Introduction to Fuel Cells

FHI-Seminar
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• Net reactions and ideal potentials (Nernst Equation)
• Actual performance and energy losses
• Atomistic view of electrodes
  – Double layer models
  – Potentials
  – Capacity model
  – Charge distribution
• Problems for fuel cell modeling:
  – Electrode / Interface
  – Membrane
  – H₂ storage
In 1839, William Grove, a British jurist and amateur physicist, first discovered the principle of the fuel cell. Grove utilized four cells, each containing hydrogen and oxygen, to produce electric power which was then used to split the water in the smaller upper cell into hydrogen and oxygen.
Why Fuel Cells?

- Limitation of fossil energy resources
- Increasing CO$_2$ emission
- Global warming
- Transport problems
- .....
Pros – Cons (Ideal Situation)

+ 
  • Direct energy conversion (no combustion)
  • Low emissions
  • No moving part in the energy converter
  • Quiet
  • High availability of lower temperature units
  • Siting ability
  • Fuel flexibility
  • Remote/unattended operation
  • Small size

— 
  • High market entry cost, production cost
  • Unfamiliar technology to the power industry
  • Almost no infrastructure
  • Still at level of development
Working principle
Fuel Cell Types
Fuel Cell types

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Temperature</th>
<th>Oxidant</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Anode</th>
<th>Fuel</th>
<th>Applications</th>
<th>Status quo</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>80 °C</td>
<td>O₂</td>
<td>O₂/ H₂O</td>
<td>OH⁻</td>
<td>H₂</td>
<td>H₂/O₂</td>
<td>Transport, space, ships</td>
<td>50-100 kW, can be bought, expensive</td>
</tr>
<tr>
<td>PEM</td>
<td>80 °C</td>
<td>O₂/ H₂O</td>
<td>H₂</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H₂/O₂</td>
<td>transport, cars, space, houses, ships, mobile appl.</td>
<td>20 kW, high efficiency</td>
</tr>
<tr>
<td>PAFC</td>
<td>200 °C</td>
<td>O₂</td>
<td>H₂</td>
<td>CO₂⁻</td>
<td>H⁺</td>
<td>H₂/O₂</td>
<td>100 MW plants 50-500 kW block heating plants</td>
<td>100 kW prototype</td>
</tr>
<tr>
<td>MCFC</td>
<td>650 °C</td>
<td>CO₂</td>
<td>CO₂⁻</td>
<td>H⁺</td>
<td>O⁻</td>
<td>H₂/O₂</td>
<td>100 MW plants 50-500 kW block heating plants</td>
<td>25 kW prototype</td>
</tr>
<tr>
<td>SOFC</td>
<td>1000 °C</td>
<td>O₂</td>
<td>air</td>
<td>O⁻</td>
<td>H⁺</td>
<td>H₂/O₂</td>
<td>100 MW plants 50-500 kW block heating plants</td>
<td>100 kW prototype</td>
</tr>
</tbody>
</table>

η: Efficiency

- AFC: 50-65%
- PEM: 50-80%
- PAFC: 35-45%
- MCFC: 45-60%
- SOFC: 50-60%

Status quo: 50 kW, high efficiency
Fuel Cell Overview

Electrode catalysis:
- Make more efficient
- Reduce overpotential

Electrolyte:
- Less expensive
- More efficient
- Wide operation temperature range

H₂ storage:
- Carbon Nanotubes
- Metal Hydrides

Diagram:
- Hydrogen from Tank
- Oxygen from Air
- Electrical Circuit
- Proton Exchange Membrane
Pros – Cons (specific)

- **PEMFC:**
  - Solid electrolyte → excellent resistance to gas crossover
  - Working temperature ~80°C → short startup time
  - Can work at high current densities compared to other cells

- Low CO tolerance (~ppm level)
- Low temperature
- Unefficient to use rejected heat for cogeneration of additional power
- Difficult heat and water management limit the operating power densities
Pros – Cons (specific)

• **AFC:**
  - Excellent performance on $\text{H}_2$ and $\text{O}_2$ compared to other cells due to active $\text{O}_2$ electrode kinetics (70% efficiency)
  - Relatively low temperatures ($\sim 80^\circ\text{C}$)
  - Wide range of possible electrocatalysts
  - Very clean fuel required, since small contaminations dissociate alkaline base,
  - $\text{CO}_2$ poisoning
  - Significant pressure difference across the membrane is required
  - Large Pt quantity is needed if harsh conditions

