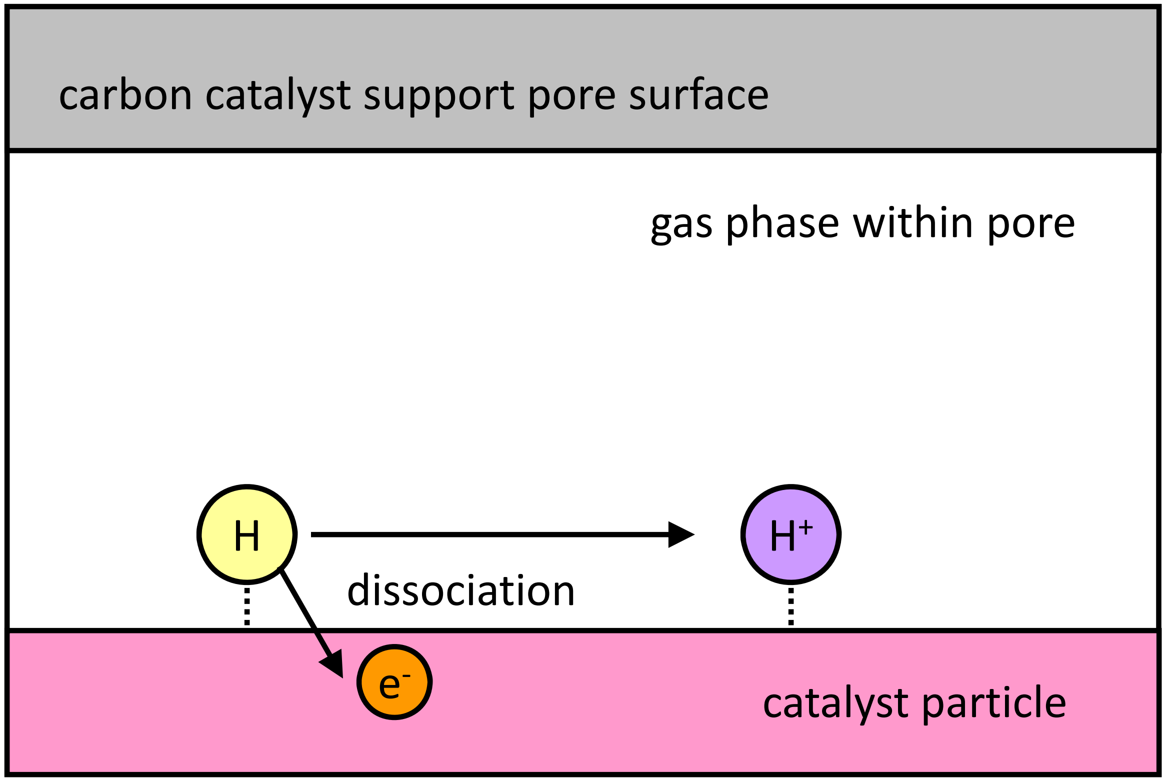
Step 3. H_2 diffuses across surface of carbon support to catalyst surface.



