Modeling and Simulations of Electrochemical Systems in COMSOL

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COMSOL
Outline

• Why and for whom?
• Scope
• Theory
  – How Physics interfaces are constructed
  – How to select Physics interfaces and Studies
• The Modules
  – Batteries & Fuel Cells
  – Corrosion
  – Electrochemistry
  – Electrodeposition
• Hands-on tutorial
Why and for Whom?
Why and for Whom?

Understand  Predict  Innovate  Optimize  Control
Why and for Whom?

Researchers, scientists, developers

Engineers that build things
Scope
Electrochemical Systems

- Electrochemical systems are devices or processes in which an ionic conductor mediates the interconversion of chemical and electrical energy.

- The reactions by which this interconversion of energy occurs involve the transfer of charge (electrons) at the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte).
Redox Reactions

- Individual electrode reactions are symbolized as reduction-oxidation (redox) processes with electrons as one of the reactants:

\[ \text{Ox} + n\text{e}^- \iff \text{Red} \]

\( \text{Ox} = \) oxidized species
\( \text{Red} = \) reduced species
\( \text{e}^- = \) electron
\( n = \) electron stoichiometry coefficient.
Redox Reactions

Red $\rightarrow$ Ox + ne$^-$

Ox + ne$^-$ $\rightarrow$ Red
Thermochemical and Electrochemical Processes

Thermochemical process:
- Direct transfer of ions
- Oxidized species ↔ Reduced species
- Direct transfer of electrons

Electrochemical process:
- Anode: Ionic transport
- Cathode: Oxidation → Reduction
- Electron transfer: $e^-$
Energy Producing and Energy Consuming Electrochemical Processes

Energy producing processes:
- Fuel cells
- Batteries

Energy consuming processes:
- Electrowinning and electroplating
- Electromachining
- Electrosynthesis
### Spontaneous Processes and Processes that Require Energy Input

<table>
<thead>
<tr>
<th>Spontaneous process</th>
<th>Process that requires the input of energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode reaction:</strong></td>
<td><strong>Anode reaction:</strong></td>
</tr>
<tr>
<td>$2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$</td>
<td>$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$</td>
</tr>
<tr>
<td><strong>Cathode reaction:</strong></td>
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</tr>
<tr>
<td>$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$</td>
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</tr>
<tr>
<td><strong>Sum reaction:</strong></td>
<td><strong>Sum reaction:</strong></td>
</tr>
<tr>
<td>$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{Energy}$</td>
<td>$2\text{H}_2\text{O} + \text{Energy} \rightarrow 2\text{H}_2 + \text{O}_2$</td>
</tr>
</tbody>
</table>

![Diagram showing energy change](image)
Electrocatalysis

Example of reduction at the cathode

Reaction coordinate

Energy Change in electrode potential Activation energy

Reactant Product

Electrode surface

$4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$

Reactant Product
Anodic and Cathodic Reactions

- **Equilibrium**
  - Ox + e⁻ → Red
  - Free energy graph

- **Reduction**
  - Ox + e⁻ → Red
  - Free energy graph

- **Oxidation**
  - Ox + e⁻ → Red
  - Free energy graph
Transport and Electrochemical Reactions

- **Transport**
  - Diffusion, convection, and migration. The mobility and concentration of ions yields the mass transfer and Ohmic resistances in the electrolyte.

- **Electrochemical reaction**
  - Electrode kinetics for an electron charge transfer step yields potential-dependent reaction rate. The overpotential is a measure of the activation energy (Arrhenius equation -> Butler-Volmer equation)
The Overpotential

- Anodic reaction
- Cathodic reaction
- Electronic current, -
- Ionic current
- Electronic current, +
- Anodic reaction
- Cathodic reaction

$E$
Multiple Processes

- Charge balances in the electrodes and electrolyte
- Material balances
- Energy balance
- Momentum balances
The Anode Electrode Matrix
The Anodic Reactions