---

### ISS

![ISS Image]

- **Anode:** $\text{H}_2 + 2(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$
- **Cathode:** $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^-$
- **Cell:** $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$
Pros – Cons (specific)

- **PAFC:**
  - $+\ CO_2$ (of reformed fuel gas stream) resistant electrolyte
  - $+\ \text{low working temperatures} \ (\sim 200\C)$
  - $+\ \text{water boiling point is not limiting}$
  - $+\ \text{less complex fuel conversion} \ (\text{no membrane and attendant pressure drop})$

- **Cons:**
  - -- lower performance due to slow cathode reaction (37-42%)
  - -- fuel from external hydrocarbon reformation
  - -- high cost catalysts
  - -- harsh conditions
  - -- CO poisoning (water gas shift reaction required)

\[
\text{Anode: } H_2 \rightarrow 2H^+ + 2e^-
\]
\[
\text{Cathode: } \frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O
\]
\[
\text{Cell: } H_2 + \frac{1}{2} O_2 \rightarrow H_2O
\]
Pros – Cons (specific)

• **MCFC**:  
  - + higher temperatures (~650°C)  
  - less sensitive reactions and less expensive materials  
  - + Ni as catalyst  
  - + reforming within the cell  
  - + CO can directly be used as fuel  
  - + heat exhaust can be used with external gas turbine (η~80%)  
  - – very corrosive and mobile electrolyte  
  - – source of CO₂ is required at cathode to form carbonate ions  
  - – low sulfur tolerance  
  - – high temperatures (~650°C)  
  - – stainless steel as cell hardware  
  - – complex working procedure
### Pros – Cons (specific)

#### SOFC

**Pros:**
- Ceramic construction
- No hardware corrosion
- No gas crossover due to absence of liquid
- Fast kinetics
- Fast kinetics
- CO is directly usable
- No CO\(_2\) is required at cathode (as in MCFC)
- High temperature (~1000°C)
  - Fuel can be reformed within the cell

**Cons:**
- Incoming air has to preheated
- High temperature (~1000°C)
- Thermal expansion mismatch
- Sealing between cells is difficult
- Constraints on material collection
- Difficult fabricate process
- High electrical resistivity in the electrolyte
- Low performance
- High cost catalysts

### Anode and Cathode

- **Anode:** \( \text{H}_2 + O^2- \rightarrow H_2O + 2e^- \)
- **Cathode:** \( \frac{1}{2} \text{O}_2 + 2e^- \rightarrow O^2- \)
- **Cell:** \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow H_2O \)

### Solid Oxide Fuel Cell

- **Anode:** Ni
- **Cathode:** LaMnO\(_3\)
- **Electrolyte:** YSZ ZrO\(_2\)[Y\(_2\)O\(_3\)]
Ideal Performance
Nernst Equation

\[ A^+ (\text{solution}) + e^- (\text{metal}) \quad \leftrightarrow \quad \frac{1}{2} A_2 (g) \]

\[ \bar{\mu}_{A^+, \text{solution}} + \bar{\mu}_{e^-, \text{metal}} = \frac{1}{2} \bar{\mu}_{A_2, \text{gas}} \]

Electrochemical potential:

\[ \bar{\mu}_i = \mu_i + N_A e^- z_i \phi = \mu_i + z_i F \phi \]

\[ \rightarrow \bar{\mu}_i = \mu_i^{\phi} + RT \ln \frac{p_i}{p_i^{\phi}} + z_i F \phi \]

\[ \left\{ \begin{array}{l}
\bar{\mu}_{A^+, \text{solution}} = \mu_{A^+} + F \phi_{\text{solution}} \\
\bar{\mu}_{e^-, \text{metal}} = \mu_{e^-} + F \phi_{\text{metal}} \\
\bar{\mu}_{A_2, \text{gas}} = \mu_{A_2(g)} = \mu_{A_2}^{\phi} + RT \ln \frac{f}{p_i^{\phi}}
\end{array} \right. \]