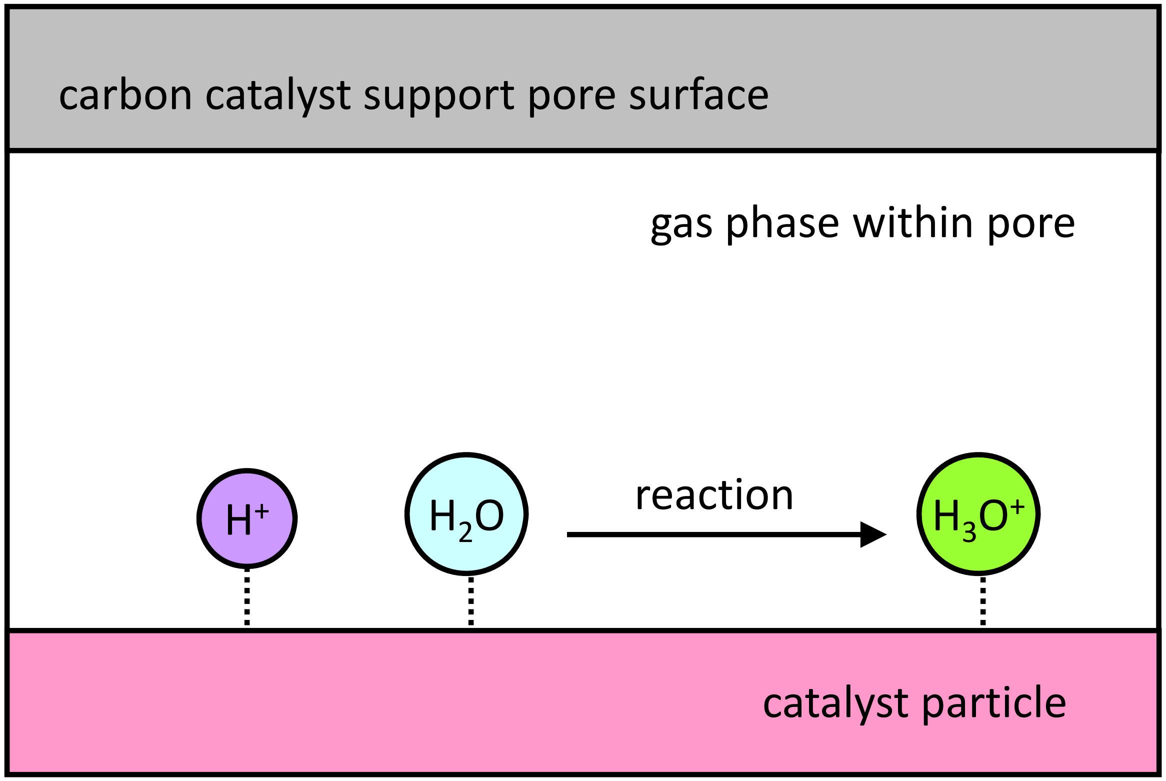
Step 4. H_2 adsorbs on catalyst surface.



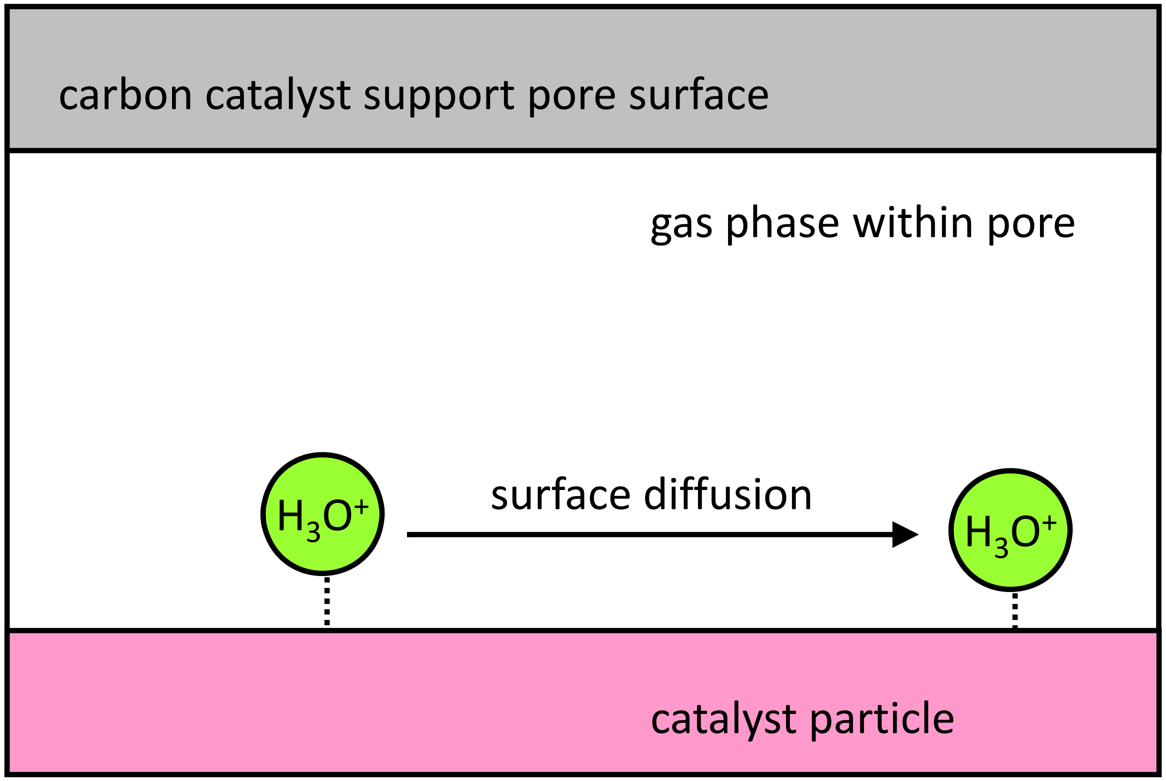
Step 5. H_2 dissociates on catalyst surface to two hydrogen atoms.



