Introduction modeling aspects—SOFC, PEMFC

Chapter 10 in course book
Phenomena and processes

- Analysis of transport phenomena: Chemical reactions coupled with gas flow, Heat transfer involving internal reforming reactions or water phase change/multi-phase flow in unit cells and stacks, catalytic layers
- Multiphysics and Multiscales
- Catalytic reactions related transport processes in compact reformers
- BOP for FC systems, including HEXs
- Specific topics, e.g., carbon deposition in SOFCs
Chemistry and Transport Phenomena to be Understood across Disparate Length Scales

**SOFC**

LSM = lanthanum-strontium-manganite (ceramic)

YSZ = yttria stabilized zirconium (ceramic)
Knowledge of the catalytic reaction mechanisms is a key for designing an anode material with a high efficiency and a long life-time, i.e., identifying reaction pathways and rate limiting steps.

SOFCs employ in general porous YSZ supported Ni or Ru as catalyst in the anodes, due to low cost and possibility for both electrochemical reactions and reforming reactions.
In PEMFCs, the incorporation of nanosized catalysts has been highly successful in increasing active areas and catalyst activity.

- Electrochemical reaction;
- Multiphase transport processes;
- Water generation/transfer processes;

In most macro scale CFD models, the CLs are treated as **interfaces**, or considered to be **isotropic**.
Function and Microstructure of CL-PEMFC

✓ **Four phases:**
- Carbon: for conduction of electrons and support of the platinum nano particles;
- Ionomer: typically Nafion®, for proton transport;
- Platinum: for electrochemical reactions;
- Pore: for reactant and product gases to diffuse;

✓ **Multi scale levels:**
- Catalyst nanoparticles \(r_{Pt} \sim 2\) nm,
- Agglomerates of carbon/Pt \(r_{a} \sim 100\) nm,
- Macroscopic device level \(L_{CL} \sim 10\) \(\mu\)m;
Research work about CLs aims to

- Reduce the cost;  
  Decrease Pt loading;
- Durability;  
  Improve Pt utilization;
- The reactions take place at the triple-phase boundaries (TPB).
  Avoid flooding;

Make clear the mechanisms of reaction, multiphase transport processes, water generation/transfer processes in thin CLs.

Long-term: Understand the multiscale transport phenomena and reactions in fuel cells.

Short-term: Bridge the models and simulation techniques across the nano-scale to micro-scale in the CLs.
Macroscopic modelling-CFD methods

- CALCHT – in-house
- ANSYS-FLUENT
- COMSOL
- OPEN FOAM
The general equation

Arbitrary variable

\[ \frac{\partial \rho \phi}{\partial t} + \frac{\partial}{\partial x_j} \rho \phi u_j = \frac{\partial}{\partial x_j} \left( \Gamma \frac{\partial \phi}{\partial x_j} \right) + S \]
Control Volume Method - Finite Volume Method

\[ \iiint_V \frac{\partial \rho U_j \phi}{\partial x_j} dV = \iiint_V \frac{\partial}{\partial x_j} \left( \Gamma \phi \frac{\partial \phi}{\partial x_j} \right) dV + \iiint_V S_\phi dV \]

Divergence theorem

\[ \iiint_S \rho \phi \vec{U} \cdot \vec{n} dS = \iiint_S \Gamma \phi \nabla \phi \cdot \vec{n} dS + \iiint_V S_\phi dV \]

Convection flux

Diffusion flux
Discretization - grid

Cartesian grid

Body-fitted grid

Unstructured grid
Terms to be determined

- Convection flux $C_f$
- Diffusion flux $D_f$
- Scalar value at a face $\Phi_f$
Convection-Diffusion Terms

- CDS - central difference scheme
- UDS - upstream scheme
- HYBRID - hybrid scheme
- Power law scheme
- QUICK
- van Leer
Pressure - Velocity Coupling

- SIMPLE (Semi-Implicit-Method-Pressure-Linked-Equations)
- SIMPLEC (SIMPLE-Consistent)
- SIMPLEX (SIMPLE-Extended)
- PISO (Pressure-Implicit-Splitting-Operators)
- SIMPLER (SIMPLE-Revised)
General Algebraic Equation – 2D case

\[ a_P \phi_P = a_E \phi_E + a_W \phi_W + a_N \phi_N + a_S \phi_S + b \]
Length scales - Computational Approaches

![Diagram showing length scales and computational approaches across different scales.](image-url)
Approaches