Charge transfer reaction
The Electrolyte

Transport of current:
diff + migr

Transport of species:
diff + migr + adv
The Cathodic Reactions

Charge transfer reaction
The Cathode Electrode Matrix

Anode

Cathode

Electronic conduction
Transport

- Flux = diff. + conv. + migration

- Current density
  \[ \mathbf{j} = F \sum_i z_i \mathbf{N}_i \]

- Electroneutrality
  \[ \text{sum of charges} = 0 \]

- Perfectly mixed
  primary and secondary

\[ \mathbf{j} = F \left( \sum_i -z_i D_i \nabla c_i + \mathbf{u} \sum_i z_i c_i - \nabla \phi \sum_i (z_i)^2 m_i F c_i \right) \]

\[ \mathbf{j} = - \left( \frac{F}{\kappa} \sum_i (z_i)^2 m_i F c_i \right) \nabla \phi \]

\[ \kappa = \text{conductivity} \]
Conservation of Species and Charge

- Conservation of species
  n-1 species, n:th through charge conservation

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot \left(-D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_i \right) + R_i
\]

- Conservation of current

\[
\nabla \cdot \mathbf{j} = \nabla \cdot \left(F \left( \sum_i -z_i D_i \nabla c_i - \nabla \phi_i \sum_i (z_i)^2 m_i F c_i \right) \right)
\]

- Net current is not accumulated, produced or consumed in the bulk electrolyte

\[
\nabla \cdot \left(F \left( \sum_i -z_i D_i \nabla c_i - \nabla \phi_i \sum_i (z_i)^2 m_i F c_i \right) \right) = 0
\]

- For primary and secondary cases

\[
\nabla \cdot (-\kappa \nabla \phi_i) = 0
\]
Selecting Physics Interfaces

• Primary current density distribution
  – Accounts only for Ohmic effects in the simulation of current density distribution and performance of the cell

• Secondary current density distribution
  – Accounts only for Ohmic effects and the effect of electrode kinetics in the simulation of current density distribution and performance of the cell

• Tertiary current density distribution
  – Accounts for Ohmic effects, effects of electrode kinetics, and the effects of concentration variations on the performance of a cell
Selecting Physics Interfaces

• Non-porous electrodes
  – Heterogeneous reactions
  – Typically used for electrolysis, metal winning, and electrodeposition

• Porous electrodes
  – Reactions treated as homogeneous reaction in models although they are heterogeneous in reality
  – Typically used for batteries, fuel cells, and in some cases also for electrolysis

• Electrolytes
  – Diluted and supporting electrolytes
  – Concentrated electrolytes
  – ”Free” electrolytes with forced and free convection
  – ”Immobilized” electrolytes through the use of porous matrixes, negligible free convection, rarely forced convection
  – Solid electrolytes, no convection
Selecting Studies

- Stationary
- Transient
  - With double-layer effects
  - Dynamic load curves
  - Constant Current – Constant Voltage mode switching by the use of Events
  - Cyclic Voltammetry in Electroanalysis
- Frequency domain
  - Impedance spectroscopy (AC-impedance, electrochemical impedance)
“Always Check Your Results” (B. Finlayson)

• Verification
  – Does the numerical solution converge?
    • Tolerances, mesh resolution
  – “Are you solving the equations right?”

• Validation
  – Input data and sensitivity to this data
  – Comparison with known studies in literature
  – Qualitative and quantitative comparison with experimental observations
  – “Are you solving the right equations?”
References to the Theory Part

• “Modern Electrochemistry”, J.O’M. Bockris, A.K.N. Reddy
The Batteries & Fuel Cells Module

Spiral wound Li-ion battery

Serpentine fuel cell flow field

Lead-acid battery electrode

Water-cooled Li-ion battery pack
The Batteries and Fuel Cells Module

- **Specialized tool:**
  - Models and simulates all major types of battery and fuel cell applications

- **Ease-of-use**
  - Tailored functionality/interfaces for:
    - Primary, secondary and tertiary current density distribution
    - Porous and gas diffusion electrodes
    - Dilute and concentrated electrolytes