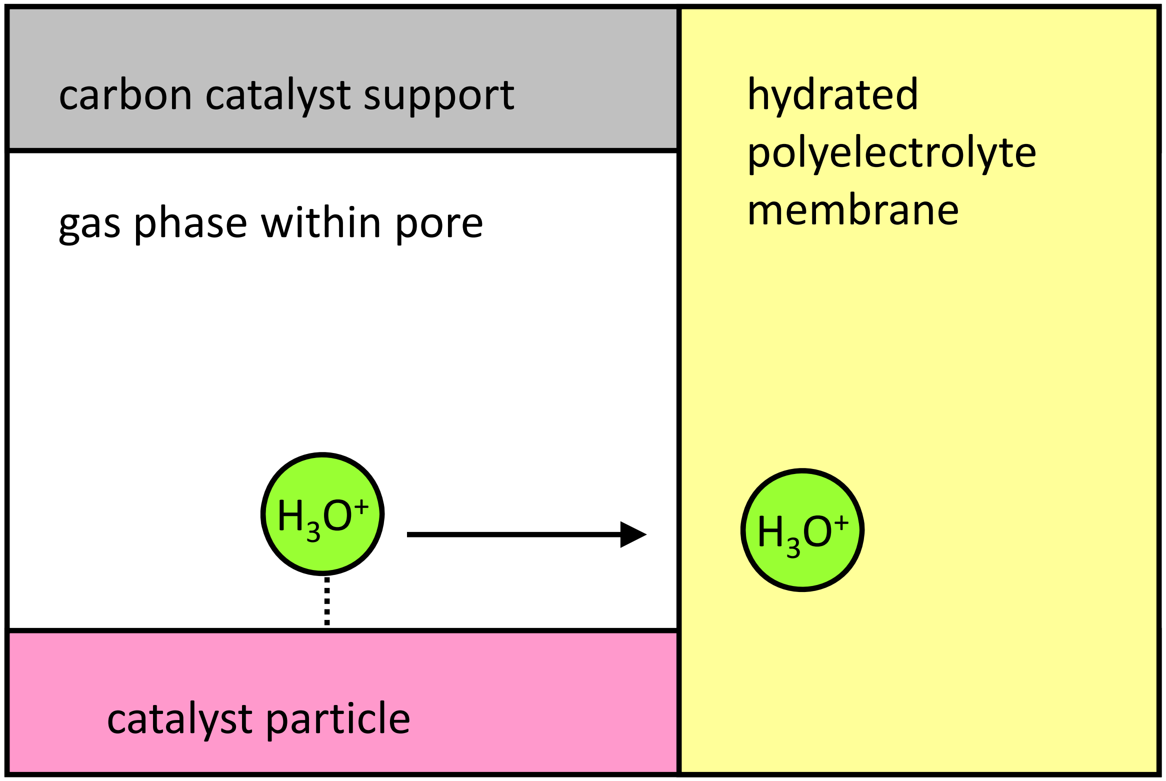
Step 6. Hydrogen atom dissociates on catalyst surface to proton and electron.



