Analysis of degradations of PEMFC combining Pore-Network Modelling of GDL and Performance Modelling

S. Pulloor Kuttanikkad\textsuperscript{a, b}, J. Pauchet\textsuperscript{a}, M. Prat\textsuperscript{b}, P. Schott\textsuperscript{a}

\textsuperscript{a} Commission for Atomic and Alternative Energies (CEA, Grenoble, France)
Laboratory of components for Fuel Cells and Electrolyseurs, and of Modelling (LCPEM)

\textsuperscript{b} Institute of Fluid Mechanics of Toulouse, France
Inputs for the study

Aim: Evaluate if the loss of hydrophobicity of GDL is a good candidate to explain performance’s degradation of PEMFC

Consider GDL with non uniform and probably mixed wettability (hydrophilic and hydrophobic zones) that will vary with time (degradation)
Context of two-phase modelling in GDL

- Classical REV approach (Darcy)
  - is doubtful for modelling two-phase flows in GDL (thin, no sufficient scale separation, mixed wettability...)
  - does not take into account explicitly local properties => difficult to link local modification to performance

- Alternative solution: Pore Network Modelling (PNM)

  Develop a 3D PNM to analyze two-phase-flows in GDL taking into account local loss of hydrophobicity
Methodology to link micro-scale degradation to performance degradation

Pore scale (t) → Effective Properties (t) (REV Darcy scale) → Performance (U,I) (t)

Develop pore network model

Apply performance model

Inputs
1. Structure
2. Pore size, Throat size
3. Wettability

1. Permeability
2. Effective diffusion
3. Capillary pressure
4. Relative permeability
5. Etc.

Compare with experiments (degradation rate)
Content

• Pore network modelling
  • brief description of the method
  • study of water invasion in thin porous layer such as GDLs
    • uniform wettability
    • non uniform (mixed) wettability
  • effect of loss of hydrophobicity on properties of GDL (gas diffusion)

• Performance modelling
  • brief description of the model
  • effect of GDL’s degradation on cell performance

• some topics for next steps
Porous medium ≈ network of pores and bonds
randomly distributed according to PSD and TSD (pore and throat size distribution of the porous medium)

*Oren et al., SPE J, 1998*
PNM: compute one-phase flow

Local Poiseuille law in each bond

\[ q_{ij} = \frac{g_{ij}}{\mu} \Delta P_{ij} \]

- Flow rate in the bond
- Bond hydraulic conductance (depends on bond hydraulic diameter and length)
- Pressure difference between two adjacent pores
- Fluid viscosity

Same for diffusion (Fick)

\[ J_A = -D_{AB} \text{grad} C_A \]

Same for heat flux…
PNM: compute two-phase flow

Small capillary number => flow controlled by capillary effects

Capillarity inside bonds/pores

Surface tension

\[ p_c = \frac{2\gamma \cos \theta}{r} \]

Local contact angle

Two-phase invasion algorithm: Invade the bond of lowest \( P_c \)

(Blunt algorithm for hydrophilic bonds)
Uniform wettability: experimental validation (hydrophobic case)

$\begin{align*}
    t_4 & > t_3 \\
    t_3 & > t_2 \\
    t_2 & > t_1 \\
    t_1 & \\
\end{align*}$

Breakthrough point

Porous media = hydrophobic grains

Experiments (liquid water in white)  Simulation (liquid water in black)

Good agreement between PNM and experiments

O. Chapuis et al., J. of PowerSource (2008)
Uniform wettability: liquid pattern as a function of contact angle

Hydrophobic (Capillary fingerings) $\theta_{\text{gas}}$ Hydrophilic (Flat traveling front)

\[ \theta_E = 160^\circ, 140^\circ, 120^\circ, 100^\circ, 80^\circ, 60^\circ, 40^\circ, 20^\circ \]

O. Chapuis et al., J. of Power Source (2008)
Fingering regime (hydrophobic media) will delay water flooding

Hydrophobic (fingering regime)

Hydrophilic (compact regime)

O. Chapuis et al., J. of Power Source (2008)

water removal with a significant fraction of pore space free for gas transport => delay of flooding
PNM with mixed wettability to simulate loss of hydrophobicity

Increase $f$ to mimic loss of hydrophobicity

Simulate SGL type GDL with a 3D regular network and TSD measured by Hg porosimetry
Percolation threshold $f_c$

For $f < f_c$ invasion through hydrophilic and hydrophobic pores

For $f \geq f_c$ invasion through hydrophilic pores only

$f_c$ is a function of GDL’s PSD and TSD
Tow-phase pattern as a function of $f$ (degradation)

$f = 0$

invasion percolation pattern

$f = f_c$

hydrophilic pore sub-network

Pattern becomes increasingly compact for $f > f_c$
Diffusion does not decrease a lot as long as $f < f_c$  

$\Rightarrow$ small influence of PTFE loss

$D_{\text{eff}} / D \ (\text{PNM})$

$D_{\text{eff}} / D \ (\text{Eq. (5)})$

$S_{BT}$

$f_c$

$0$

$0.2$

$0.4$

$0.6$

$0.8$

$SGL \ GDL$

$0$

$20$

$40$

$60$

$80$

$100$

$\text{Degradation}$

$\text{Overall saturation at breakthrough}$

$\text{Diffusion rapidly drops down for } f > f_c$

$\Rightarrow$ large influence of PTFE loss

$\Rightarrow$ small influence of PTFE loss

Flooding will increase as a function of time

Compared to PNM, classical models seem to over-estimate gas diffusion and under-estimate the effect of liquid saturation.
Performance modelling: description of the model

Inputs: properties of components (diffusion, permeability…), geometry, working conditions…

Outputs: polarisation curve (U,I), distribution of current density, reactant activity, temperature, liquid saturation…

Cell model

Coupling: heat and mass (two-phase) transfer, charge transfer, electrochemistry (Butler-Volmer)
Effect of GDL’s degradation on performance

Simulation of one experimental case of DECODE

Existence of liquid water in the cell => potential effect of hydrophobicity loss

For the time being, f(t) is unknown

analyze as a function of f (and not as a function of t)

• PNM => effective properties (k, Deff…) as a function of f
  • then calculate U(f)
Effect of GDL’s degradation on performance

Gas diffusion will decrease due to degradation
Classical models (Bruggeman, Eq. 5) under-estimate this effect

Loss of PTFE =>
• decrease of Deff
• decrease of U (@ I=cte)
• increase of current density differences in the cell (inlet/outlet)
• make progress liquid water up to the inlet
• increase flooding
Some topics for next steps

- Measure $f(t)$ to calculate $U(t)$ and to compare with experiments

- include
  - real structure (morphological network, PSD, TSD, local wettability?)
  - condensation ($dT = 1-4 \, ^\circ C$, results Chameau project)
  - multiple injection points and couple the layers

Numerous breakthrough points will have an effect on two-phase pattern and on diffusion

Eikerling et al., Physics Today, 2006
Analysis of degradations of PEMFC combining Pore-Network Modelling of GDL and Performance Modelling

Thank you for your attention

This work has been performed within the European project DECODE. The financial support of the 7th Framework Programme (Grant Agreement 213295) is gratefully acknowledged.

Some images are part of French National Project CHAMEAU (PAN-H ANR 2006)