Beyond the atomic-scale (molecular dynamics) and below the conventional continuum scale (CFD)

Pseudo-particle models

- Lattice-based pseudo-particle models
  - Lattice Boltzmann (LB or LBM)

- Off-lattice pseudo-particle models
  1. Coarse-Grained Molecular Dynamics (CG-MD)
  2. Dissipative Particle Dynamics (DPD)
  3. Smoothed particle hydrodynamics (SPH)
Reconstruction of Catalyst Layer

✓ **Methods:**

- Experimental imaging (TEM, SEM etc.)
- Computer simulation
  - stochastic
  - semi-deterministic
  - regular
From Nano-scale to Microscale

Computer modeling from 1st principles to Microscale

Three levels of molecular modeling:

First-principles (Quantum Mechanics)
- nuclei
- electrons
- atoms
- molecules

Classical Molecular Mechanics
- atoms
- molecules

Microscale soft matter
- coarse-grained molecules
- soft matter

The problem: Larger scale ⇔ more approximations
For the macroscale modeling approaches using the continuum formulation, many commercial codes (like ANSYS-FLUENT and COMSOL) and their specific fuel cell modules have been considered as well as in-house softwares (at universities and institutes) have been used.

Open source codes like Open Foam are also available with some fuel cell modules and used frequently.

To handle systems that couple several scales, a theoretical and computational platform including a first principle is needed. This can be built up at least partly by available open-source codes.

The Atomic Simulation Environment (ASE) is a common part of a simulation tool developed at DTU, Denmark. It can be used to run molecular dynamic simulations when the atomic numbers and positions are given (all atom modelling).

The Visual Molecular Dynamics (VMD) software is a molecular visualization program for display, animation and analysis of large biomolecular systems using 3D-graphics and built-in scripting. The coarse graining (CG) builder module in VMD can be employed to, e.g., transform unit structures to CG beads.

GROMACS (Groningen Machine for Chemical Simulation) is a molecular dynamics simulation package originally developed at University of Groningen, Netherlands. As the coordinates of the CG beads are at hand, the CG-MD method can be implemented in the GROMACS package.

PACKMOL packs molecules in defined space regions and create a starting point for MD simulations. The packing makes sure that short range repulsive interactions do not disrupt the simulations.

LAMMPS (large scale atomic/molecular massively parallel simulator) can be applied to calculate, e.g., the thermal properties, thermal behavior and temperature distribution inside a porous SOFC anode.

The Lattice Boltzmann method can be applied as a microscale model of an SOFC anode using the programs PALABOS with PYTHON and MATLAB together with PARAVIEW.
Objectives - small scale modeling

a) Establishing nano/micro-scale structure of porous anode for SOFC
b) Calculating thermal properties, mainly thermal conductivity, thermal expansion coefficient and equilibrium lattice constant
c) Predicting thermal behavior and temperature distribution inside the porous anode
Methodology

In general, an AA-CG-MD method is employed for reconstruction of nanostructures, calculation of thermal properties, and analysis of thermal behavior and temperature distribution inside the porous anode for SOFC.

a) AA: all-atom modeling
b) CG: coarse-graining modeling
c) MD: molecular-dynamics modeling
Modeling

a) **ASE**: all-atom models of Ni, YSZ and Ni-YSZ particles

b) **VMD**: coarse-graining model of Ni-YSZ beads and force field parameters

c) **GROMACS**: nanostructure of Ni-YSZ cermet with a targeted box of 50 nm³

d) **LAMMPS**: thermal properties, thermal behavior and temperature distribution inside the porous anode
Example SOFC modeling – CFD based

Schematics of a composite anode duct
Example SOFC modeling

Dimensionless axial velocity contours ($U/U_{in}$) along the main flow direction.
Example SOFC modeling

CH$_4$ mass concentration
Example SOFC modeling

Temperature distribution along the main flow direction
Final Remarks

• In fuel cells, multiphysics transport phenomena are involved, and coupling of complex transport phenomena and reaction kinetics takes place at molecular or particle levels. The characteristics are often treated as a black box measured as boundary conditions or overall mean-field parameters.

• Various model approaches have been developed for fuel cell components and their systems with different levels of details, mainly based on macroscopic continuum approaches (CFD and BOP).

• On-going research includes understanding catalytic reactions mechanisms and effects on various transport processes in porous catalytic layers by multiscale and multiphysics model development.

• Integration with CFD codes based on hybrid methodology.