\[ \leftrightarrow (\mu_{A^+} + F \phi_{\text{solution}}) + \mu_{e^-} + F \phi_{\text{metal}} = \frac{1}{2} \mu_{A_2(g)} \]
Nernst Equation

\[
\Delta \phi = \frac{1}{F} (\mu_{A^+}^0 + \mu_e^- - \frac{1}{2} \mu_{A_2}^0) + \left(\frac{RT}{F}\right) \ln \frac{a_{A^+}}{f^{1/2}}
\]

\[
\Delta \phi = \Delta \phi^0 + \left(\frac{RT}{F}\right) \ln \frac{a_{A^+}}{f^{1/2}}
\]

\[
\Delta \phi = \Delta \phi^0 + \left(\frac{RT}{F}\right) \ln \frac{Ox}{Red}
\]

<table>
<thead>
<tr>
<th>Cell Reactions(^a)</th>
<th>Nernst Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2 + \frac{1}{2}O_2 \rightarrow H_2O)</td>
<td>(E = E^\circ + \left(\frac{RT}{2F}\right) \ln \left[\frac{P_{H_2}}{P_{H_2O}}\right] + \left(\frac{RT}{2F}\right) \ln \left[\frac{P_{O_2}^0}{P_{H_2O}}\right])</td>
</tr>
<tr>
<td>(H_2 + \frac{1}{2}O_2 + CO_2(a) \rightarrow H_2O + CO_2(g))</td>
<td>(E = E^\circ + \left(\frac{RT}{2F}\right) \ln \left[\frac{P_{H_2}}{P_{H_2O}}\left(P_{CO_2}\right)<em>{(g)}\right] + \left(\frac{RT}{2F}\right) \ln \left[\frac{P</em>{O_2}^0}{\left(P_{CO}<em>2\right)</em>{(g)}}\right])</td>
</tr>
<tr>
<td>(CO + \frac{1}{2}O_2 \rightarrow CO_2)</td>
<td>(E = E^\circ + \left(\frac{RT}{2F}\right) \ln \left[\frac{P_{CO}}{P_{CO_2}}\right] + \left(\frac{RT}{2F}\right) \ln \left[\frac{P_{O_2}^0}{P_{CO_2}}\right])</td>
</tr>
<tr>
<td>(CH_4 + 2O_2 \rightarrow 2H_2O + CO_2)</td>
<td>(E = E^\circ + \left(\frac{RT}{8F}\right) \ln \left[\frac{P_{CH_4}}{P_{H_2O}}\right] + \left(\frac{RT}{8F}\right) \ln \left[\frac{P_{O_2}^0}{P_{CO_2}}\right])</td>
</tr>
</tbody>
</table>

\(\text{FC reactions and their corresponding Nernst equations}\)

\(\begin{align*}
\text{P} & - \text{gas pressure} \\
\text{R} & - \text{universal gas constant} \\
\text{T} & - \text{temperature (absolute)}
\end{align*}\)
Nernst Equation

$$\Delta \phi = \Delta \phi^\circ + \left( \frac{RT}{\nu F} \right) \ln \frac{O_x}{Red}$$

Temperature dependence of H$_2$/O$_2$
Ideal Potential

Ideal voltage (for oxidation of hydrogen) as a function of cell temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25°C</th>
<th>80°C</th>
<th>100°C</th>
<th>205°C</th>
<th>650°C</th>
<th>800°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(298K)</td>
<td>(353K)</td>
<td>(273K)</td>
<td>(478K)</td>
<td>(923K)</td>
<td>(1073K)</td>
<td>(1373K)</td>
</tr>
<tr>
<td>Cell Type</td>
<td>PEFC</td>
<td>AFC</td>
<td>PAFC</td>
<td>MCFC</td>
<td>ITSOFC</td>
<td>SOFC</td>
<td></td>
</tr>
<tr>
<td>Ideal Voltage</td>
<td>1.18</td>
<td>1.17</td>
<td>1.14</td>
<td>1.03</td>
<td></td>
<td></td>
<td>0.91</td>
</tr>
</tbody>
</table>
Actual Performance
Actual Performance