- **Multiphysics**
  - Flow, electric fields, and heat transfer with electrochemical reactions

Temperature distribution in a PEMFC equipped with passive self-breathing electrodes
Targeted Batteries and Fuel Cell Systems

- **Batteries:**
  - Lithium-ion
  - All-solid-state lithium-ion
  - Nickel-metal hydride
  - Lead-acid
  - Nickel-cadmium

- **Flow Batteries:**
  - Vanadium redox
  - Soluble lead-acid

- **Fuel Cells:**
  - Proton exchange membrane, high and low temperature
  - Solid oxide
  - Molten carbonate
  - Direct methanol

Discharge-recharge cycle for a lithium-ion battery simulated with the Lithium-ion battery interface.
Battery Modeling and Simulations in COMSOL

- Battery unit cells:
  - Current collectors and feeders
  - Porous electrodes
  - Pore electrolyte
  - Electrolyte

The scope of a typical model incorporates relatively detailed descriptions, such as intercalation and modeling of the SEI on the surface of the particles in porous electrodes.
The Battery Modeling Interfaces

- Lithium-ion battery
  - Charge balances in the electrodes and electrolyte
  - Material balances for the salt
  - Energy balance including electrochemical reactions
  - Material balance of intercalating species in electrode particles
  - Solid electrolyte interface on electrode particles
- Battery with binary electrolyte
  - Generic interface for batteries with concentrated binary electrolytes
- Lead-acid battery
  - Porosity variation within electrodes coupled to electrode reactions and material balances
  - Material balance for the salt in the electrolyte
- Generic physics interfaces
  - Primary Current Distribution
  - Secondary Current Distribution
  - Tertiary Current Distribution, Nernst-Planck
- Predefined couplings with Heat Transfer interfaces, including heat sources from electrochemical reactions
Fuel Cell Modeling and Simulations

- Fuel cell unit:
  - Current collectors and feeders
  - Gas channels
  - Gas diffusion electrodes (GDE)
  - Pore electrolyte
  - Electrolyte

Unit cell consisting of current collectors, gas channels, gas diffusion electrodes, electrolyte, and pore electrolyte.
The Fuel Cell Modeling Interfaces

- **Secondary Current Distribution**
  - Include electrode kinetics:
    - Exchange current density
    - Equilibrium potential
    - Charge transfer coefficients
    - User-defined expressions
  - Double layer currents

- **Predefined coupling with Chemical Species Transport interfaces**
  - Mass transport in gas channels
  - Mass transport in GDEs
  - Transport of charged species in supporting electrolyte

- **Predefined coupling with Heat Transfer interfaces**
  - Heat sources from electrochemical reactions and Joule heating
Generic Electrochemistry Interfaces

- Porous and non-porous electrodes
  - Arbitrary number of electrode reactions
    - Butler-Volmer reaction
    - Tafel reactions
    - User-defined current density option for full versatility
  - Double layer capacitance
- Electric conduction (electrons)
  - Porous and non-porous domains
  - Thin layers (shells)
  - Floating potential surfaces
- Mass and charge transport
  - Transport of neutral species and ions
  - Nernst-Planck, with or without electroneutrality
  - Supporting electrolytes
- Electroanalysis
  - Cyclic Voltammetry
- Momentum transport
- Heat transfer

Discharge curves of an all-solid-state lithium-ion battery modeled by a combination of generic interfaces for mass transport and current distribution.
The Physics Interfaces, Summary

- Electrochemistry

- Chemical Species Transport
  - of Diluted Species
  - of Concentrated fluids
  - in Free and porous media

- Fluid flow
  - Single-Phase Flow
  - Porous Media Flow
  - Free and Porous Media Flow

- Heat Transfer
  - in Fluids
  - in Solids
  - in Porous Media
The Batteries & Fuel Cells Material Library