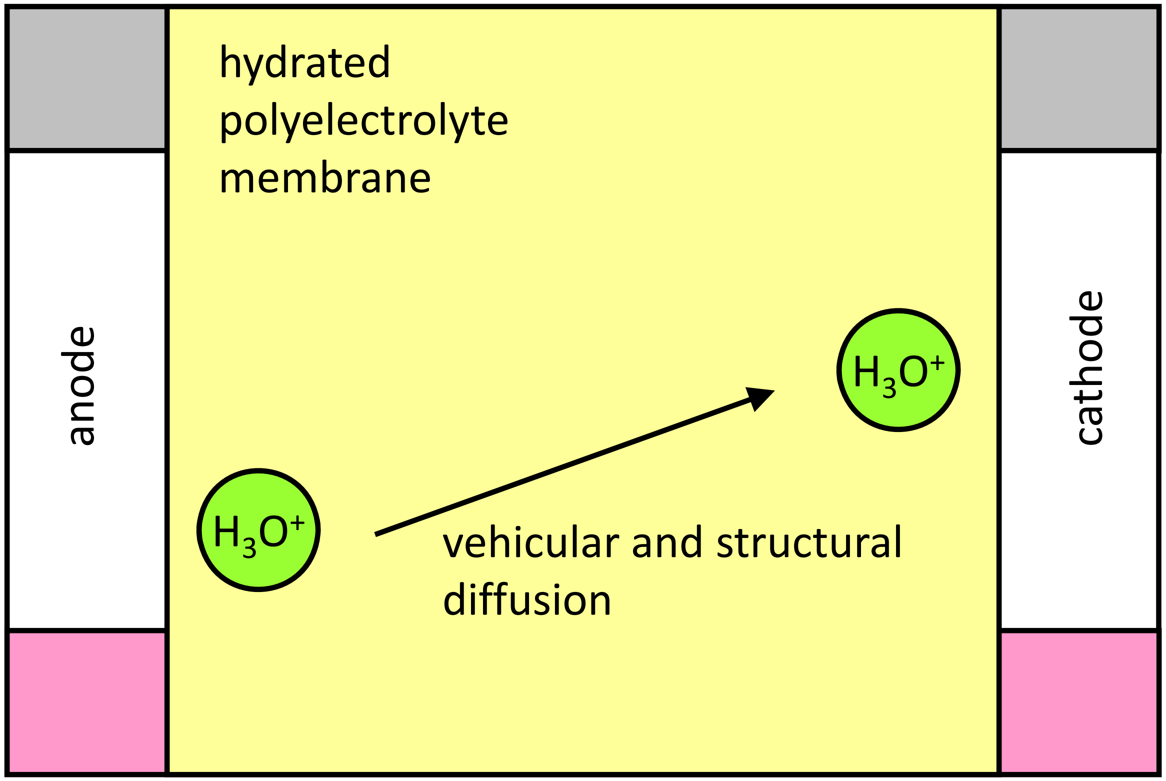
Step 7. Proton joins with water to form hydronium ion.



Step 8. Hydronium ion diffuses across catalyst particle surface.



Step 9. Hydronium ion diffuses into hydrated polyelectrolyte membrane.



Step 10. Charge diffuses across hydrated polyelectrolyte membrane

Diffusivity and Conductivity

For charge, the proton conductivity of the membrane is the important transport property. In many simulations and in some experiments, such as PFG-NMR, it is the diffusivity that is measured.

The diffusivity can be approximately related to the conductivity via

$$D = \left(\frac{RT}{|z|^2 F^2}\right)\frac{\sigma}{c}$$

Where R is the gas constant, T is temperature, z is the charge of the ion, F is Faraday's constant, σ is the conductivity and c is the concentration.

One immediately observes that at low concentrations, the conductivity will scale linearly will the concentration whereas the diffusivity is independent of concentration. At higher concentrations, the concentration dependence of the diffusivity remains much weaker than that of the conductivity.

Conclusions

Water management in fuel cells is critical.
Without water management the membrane will dehydrate , leaving an inhomogeneous membrane with poor performance properties.

There are many elementary transport steps in the movement of a proton from a hydrogen feed stream on the anode side of the fuel cell to its departure as part of a water molecule on the cathode side.

Understanding which of these steps is rate limiting is important to developing next generation nanostructured membrane electrode assemblies.