- Concentration Polarization → reactions reduce educt concentrations $\eta_{\text{conc}}$
- Activation Polarization → Rates of electrochemical reactions $\eta_{\text{act}}$
- Ohmic Polarization → resistance of ion flow $\eta_{\text{ohm}}$
Concentration Polarization

Rate of mass transport to an electrode surface can be described by Fick’s first law of diffusion:

\[ i = \frac{\nu F D (c_{\text{bulk}} - c_{\text{surface}})}{\delta} \]

\((D: \text{diffusion coefficient}, c_i: \text{concentration}, \delta: \text{thickness of diffusion layer})\)

The limiting current \(i_L\) is a measure of the maximum rate at which reactants can be supplied to an electrode and occurs at \(c_{\text{surface}} = 0\):

\[ i_L = \frac{\nu F D c_{\text{bulk}}}{\delta} \]

\[ \longleftrightarrow \frac{c_{\text{surface}}}{c_{\text{bulk}}} = 1 - \frac{i}{i_L} \]

Nernst equation for reactant species at equilibrium is:

\[ \Delta \phi_{i=0} = \Delta \phi^0 + \left(\frac{RT}{\nu F}\right) \ln c_{\text{bulk}} \]

When current flows \(c_{\text{surface}}\) is less than \(c_{\text{bulk}}\) and

\[ \Delta \phi = \Delta \phi^0 + \left(\frac{RT}{\nu F}\right) \ln c_{\text{surface}} \]

Potential difference produced by a concentration change:

\[ \eta_{\text{conc}} = \Delta \phi_{i=0} - \Delta \phi = \left(\frac{RT}{\nu F}\right) \ln \frac{i}{i_L} \]

\[ \longleftrightarrow \eta_{\text{conc}} = \left(\frac{RT}{\nu F}\right) \ln \frac{i}{i_L} \]
Activation Polarization

The activation polarization is customarily expressed by a semi-empirical equation, called Tafel equation:

\[ \eta_{\text{act}} = \left( \frac{RT}{\alpha \nu F} \right) \ln \frac{i}{i_0} \]

Here \( \alpha \) is the electron transfer coefficient of the reaction at the electrode, and \( i_0 \) is the exchange current density.

The usual form is given by \( \eta_{\text{act}} = a + b \log i \)
where \( a = (-2.3RT/\alpha \nu F) \cdot \log i_0 \) and \( b = 2.3RT/\alpha \nu F \).

B is called the Tafel slope.
Actual Performance

Sum of electrode polarization: 

\[ \eta_{\text{anode}} = \eta_{\text{act,a}} + \eta_{\text{conc,a}} \]

\[ \eta_{\text{cathode}} = \eta_{\text{act,c}} + \eta_{\text{conc,c}} \]

The effect is to shift the potential of an electrode \((\Phi_{\text{electrode}})\):

\[ \Phi'_{\text{cathode}} = \Phi_{\text{cathode}} - |\eta_{\text{cathode}}| \]

\[ \Phi'_{\text{anode}} = \Phi_{\text{anode}} + |\eta_{\text{anode}}| \]

\[ \Phi_{\text{cell}} = \phi_{\text{cell}} = \Phi_{\text{cathode}} - |\eta_{\text{cathode}}| - (\Phi_{\text{anode}} + |\eta_{\text{anode}}|) - I \cdot R \]

\[ \Phi_{\text{cell}} = \Delta \Phi - |\eta_{\text{cathode}}| - |\eta_{\text{anode}}| - I \cdot R \]

Current flow reduces cell voltage due to electrode and ohmic polarization

\[ \Phi_{\text{cell}} = \Delta \phi = \Delta \phi^\circ + \left( \frac{RT}{\nu F} \right) \ln \frac{O_x}{\text{Red}} - |\eta_{\text{cathode}}| - |\eta_{\text{anode}}| - I \cdot R \]

Goal: Minimize the polarization
Electric Double Layer
Steps of electrochemical reaction:

1. Transport of reactants to electrode

2. Adsorption of reactants at electrode (maybe dissociative ads.)
   e.g. H₂ → H₂,ads; H₂,ads ↔ 2H_ads; H₂ ↔ H⁺ + A⁻

3. Electron transfer through phase boundary
   e.g. H⁺ + e⁻ ↔ H_ads

4. Follow-reactions at electrode surface and desorption
   e.g. 2H_ads → H₂(g)

5. Removing reaction products to solution
Electron Transfer

$E_F$: Fermi-level of metal

$a$: Tunnel distance

$\Phi$: Work function of metal

$EA$: Electron affinity

$EA > \Phi$ for reduction

$\Phi - EA$ should be small

Open circuit: Reaction takes place until equilibrium at electrode

equilibrium potential $\varphi_0$

Opposite charge distribution in metal and electrolyte
Double-Layer

Potential is a result of the charge distribution

- Electroneutral!