- Included library based on literature data for the most common electrode and electrolyte materials for Lithium-ion, NiMH and lead acid batteries:
  - Electrolyte conductivities
  - Equilibrium potentials
  - Diffusion coefficients
  - Activity coefficients
  - Transport numbers
  - Densities
  - Heat capacities

*All listed properties not available for all listed materials
Study Types

• Stationary

• Transient
  – With double-layer effects
  – Dynamic load curves
  – Constant Current – Constant Voltage mode switching by the use of Events
  – Cyclic Voltammetry in Electroanalysis

• Frequency Domain
  – AC-Impedance Spectroscopy
Supporting Capabilities in COMSOL

- **Extended physics:**
  - Single-phase and multiphase flow: Extended laminar flow capabilities and turbulent flows in the CFD Module
  - Cooling: Extended thermal transport capabilities in the Heat Transfer Module
  - Thermal Expansion in the Structural Mechanics Module
  - Equation-based modeling

- **Material properties and parametric estimation:**
  - Thermodynamics and reaction kinetics in Chemical Reaction Engineering Module
  - Parametric estimation in Optimization Module

- **CAD capabilities:**
  - Include designs with the CAD Import Module
  - Parametric sweeps on geometry
  - LiveLink add-ons available for a number of common CAD software

Air cooling of a cylindrical lithium-ion battery using the Heat Transfer Module together with the Batteries & Fuel Cells Module
Corrosion Module

General Introduction
Contents

• Overview
  – Purpose
  – Described processes
  – Described phenomena

• Corrosion and corrosion protection, examples

• The Corrosion Module interfaces and their theoretical background

• Concluding remarks
Purpose

- Space-dependent modeling and simulation of corrosion of metallic structures
  - Understand corrosion processes in the context of a given geometry
  - Optimize design to minimize corrosion

- Space-dependent models of corrosion protection of metallic structures
  - Design and optimize corrosion protection systems and operational conditions for a given geometry

Electrolyte potential surrounding a zinc galvanized nail with the iron core exposed at the point of the nail.
Described Processes

- Space-dependent models of corrosion of metallic structures in water
  - Galvanic corrosion
  - Crevice corrosion
  - Pitting corrosion
  - Corrosion due to stray currents

- Space-dependent models of corrosion protection of metallic structures
  - Cathodic protection using external current (impressed current cathodic protection, ICCP)
  - Cathodic protection with sacrificial anodes
  - Anodic protection (for example, small passivating currents that stabilize oxide films)

Initial and deformed geometry before and after galvanic corrosion modeled using a moving mesh.
Described Phenomena

- Material, current, and charge conservation in the electrolyte
- Electric current conservation in the metallic structures
- Electrode kinetics with activation and concentration overpotential couple the electrolyte potential with the potential of the metallic structure at the metal surfaces
- Multiple reactions at the metal surface, where the mixed potential determines if a surface corrodes or is protected
- Effect of geometry deformations and formation of resistive films on electrode surfaces
Corrosion Module Interfaces

- Current and potential distribution based on:
  - Current and charge balances
  - Material transport
  - Fluid flow
  - Heat transfer

- Corroding surfaces:
  - Electrode reactions coupled to surface species balances
  - Fixed and moving boundaries coupled to surface species balances

- Stationary and transient studies

Physics list in the GUI of the Corrosion Module
Examples
Galvanic Corrosion

- Corrosion caused by two different metals being in electronic contact and also sharing the same electrolyte.

Galvanic corrosion simulation with moving mesh. The figure shows the potential and current in the electrolyte. The two metal surfaces are aligned and flat at the beginning of the simulation. (The model is included in the Corrosion Module Model Library.)
Crevice Corrosion

- Crevice corrosion of stainless steel in water

Calculated concentration profiles in a crevice. The role of parameters such as pH inside the crevice, external potential, acid/base concentration of the solution and crevice geometry is studied. (From the Corrosion Module Model Library.)
Crevice Corrosion with Deformation

- Crevice corrosion of nickel in acid of high conductivity

Simulation of corrosion of Ni in a lab cell.

