Multi-scale modeling to boost fuel cell performance: From pore-scale simulations to better efficiency and durability

Original

Availability:
This version is available at: 11583/2515681 since:

Publisher:

Published
DOI:

Terms of use:
openAccess
This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)
Multi-scale modeling to boost fuel cell performance: From pore-scale simulations to better efficiency and durability

Uktam Salomov, Pietro Asinari

Multi-Scale Modelling LAB – SMaLL (www.polito.it/small)

ARTEMIS (http://www.artemis-htpem.eu/)

POLITECNICO DI TORINO
Motivation: High Temp. PEM Fuel Cells

- membrane-electrode-assembly
  - gasket
  - catalyst
  - bipolar plate
  - gas diffusion layer
  - polymer electrolyte membrane

Principle of an acidic fuel cell:
- unused H₂
- water
- hydrogen
- oxygen
- LT: 25-80 °C
- MT: 80-120 °C
- HT: 120-200 °C

ECoMaTech, 19-21 September, 2013, Bled (Slovenia)
Two main issues preventing widespread commercialization of PEMFC:

- High cost
- Durability (degradation)

Study case:
Electrode = Catalyst + GDL
- the most expensive (~60% of full cost of cell)
- the most vulnerable part prone to degradation processes

Solution!!!
Optimization of Pt loading of catalyst layers and analysis of carbon support via investigation of the undergoing physico-chemical mechanisms of degradation processes
HT PEMFC: degradation of electrodes

- Open circuit voltage
- Start/stop cycles
- Fuel starvation in anode
- Air starvation in cathode
- Load cycles
- Freeze/thaw cycles

- Carbon corrosion
- Formation of unsupported Pt particles
- Pt oxidation and dissolution
- Oxidation current at anode supplied by side-reaction

- Carbon dioxide formation
- Phosphoric acid depletion

- Loss of Pt surface area
- Loss of ECSA

- Pt particle growth
- Voltage degradation

Colors:
- Red: Condition
- Green: Degradation mechanism
- Blue: Measurable effect
**Degradation of electrodes: phosphoric acid loss**

Phosphoric acid depletion:

- Loss of ionic conductivity

  

  • Acid loss may occur through several mechanisms such as:
    - diffusion
    - capillary transport
    - membrane compression
    - evaporation
    - leaching by condensed water during shutdown and cold start


  • PA loss as a function of flow rate, temperature, operating conditions

Y. Oono et al., Journal of Power Sources, 210 (2012) 366
Pore-scale modeling of the fluid flow through the electrodes of HT PEMFC
Morphological model: main steps

- Development of the reliable algorithm for reconstruction of micro-morphology of electrodes (GDL, CL)
- Challenge for numerical tools and mathematical models for specific degradation phenomenon
- Validate the proposed algorithm and numerical tools computing macroscopic transport coefficients
- Development of mitigation strategy using virtual realization of system
Reconstruction: MEA’s real structure SEM images

GDL has mainly **ordered** structure  
Example: Celtec by BASF®  
Structure: **woven (nonwoven)** like  
Approach: **deterministic (stochastic)**

CL has **irregular** structure  
Example: Celtec by BASF® VulcaN XC – 72R  
Structure: **aggregation** of particles  
Approach: **stochastic** based on clusterization of particles
LBM is the discretization of not only physical space, but also velocity space, which means that particle velocities are restricted to a finite set of orientations. 

- LBM solves the following Lattice Boltzmann equation:

\[ f_i(\vec{x} + \vec{c}_i \Delta t, t + \Delta t) = f_i(\vec{x}, t) - \frac{[f_i(\vec{x}, t) - f_i^{eq}(\vec{x}, t)]}{\tau} \]

  - Streaming
  - Collision

- It should be noted that in this algebraic equation, “non-locality (streaming term, S) is linear and non-linearity (collision term, C) is local” [Sauro Succi, 2001]

- In LBM fluid models, like BGK or single relaxation time

**Numerical tool:** Lattice Boltzmann Method

- Very complex geometry
- Parallel computation
- Gas rarefaction effect

**Computational domain size is ~100 Mcells**
Numerical tool: PALABOS

Palabos (www.palabos.org) is an open-source CFD solver based on the lattice Boltzmann method.