$\varphi_0$ - $\varphi_L$

- Equilibrium: dynamic equilibrium of charge transfer in both directions of phase boundary

- Electrochemical process only if coupled with reduction (oxidation) at opposite electrode

- Open circuit: EMK = $\varphi_0$ of galvanic cell
At a certain electrode potential (potential of zero charge) the electrode surface charge vanishes: \( q = 0, \sigma = 0 \)

This can be measured polarographically measuring \( I \) for different \( \phi \)

![Diagram of PSZ-Potential of Zero Charge](image)
Remove electrolyte without changing the charge distribution of the metal (surface)

Region 1: Test charge feels Coulomb potential at far distances
Region 2: Surface charge is not a point charge
Region 3: Test charge feels surface charges
Detailed view of Double-Layer

**Physisorption:**
- electrostatic interaction between charges
- charge-dipol interaction
- polarisation of molecules and ions
- dispersion forces, vdW forces
- Attachment of opposite charged ions and molecule-dipols

**Chemisorption:**
- chemical interaction between particles and metal
Detailed view of Double-Layer

Inner Helmholtz Plane:
plane of adsorbed species
(direct electrode contact)

Inner Helmholtz Layer:
Area of reactions with desolvated particles

Outer Helmholtz Plane:
plane of closest possible solvated particles

Outer Hemholtz Layer:
Area of redox reaction between solvated particles
Condensator Model of Double-Layer o.H.p. model

Charge density on metal surface: \( \sigma_e = q / A \)

equivalent charge density in o.H.p. \( \rightarrow \) electric double layer

Integral double layer capacity (relative to psz level):
\[
C_D = \frac{q}{\varphi_e - \varphi_{pzc}} \quad \lim_{q \to 0} \frac{q}{\varphi_e - \varphi_{pzc}} = C_D
\]

Differential double layer capacity:
\[
\tilde{C}_D = \frac{\partial q}{\partial \varphi_e}
\]

\[
\frac{\partial C_D}{\partial \varphi_e} = \frac{1}{\varphi_e - \varphi_{pzc}} \cdot \frac{\partial q}{\partial \varphi_e} - \frac{q}{(\varphi_e - \varphi_{pzc})^2}
\]

\[
(\varphi_e - \varphi_{pzc}) \frac{\partial C_D}{\partial \varphi_e} = \tilde{C}_D - C_D
\]

\[
\tilde{C}_D = C_D + (\varphi_e - \varphi_{pzc}) \frac{\partial C_D}{\partial \varphi_e}
\]

Measurement of differential capacity with DC methods, electrocapillar-experiments
Condensator Model of Double-Layer o.H.p. model

$C_D$: Double layer capacity
$R_S$: Electrolyte resistance
$C_{ref}$: Capacity of reference electrode (usually neglected)

Measurement by potential drop method:

$$U = U_R + U_C = I \cdot R_S + \frac{q}{C_D}$$

$$I = \frac{d}{dt} \left( -\frac{q}{R_S \cdot C_D} + \frac{U}{R_S} \right)$$

Solving Diff. Eq. for $q$, then integrate over $t$:

$$q = U \cdot C_D \left[ 1 - \exp \left( -\frac{t}{R_S \cdot C_D} \right) \right]$$

Evaluate $I$:

$$I = \frac{U}{R_S} \exp \left( -\frac{t}{R_S \cdot C_D} \right) \Rightarrow \ln I = \ln \left( \frac{U}{R_S} \right) - \frac{t}{R_S \cdot C_D}$$
Models for electric double layer

Helmholtz (1853) static double layer

Gouy (1910) and Chapman (1913) diffuse double layer

Stern (1924) static and diffuse double layer (combination)

New model also include:

• Specific adsorption at electrode
• Ion-metal, molecule-metal interaction and catalytic effects
• Structure of conduction bands
• Overlap between valence band and conduction band at phase boundary
• Dielectric filling of double layer
• Deformation of conduction band
Stern Model

Double layer without adsorption of ions (charges) within the i.H.l.

