Advanced Particle-Based 3D Modeling of Fuel Cell Electrodes

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COMSOL CONFERENCE
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Solid Oxide Fuel Cells

Main characteristics
- Electricity from H₂ and air
- Solid electrolyte
- 600-1000°C
- Porous composite electrodes

\[
\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \quad H_2 + O^{2-} \rightarrow H_2O + 2e^-
\]

Efficiency and degradation

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**picture taken from V.A.C. Haanappel et al., J. Power Sour. 141 (2005) 216-226
3D tomography & electrode microstructure

FIB-SEM

X-ray nano-CT*

*picture adapted from Shearing et al., J. Eur. Ceram. Soc. 30 (2010) 1809
Averaged results from 3D modelling

Simulating physics and electrochemistry *within* the 3D microstructure

*picture adapted from Carraro et al., Electrochim. Acta 77 (2012) 315

**picture adapted from Häffelin et al., J. Electrochem. Soc. 160 (2013) F867

Full 3D microstructural details to get...

*averaged* electrochemical response

...which can be predicted by continuum models too

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*picture adapted from Carraro et al., Electrochim. Acta 77 (2012) 315

**picture adapted from Häffelin et al., J. Electrochem. Soc. 160 (2013) F867
Motivation

• 3D simulations must go *beyond* what 1D macro-homogeneous models can do

• 3D simulations should assess:
  o heterogeneous distributions
  o hot spots which may trigger localized degradation phenomena
  o *truly* three-dimensional properties

There is the need to exploit the **full potential** of simulations combined with 3D tomography
A novel approach to fully exploit 3D data

Resolve individual particles

Tomographic microstructure

3D electrochemical model

linking electrochemical behavior to individual particles

\[ \nabla \cdot (-D_k \nabla C_k) = 0 \]

\[ \nabla \cdot (-\sigma \nabla V) = 0 \]

\[ i_{TPB} = i_0 \prod_k p^{\xi_k} \left( \frac{a_{F\eta}}{RT} - e^{-\frac{(1-a)F\eta}{RT}} \right) \]

*Quiq3D by IQM Elements, London
**Workflow**

1. Produce the mesh (Synopsys Simpleware)

2. Solve the model (Comsol Multiphysics)

3. Export and process the results (Comsol Multiphysics + Matlab)
1) Mesh in Synopsys Simpleware

INPUT = segmented microstructural dataset

PROCEDURE
1. Assign isolated islands smaller than 125 voxels to the adjacent phase

2. Produce the mesh (smart mask smoothing, coarseness factor -15)

OUTPUT = Nastran mesh file (~ 40 M mesh elements)
2) Model in Comsol

INPUT = Nastran mesh file

PROCEDURE
1. Import the mesh
2. Define geometric entities (Boolean operations)
2) Model in Comsol

PROCEDURE

3. Set the physics (General Form PDE Interface)

\[
\begin{align*}
\text{Ni:} & \quad \nabla \cdot I_e = 0 \quad I_e = -\sigma_e \nabla V_{Ni} \\
\text{ScSZ:} & \quad \nabla \cdot I_O = 0 \quad I_O = -\sigma_O \nabla V_{ScSZ} \\
\text{Pore:} & \quad \nabla \cdot N_H = 0 \quad N_H = -D_H \frac{P}{RT} \nabla y_H
\end{align*}
\]

4. Set the reaction rate as an edge source
5. Select stationary solver (segregated)
6. OPTIONAL: Reduce element order
7. Solve in cluster (> 150 GB RAM)
3) Export data (Comsol + Matlab)

INPUT = solved model (field variables within the domains)

PROCEDURE*
1. Export data in Gauss points
2. Use an in-house Matlab code to interpolate values in Gauss points to a regular grid

OUTPUT = Field variables in grid to be overlaid with microstructure & particles

*Lettin Comsol export as a regular grid is too slow.*
Inhomogeneous current distribution

Ni/ScSZ anode

- Inhomogeneous distribution of current transferred by particles
- **Good** particles have more connections, **bad** particles are disconnected
Localized Joule heating and particle dispersion

8% of particles experience more current than what continuum models predict.

The wider the particle dispersion, the more inhomogeneous the current distribution.

Hot spots and localized Joule heating.
• **Good** particle for *transferring* current have connections but small reaction sites
• **Good** particles for *producing* current have reaction sites but small connections
• Particles which **excel** in both functions are a tiny fraction (~1 % of the total)

*Connections and reaction sites* (TPBs) are **mutually exclusive** conditions
an advanced design is required by **decoupling** the functionalities
Conclusions

• 3D tomography + physically-based simulation + resolving particles

• Comsol coupled with Synopsys Simpleware and Matlab

• Some tricks to handle big models… a lot of room for improvement!

• There is more 3D information in outliers than in mean trends
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Have a look at the paper!!!

A novel approach for the quantification of inhomogeneous 3D current distribution in fuel cell electrodes

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Thank you!
Backup slides
• Inhomogeneous distribution of current **produced** by particles
• **Good** particles have more TPBs, **bad** particles have less or no TPB
Localized Joule heating and particle dispersion

Localized Joule heating

8% of particles experience more current than what continuum models predict

Hot spots and localized Joule heating

Particle dispersion

The wider the particle dispersion, the more inhomogeneous the current distribution

Coarsening may induce further coarsening
Macro-homogeneous modelling

Phase-resolved

- Gas transport
- Charge transport

Electrochem. reaction

Continuum

\[ \nabla \cdot \left( \frac{\varepsilon_g}{\tau_g} D_k \nabla C_k \right) = \frac{i_{TPB}^v}{n_k F} \]

\[ \nabla \cdot \left( \frac{\varepsilon_s}{\tau_s} \sigma \nabla V \right) = \pm i_{TPB}^v \]

Averaged microstructural properties to get averaged electrochemical response

*picture adapted from Bertei et al., Int. J. Hydrog. Energy 41 (2016) 22381
• Inhomogeneous distribution of current transferred by particles
• **Good** particles have more connections, **bad** particles are disconnected
Electrochemical modelling approach

Model-based design approach

3D tomography: microstructure

Impedance spectroscopy: electrochemistry

Fabrication

Characterization

Modelling

Simulation & validation

Physically-based model

Z_{Im} [Ω cm²]

Z_{Re} [Ω cm²]

Simulation & validation

650°C
600°C
750°C
700°C

exp.
sim.

YSZ
Ni
ScSZ
stagnant layer

(1) Bertei et al., Int. J. Hydrogen En. 41 (2016) 22381-22393
Advanced microstructural characterisation tools

Particle analysis (proprietary)
- Watershed algorithm to identify particles
- Statistics of neighbours, contact areas, TPB, etc.

Tortuosity factor (open-source)*
- Solves Fick law in 3D voxels
- Segmented or gray-scale datasets
- Extended to diffusion impedance

* S.J. Cooper et al., SoftwareX 5 (2016) 203-210