Palabos ingredients:

- **Physics:** In/weakly compressible, non-thermal Navier-Stokes equations; flows with body-force term, thermal flows with Boussinesq approximation, single-component multi-phase fluids (Shan/Chen model), free surface flows (volume-of-fluid approach), static Smagorinsky model for fluid turbulence.
- **Basic fluid models:** BGK, MRT, regularized BGK, LW-ACM, entropic model.
- **Straight-wall boundary conditions:** Zou/He, Inamuro, Skordos, regularized BC, simple equilibrium, bounce-back, periodic.
- **Off-lattice boundary conditions:** GUO model, generalized off-lattice BC.
- **Grid:** D2Q9, D3Q13, D3Q15, D3Q19, and D3Q27.
- **Parallelism:** parallelized with MPI for shared-memory and distributed-memory platforms, including I/O operations that are implemented in terms of MPI’s Parallel I/O API.
## Validation: Gas diffusion layer

<table>
<thead>
<tr>
<th></th>
<th>Woven [Celtec BASF®]</th>
<th>Non-woven [Freudenberg]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thickness @0.025MPa</strong></td>
<td>400 μm</td>
<td>256 μm</td>
</tr>
<tr>
<td><strong>Computational domain</strong></td>
<td>534 Mcells</td>
<td>67 Mcells</td>
</tr>
<tr>
<td><strong>Fiber diameter</strong></td>
<td>7 μm</td>
<td>7 μm</td>
</tr>
<tr>
<td><strong>Porosity</strong></td>
<td>0.78</td>
<td>0.75</td>
</tr>
<tr>
<td><strong>Computed Permeability</strong></td>
<td>0.44x10^{-12} m^2</td>
<td>3.2x10^{-12} m^2</td>
</tr>
<tr>
<td><strong>Actual permeability</strong></td>
<td>0.50x10^{-12} m^2</td>
<td>2-3x10^{-12} m^2</td>
</tr>
</tbody>
</table>

## Validation: Catalyst layer

<table>
<thead>
<tr>
<th>Clustering Name</th>
<th>40 nm</th>
<th>400 nm</th>
<th>1500 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computational domain</td>
<td>8 Mcells</td>
<td>8 Mcells</td>
<td>16 Mcells</td>
</tr>
<tr>
<td>Carbon support particles diameter</td>
<td>40 nm</td>
<td>40 nm</td>
<td>40 nm</td>
</tr>
<tr>
<td>Computed Permeability</td>
<td>1.1x10^{-16} m²</td>
<td>4.8x10^{-15} m²</td>
<td>0.4x10^{-13} m²</td>
</tr>
<tr>
<td>Increase of permeability</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual permeability</td>
<td>1.0x10^{-13} m²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Validation: Effect of redistribution of Pt particles on flow field

<table>
<thead>
<tr>
<th>Name</th>
<th>Non-distrib</th>
<th>Distributed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computational domain</td>
<td>2.1 MNodes</td>
<td>2.1 MNodes</td>
</tr>
<tr>
<td>Average cluster size</td>
<td>1500 nm</td>
<td>1500 nm</td>
</tr>
<tr>
<td>Computed flow rate</td>
<td>$0.31 \times 10^{-6}$</td>
<td>$2.3 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Redistribution of catalyst particles inside the microstructure leads to considerable increase of mass flow rate.

This provides an additional tunable parameter of the morphological model.
Mitigation strategy: Redistribution of Pt particles in CL

The goal of proposed morphological model is to design a strategy in order to enhance PEMFC performance and to mitigate degradation phenomena by improving mass transport processes.

Two virtual realizations of morphological model are considered in regards to Pt distribution:

1. Homogeneous
2. Exponential decay
There are quantitative changes (scale factor), but also qualitative changes in the flow field (streamlines). Thus, redistribution of catalyst particles inside the microstructure leads to considerable increase of overall mass flow rate and changing flow field near membrane (flow rate almost zero).
High Temperature PEM FC single MEA performance simulation
Single MEA structure

- Anode (H2) and Cathode (air) gas channels
- Gas diffusion layers (GDL)
- Catalyst layers (CL)
- Membrane
**MEA secondary current distribution**

Electrolyte: Poisson equation

\[ \nabla \cdot i_l = Q_l, \quad i_l = - \sigma_l \nabla \varphi_l \]

Porous electrodes: mixture of Poisson eqs of electrodes and electrolyte.

Electrode kinetics:
Linearized Butler-Volmer for anode CL

\[ i_a = i_{a,0} \left( \frac{c_{H_2}}{c_{H_2,ref}} \right)^{0.5} \left( \frac{\alpha_a F \eta_a}{RT} \right) \]

Cathodic Tafel equation for cathode CL

\[ i_c = -i_{c,0} \left( \frac{c_{O_2}}{c_{O_2,ref}} \right) \exp \left( \frac{\alpha_c F \eta_c}{RT} \right) \]
Transport mechanisms

Transport of concentrated species:
- Compartments: Channel, GDL and CL
- Anode: Hydrogen and water
- Cathode: Oxygen, water and nitrogen
- Momentum transfer: Navier-Stokes and Brinkman equations
- Coupling with Poisson equations as sources and sinks at porous electrode (catalyst layer)
CL with different Pt distribution

C1: Exponential decay
C2: Homogeneous (today)
C3: Exponential increase
Single MEA performance simulation

Region with higher performance $Pc_1 > Pc_2$

C1: Exponential decay
C2: Homogeneous (today)
C3: Exponential increase

~15-20% performance range

$Rc_1 > Rc_2 > Rc_3$
Thank you for your attention!