Modeling of water and oxygen transport in electrolyzers – multi-phase flow on the Darcy scale

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https://www.sergeferrari.com/references/serge-ferrari-board-energy-observer
Hydrogen demand in transportation:

- Hydrogen ship (2017 Saint-Malo)
- Fuel cell bus (2005 London)
- Fuel cell aircraft (HY4, 2016)
- Fuel cell cars (2007)
- Hydrail (from 2021 Buxtehude-Cuxhaven)
Hydrogen can be produced with **electrolyzers**

Example:
Proton exchange membrane water electrolyzer (PEMWE) cells

(www.h-tec.com/de/education)

**Electrolyzers are also discussed for energy storage**
Electrolyzers

Oxygen evolution reaction

\[ \text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + 2\text{e}^- + \frac{1}{2}\text{O}_2 \]

Bipolar Plate - Ti plate with engraved flow channels
PTL - Porous transport layer
MEA - Membrane electrode assembly
Electrolyzers

PEM Water Electrolysis: \[ 2H_2O \leftrightarrow 2H_2 + O_2 \]
**Electrolyzers**

Porous transport layer

Titanium, hydrophilic

Thickness ~ 1 mm

300 μm
Efficiency of the cell: as much current density (→ hydrogen) as possible with as little cell voltage as possible

Polarization curve

Current density \(i\) [A/cm\(^2\)]

As much water at the membrane as possible

Modeling of fluid transport processes to reduce losses
Boundary condition membrane, in: \( \text{O}_2 \), out: \( \text{H}_2\text{O} \)

According to Butler Volmer equation (simplified)

\[
i = i_{ref} \left( \frac{c_{\text{H}_2\text{O}}}{c_{ref}} \exp \left( \frac{\eta A}{RT} \right) \right) \quad i \rightarrow \text{number of electrones}
\]
\[
\rightarrow \text{number of molecules}
\]
Outline

- Multi-phase flow on the Darcy scale: Modeling approach
- Comparison model to observations
- Conclusions
Question: Can Darcy scale models be used to describe and predict the processes in the porous transport layer?

Darcy scale: Control volume over an REV

→ Pore space no longer resolved

Change of ... with time equals fluxes in and out plus sources
Darcy scale model of two-phase flow

Two fluids: Oxygen (gas phase) and water (liquid phase)

Mass balance for each fluid (here identical with component):

$$\Phi \frac{\partial S_\alpha \rho_\alpha}{\partial t} + \nabla \cdot [\bar{q}_\alpha \rho_\alpha] = s_\alpha$$

$S_\alpha$: Volume percentage of phase $\alpha$ in pore space [-]

$$S_{\text{liquid}} + S_{\text{gas}} = 1$$

$\bar{q}_\alpha$: Specific discharge of phase $\alpha$  \quad \rho_\alpha$: Density of phase $\alpha$

5 unknowns: one saturation, 4 components of spec. discharge

Parameters and fluid properties: Porosity, density
Darcy scale model of two-phase flow

**Assumption:** specific discharge of each fluid follows a Darcy law (despite the fact that a second fluid flows at the same time and that the fluid might not form a connected pathway)

\[
\vec{q}_\alpha = -\frac{K_\alpha(S, \ldots)}{\mu_\alpha} \vec{\nabla}(p_\alpha + \rho_\alpha g z)
\]

3 unknowns: one saturation \( S \), two phase pressures \( p \)
\[ \rightarrow \] 1 constitutive relation

New parameters and fluid properties:
Permeability for both fluids, viscosities
Darcy scale model of two-phase flow

**Assumption:** Pressure difference between liquid and gas phase is a unique function of the fluid saturation (capillary pressure saturation), despite the fact that fluids are not static

\[ p_{\text{non wetting}} - p_{\text{wetting}} = p_c(S) \]

Here: \( p_{\text{gas}} - p_{\text{liquid}} = p_c(S_{\text{liquid}}) \)

2 unknowns, could be chosen in different ways, here: saturation gas phase, pressure liquid phase