**o.H.l.: static double layer**, free of charges $\rho(x) = 0$

Poisson equation with conditions:

\[
\frac{\partial^2 \varphi}{\partial x^2} = 0 \\
0 \leq x < a \quad ; \quad \varphi(x = 0) = \varphi_e; \quad \varphi(x = a) = \zeta
\]

$\zeta$: Zeta-Potential at the boundary between static Helmholtz layer and diffuse layer

$\rightarrow$ Distance-dependency of potential:

\[
\varphi(x) = \varphi_e - \frac{\varphi_e - \zeta}{a} x
\]

**Diffuse double layer**: Electrolyte beyond the o.H.l. (bulk solution) $\rho(x) \neq 0$

Poisson equation:

\[
\frac{\partial^2 \varphi}{\partial x^2} = -\frac{1}{\varepsilon_0 \varepsilon} \rho(x)
\]
Stern Model

Diffuse double layer

Conditions: \[ \varphi(x = \infty) = \varphi_L, \quad \varphi(x = a) = \zeta, \quad a \leq x < \infty \]

Boltzmann-Ansatz for the charge distribution within the electrolyte

\[ \rho(x) = \sum_i n_i^0 z_i e_0 \exp \left[ -\frac{z_i e_0 \varphi(x)}{kT} \right] \]

Insert into Poisson equation:

\[ \frac{\partial^2 \varphi}{\partial x^2} = -\frac{1}{\varepsilon_0 \varepsilon} \sum_i n_i^0 z_i e_0 \exp \left[ -\frac{z_i e_0 \varphi(x)}{kT} \right] \]

If \[ \left[ \frac{z_i e_0 \varphi(x)}{kT} \right] \ll 1 \Rightarrow \text{small concentrations} \Rightarrow \text{Taylor expansion} \]

\[ \rho(x) = \sum_i n_i^0 z_i e_0 \left( 1 - \frac{z_i e_0 \varphi(x)}{kT} + \cdots \right) \Rightarrow \rho(x) = -\frac{e_0^2 \varphi(x)}{kT} \sum_i n_i^0 z_i^2 \]

\[ \frac{\partial^2 \varphi}{\partial x^2} = \frac{1}{\varepsilon_0 \varepsilon} \frac{e_0^2 \varphi(x)}{kT} \sum_i n_i^0 z_i^2 = \kappa^2 \varphi(x) \]

Solution of the partial differential equation: \[ \varphi(x) = A \exp[-\kappa x] + B \exp[\kappa x] \]
Stern Model

Diffuse double layer

Conditions:

1. Condition: \( B = 0 \Rightarrow \varphi(x) = A \exp[-\kappa x] \)

2. Condition: \( \varphi(a) = \zeta \)

\[
\varphi(a) = A \exp[-\kappa a] = \zeta \Rightarrow A = \zeta \exp[\kappa a]
\]

\[
\varphi(x) = \zeta \exp[-\kappa(x - a)]
\]

Debye-distance: \( \kappa^{-1} \approx \sqrt[3]{\frac{T}{\sum n_i^0 z_i}} \)

t Center of charge in the diffuse double layer

For \( x = \kappa^{-1} \):

\[
\varphi(\kappa) = \zeta \exp[-\kappa(\kappa^{-1} - a)] \approx \frac{\zeta}{e}
\]

Charge-density

\[
\rho(x) = -\varepsilon \varepsilon_0 \kappa^2 \zeta \exp[-\kappa(x - a)] = -\zeta \frac{\varepsilon_0^2}{kT} \exp[-\kappa(x - a)] \sum n_i^0 z_i^2
\]
Stern Model

Diffuse double layer

Small $\kappa \rightarrow$ broad double layer extends into electrolyte region

$\zeta$ of the o.H.p. can be replaced by the electrode potential

Electric Field:

\[
E = -\nabla \phi = -\frac{\partial \phi(x)}{\partial x} \hat{e}_x
\]

$x<\alpha$: $E(x) = \frac{\phi_e - \zeta}{\alpha}$

$x\geq\alpha$: $E(x) = \zeta \kappa \exp[-\kappa(x-\alpha)]$

Continuous transition at $x = \alpha$:

\[
\frac{\phi_e - \zeta}{\alpha} = \zeta \kappa \exp[-\kappa(\alpha-\alpha)]
\]

\[
\phi_e - \zeta = \zeta \kappa \alpha
\]

\[
\zeta = \frac{\phi_e}{(\kappa \alpha + 1)}
\]

Charge density as a function of the electrolyte concentration and electrode potential:

\[
\phi(x) = \frac{\phi_e}{(\kappa \alpha + 1)} \exp[-\kappa(x-\alpha)]
\]

\[
\rho(x) = -\frac{\phi_e}{(\kappa \alpha + 1)} \kappa^2 \exp[-\kappa(x-\alpha)]
\]
Stern Model

Diffuse double layer

Low concentrations: $\kappa a << 1$: $\zeta \approx \varphi_e$ Potential-drop within the o.H.I. is almost zero

High concentrations: $a < \kappa$: $\zeta = \frac{\varphi_e}{(\kappa a + 1)}$

Potential-drop within the o.H.I. increases with increasing concentrations, linearisation of Poisson equation may be critical!

Charge of the diffuse layer

\[
q_{\text{diff}} = -\varepsilon_0 \varepsilon A \zeta^\infty_a \exp[-\kappa(x-a)] \, dx = -\varepsilon_0 \varepsilon A \zeta^\infty_a \left[ -\frac{1}{\kappa} \exp[-\kappa(x-a)] \right]_a
\]

\[
q_{\text{diff}} = -\varepsilon_0 \varepsilon A \zeta
\]

Capacity of static double layer:

\[
\tilde{C}_D = \frac{\varepsilon_0 \varepsilon A}{a}
\]

Capacity of diffuse double layer:

\[
\tilde{C}_{\text{diff}} = \frac{\partial |q_{\text{diff}}|}{\partial \zeta} = \varepsilon_0 \varepsilon A / \kappa^{-1}
\]

$\Rightarrow$ Plate condensator at distance $\kappa$
Problems for Fuel Cell Modeling

Electrodes / Interfaces
Current problems for modeling I

- Morphology of the catalyst
  In order to provide a large surface area for simultaneous catalysis, Pt nanoparticles are used instead of (semi-) infinite systems.
  However:
  - Nanoparticles have structural and electronic properties, which might strongly depend on size and shape (e.g. Quantum Size Effects).
  - Nanoparticles combine a variety of different functional groups: different surfaces, steps, kinks, tips, vacancies, ...), having different properties.

\[ E_b = 0.49 \text{eV} \quad \text{and} \quad E_b = 1.10 \text{eV} \]
• **Influence of the support**
  
  - Pt nanoparticles are attached to larger Carbon particles (~50nm), which will change their structures.
  
  *Smaller particles $\rightarrow$ less deformation, close to spherical structure*
  
  *Larger particles $\rightarrow$ strong deformation, ellipsoidal shape*
  
  - Pt nanoparticles are assumed to be 2-5nm in diameter. However, due to relatively low diffusion barriers agglomeration may occur to create larger particles. (again having modified properties)
  
  - Supporting material:
    - Pd particles on Au have $\sim$10 times higher reactivity than Pd particles on Cu
Current problems for modeling III

- Bulk region should have structural properties (density, distribution, …) of bulk Nafion, otherwise system need to be expanded.

- Water layer forms between electrode and membrane (will be different in presence of E-field)
Current problems for modeling IV

• Reactive Environment
  – Cathode is surrounded by a variety of different compounds:
    • \( H_2O \) of the electrolyte, and reaction product
    • \( H_3O^+ \) as proton carrier (surrounded by water molecules)
    • \( O_2 \) gas as reaction component
    • Different reaction intermediates
      (e.g. \( O, H, OH, OOH, HOOH, \ldots \))
    • Impurities in the fuel (e.g. \( CO, No_x, \ldots \))

→ The environment might influence the structure, stability, and composition of the Pt nanoparticles (or certain functional groups).
→ This may vary for different \( T \) and \( p \) conditions
Current problems for modeling V