**Parameters and fluid properties:**
Densities, viscosities \( \rightarrow \) Thermodynamics, nothing fancy
Porosity
Permeabilities, capillary pressure – saturation relation
Darcy scale model of two-phase flow

Capillary bundle model: Capillary pressure – saturation relation

Pressure jump across interface: Capillary pressure

\[ p_c = \frac{2\sigma \cos(\Theta)}{r} \]

If \( p_{nw} - p_w > \frac{2\sigma \cos(\Theta)}{r} \):

Non-wetting fluid is present, otherwise wetting fluid is present
Darcy scale model of two-phase flow

Capillary bundle model: Capillary pressure – saturation relation

Pressure distribution hydrostatic in both fluids

\[ p_{nw} = \rho_{nw}gz \]

\[ p_{w} = \rho_{nw}gz \]

\[ p_{c} = p_{nw} - p_{w} \]
Darcy scale model of two-phase flow

Capillary pressure – saturation relation:
Darcy scale model of two-phase flow

Capillary bundle model: Permeabilities

Wetting fluid: Small tubes  Non-wetting fluid: Large tubes

Permeability in one tube: Hagen Poisseuille for laminar flow

\[ K = \frac{R^2}{8} \]

Bundle of tubes filled with one fluid: arithmetic mean

\[ K = \frac{\Phi \int r^2 (\pi r^2) p(r) dr}{\frac{8}{\int (\pi r^2) p(r) dr}} \]
Darcy scale model of two-phase flow

Capillary bundle model: Permeabilities

Bundle of tubes filled with both fluids: Wetting fluid occupies the small tubes (<\(r_{\text{thr}}\)), non-wetting the large tubes (>\(r_{\text{thr}}\))

\[
K_{nw} = \frac{\Phi}{8} \frac{\int_{r_{\text{thr}}}^{\infty} r^2 (\pi r^2)p(r)dr}{\int_{0}^{\infty} (\pi r^2)p(r)dr} = K(S_{nw} = 1)k_r, nw(r_{\text{thr}})
\]

\[
K_w = \frac{\Phi}{8} \frac{\int_{0}^{r_{\text{thr}}} r^2 (\pi r^2)p(r)dr}{\int_{0}^{\infty} (\pi r^2)p(r)dr} = K(S_w = 1)k_r, w(r_{\text{thr}})
\]

Relation between threshold radius and saturation:

\[
S_w = \frac{\int_{0}^{r_{\text{thr}}} \pi r^2 p(r)dr}{\int_{0}^{\infty} \pi r^2 p(r)dr}
\]
Darcy scale model of two-phase flow

Relative permeabilities

\[ K_r^{nw}, K_r^{w} \]
Darcy scale model of two-phase flow

Summary model:

■ Basis: mass balance of the fluids
■ Assumption: specific discharge → Darcy law ("side by side flow")
■ Assumption: unique relation between fluid pressure difference and saturation (static configuration)
■ Predictive models: Parametrization of relative permeabilities and capillary pressure-saturation relation → structure of the porous medium
■ Many extensions under discussion
Outline

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Setup of the model

1d configuration

\[ p_{H_2O} = 10^5 \text{ Pa} \]

\[ S_{O_2} = 0 \]

\[ \dot{m}_{O_2, in} = \text{fix} \]

\[ \dot{m}_{H_2O, out} = \text{fix} \]

Butler-Volmer equation

\[ i = i_{ref} \left( \frac{c_{H_2O}^{\text{ref}}}{c_{H_2O}} \exp \left( \frac{\eta_A F}{RT} \right) \right) \]

• Fix \( i \)

• Calculate \( c_{H_2O} \) (model)

• Calculate \( n_A \)
Comparison model and observations

Data from the literature: Materials studied by M. Suermann et al., Journal of The Electrochemical Society 164(9), F973-F980, 2017

X-ray tomographic microscopy
Comparison model and observations

Parameters

<table>
<thead>
<tr>
<th>Property</th>
<th>T5</th>
<th>T10</th>
<th>T20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tortuosity $\tau$ [-]</td>
<td>$1.9 \pm 0.1$</td>
<td>$1.6 \pm 0.1$</td>
<td>$1.8 \pm 0.1$</td>
</tr>
<tr>
<td>Porosity $\varepsilon$ [%]</td>
<td>$30 \pm 2$</td>
<td>$35 \pm 2$</td>
<td>$33 \pm 2$</td>
</tr>
</tbody>
</table>