- Solvation effects due to solvent in the electrolyte
  - In case of PEM-FCs the electrolyte is hydrated
  - At the cathode water is generated

→ The electrode is surrounded by water molecules, which influence adsorption energies and structures. This might change the reaction mechanism, but also stabilize or destabilize certain structures (e.g. electrode, adsorbates)

→ Solvation can be treated by a two- or three-shell model
Current problems for modeling VI

- **Electrode potential**
  - Besides $T$ and $p$, the electrode potential $\varphi$ is another parameter, which influences structures and energetics.
  - Example: Au(100) surface in 0.01 M HClO$_4$ solution
    - $\varphi < 0.25 \text{V}$ quasi-hexagonal reconstruction
    - $\varphi > 0.25 \text{V}$ unreconstructed surface (H. Ibach et al., Surf. Sci. 375, 107 (1997))

- Distribution of negative and positive charges within the solution changes
- Counter charges will be on the surface of the metal electrode (whole interface is electroneutral)

$\rightarrow$ electric double layer establishes
$\rightarrow$ potential drop (strong E-field) on the electrode surface
• All previous problems deal with the system in equilibrium. However, under steady state conditions structures, compositions, and reaction mechanisms might be significantly different?

→ Use kinetic simulations to study exactly these influences.

However, in order to get reliable results all significant processes should be studied and the corresponding parameters extracted:
  Adsorptions, desorptions, diffusions, reactions, …
Electrolyte
Hydrated Nafion is a multiscale heterogeneous material.

Each level has implications on membrane performance.

Width of water domains affected by electrostatic repulsions and polymer elasticity.
Coarseness of the surface affects viscous movement of the ion.
Sensitive parameter for conductivity and permeation.

Ions exert dielectric friction on H+ mobility.

Rational approach to the study of PEM: experiments and simulation are complementary.

<table>
<thead>
<tr>
<th>Blockiness of polymer</th>
<th>Backbone flexibility</th>
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</thead>
<tbody>
<tr>
<td>Side chain length</td>
<td>Backbone hydrophobicity</td>
</tr>
<tr>
<td>Acidity of ionomer</td>
<td>Equivalent weight</td>
</tr>
<tr>
<td>Counter ion</td>
<td>Charge localization</td>
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<tr>
<td>Water content</td>
<td>Side chain flexibility</td>
</tr>
<tr>
<td>Temperature</td>
<td>Side chain polarity</td>
</tr>
<tr>
<td>Architecture of side chain</td>
<td>Confinement</td>
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</table>

<table>
<thead>
<tr>
<th>Microphase segregation</th>
<th>Counter ion migration</th>
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<tbody>
<tr>
<td>Water diffusion</td>
<td>Hydronium transport</td>
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<tr>
<td>Mechanical properties</td>
<td>Patchiness of the water/PE interface</td>
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<tr>
<td>Water's electroosmotic drag</td>
<td>Interfacial free volume</td>
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<tr>
<td>Maximum water uptake</td>
<td>Degree of crystallinity</td>
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<td>Water evaporation</td>
<td>T of glass transition(s)</td>
</tr>
<tr>
<td>Extent of ionomer solvation</td>
<td>Water percolation</td>
</tr>
</tbody>
</table>
Effect of polymer sequence

Blockiness affects the extent of nanophase segregation (is better for the blocky polymer) and water-polymer interface heterogeneity.

Effect of water content

We compute a water percolation threshold that is in agreement with the one inferred from conductivity. The percolation of the hydrophilic phase is necessary for proton conductivity.

Water diffusion is ~25% faster in the more segregated structure. Experimental results between blocky and random. Vehicular diffusion of hydronium is comparable for both sequences (no exp). Activation energies of water diffusion in agreement with experiment.
Membrane characteristics

**Characteristics of water mobility in**

(a) Pure water, (b) neutral and ionized nafion, (c) hydrophobic slabs, (d) hydrophilic slabs, (e) neutral and ionized *homogeneous solution* of nafion fragments
H₂ storage
Doped Carbon-Based Materials

MD/MC studies:

![Graph showing hydrogen density and hydrogen uptake mass% vs. interlayer and inter-tube distance (Å).](image)

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