Size distribution [\(\mu m\)]

<table>
<thead>
<tr>
<th>Size</th>
<th>Void</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{10}$</td>
<td>16</td>
<td>34</td>
</tr>
<tr>
<td>$d_{50}$</td>
<td>40</td>
<td>68</td>
</tr>
<tr>
<td>$d_{90}$</td>
<td>68</td>
<td>110</td>
</tr>
<tr>
<td>Modal</td>
<td>18</td>
<td>46</td>
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<tr>
<td>Median</td>
<td>28</td>
<td>52</td>
</tr>
<tr>
<td>Mean</td>
<td>30</td>
<td>56</td>
</tr>
</tbody>
</table>

$K = 1.2 \times 10^{-12} m^2$

$K = 3.4 \times 10^{-12} m^2$

$K = 7.7 \times 10^{-12} m^2$

M. Suermann et al., Journal of The Electrochemical Society 164(9), F973-F980, 2017
Comparison model and observations

Lettenmeier et al., Royal Society of Chemistry 10(12), 2017
Comparison model and observations

Relative permeability calculated from Pc-S with Burdine model

\[ k_{r,w} = \left[ \frac{S_w - S_{w,r}}{1 - S_{w,r}} \right]^2 \frac{\int_0^{S_w} \frac{dS_w}{P_c^2}}{\int_0^1 \frac{dS_w}{P_c^2}} \]

\[ k_{r,nw} = \left[ 1 - \frac{S_w - S_{w,r}}{1 - S_{w,r}} \right]^2 \frac{\int_0^{S_w} \frac{dS_w}{P_c^2}}{\int_0^1 \frac{dS_w}{P_c^2}} \]
Comparison model and observations

Results: Prediction vs. Observations

T10, $p = 1 \text{ bar}, \vartheta = 50 \text{ °C}$
Comparison model and observations

Calibration: Fitting relative permeability while keeping all other parameters as measured

\[ k_{rn,T10} \text{ acc. to Burdine} \]

\[ k_{rn,T10} \text{ calibrated} \]

Relative permeability \( k_{rn} \)

Liquid saturation \( S_w \)

Relative permeability \( k_{rn} \)

Liquid saturation \( S_w \)
Comparison model and observations

Results: Dependence of performance on operating pressure

$T10, \vartheta = 50 \, ^\circ C$

$\eta_{mex, PTL}$ [mV]

- $p = 1$ bar, experiment
- $p = 10$ bar, experiment
- $p = 50$ bar, experiment
- $p = 1$ bar, calibrated
- $p = 10$ bar, transferred
- $p = 50$ bar, transferred

$i$ [A/cm$^2$]
Comparison model and observations

Results: Performance at very high current density T10

No more liquid at the cathode, water transported only as vapour
Comparison model and observations

Results: Pressure and saturation profiles in the cell

**T10**
Comparison model and observations

Results: Transferrability of the model to other materials

- Measured permeability
- Rescaled entry pressure
Comparison model and observations

Neutron radiograms of water in the porous transport layer (anode) (SEWERYN et al., Journal of the Electrochemical Society 163(11), 2016)
Comparison model and observations

Shape of a capillary pressure curve that would allow to reproduce such a behaviour

\[ P_c \]

![Diagram showing capillary pressure curve withreekness values and model comparison]

- T10
- 200 µm

- GKN Sika T05
- GKN Sika T10
- GKN Sika T20

\[ S_w \]

\[ \times 10^7 \]
Outline

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Conclusions

- Multi-phase flow models on the Darcy scale can be used to analyze the fluid transport processes in PEM electrolyzers.
- Observations that can be compared to the model are not straightforward to obtain.
- Some observations can only be reproduced if parameter functions have non-typical shapes.
- Pore scale models would be useful (ongoing work at the moment).

Thank you!