Left: Polarization curve taken from experimental data.
Right: Electrolyte potential and simulated geometry after 72 h.

The model is included in the Corrosion Module Model Library.
Corrosion due to Stray Currents

- Corrosion initiated by metallic structures being subjected to an external electric field

Cathodic Protection

- Protection of an propeller and shaft of a ship using impressed current cathodic protection (ICCP)

Right: Electrolyte (ocean) potential along the ship hull surface.
Left: Current density on propeller and shaft
Sacrificial Anode Protection

• Cathodic protection of a steel structure using sacrificial AlZnIn anodes

Potential at the surface of the metal of a detail in an offshore platform. The leg of the platform is protected by 40 sacrificial anodes.
More examples

• Anodic Protection
  – Imposes an anodic current that preserves the passivation of metal surfaces by stabilizing the protecting oxides

• CO₂ corrosion
  – Electrode kinetics in combination with the mass transport rate and equilibrium reactions of electrolyte species govern the corrosion rate

• Atmospheric corrosion
  – Formation of a thin moisture film, acting as electrolyte, on a metal surface in contact with air of varying humidity

• Formicary (ant’s nest) corrosion
  – Complex interplay between organic compounds and passivation behavior of metal surfaces causing pitting corrosion on the micro scale
The Corrosion Module Model Library

Cathodic Protection
- Ship hull
- Off-shore structure
- Rebar in concrete

Galvanic Corrosion
- With or without deformation
- Atmospheric corrosion
- Localized corrosion
- CO$_2$ corrosion

Crevice corrosion
- With or without deformation
- Similar to pitting corrosion

General Electrochemistry
- Impedance Spectroscopy
- Cyclic Voltammetry

Cyclic voltammetry tutorial done with the Electroanalysis interface
Transport of Charged and Neutral Species

- Flux in the electrolyte = diffusion + convection + migration

\[ N_i = -D_i \nabla c_i + c_i u - z_i m_i F c_i \nabla \phi_i \]
Transport of Charged and Neutral Species

- Current density

\[ j = F \sum_i z_i \mathbf{N}_i \]

\[ j = F \left( \sum_i -z_i D_i \nabla c_i + u \sum_i z_i c_i - \nabla \phi_i \sum_i (z_i)^2 m_i F c_i \right) \]

- Electroneutrality, charge conservation

\[ \text{sum of charges} = 0 \]

\[ j = F \left( \sum_i -z_i D_i \nabla c_i - \nabla \phi_i \sum_i (z_i)^2 m_i F c_i \right) \]

- Perfectly mixed primary and secondary current distribution

\[ j = -\left( F \sum_i (z_i)^2 m_i F c_i \right) \nabla \phi_i \]

\[ \kappa = \text{conductivity} \]
Conservation of Species, Current, and Charge

- Conservation of species
  n-1 species, n:th through current and charge conservation (electroneutrality)

- Conservation of current, net current is not accumulated, produced nor consumed in the bulk electrolyte

- For primary and secondary current distr. and current balance for metal structure. Shell interface for thin structures (avoid meshing across thickness of metal structures).

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot \left( -D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_i \right) + R_i
\]

Reaction rate

\[
\nabla \cdot \left( F \left( \sum_i -z_i D_i \nabla c_i - \nabla \phi_i \sum_i (z_i)^2 m_i F c_i \right) \right) = 0
\]

Electrolyte

\[
\nabla \cdot \left( -\kappa \nabla \phi \right) = 0
\]

Metal structure

\[
\nabla \cdot \left( -\kappa \nabla \phi_s \right) = 0
\]
Reactions at Metal Surfaces

• Described through kinetics expressions that include activation and concentration overpotential:

\[ j \cdot n = i \]

• Multiple reactions defined on a metal surface
  – Anodic dissolution of metals
  – Anodic reactions at active anodes, for example oxygen and chlorine evolution
  – Oxygen reduction and hydrogen evolution as competing reactions at protected surfaces
  – Heterogeneous reactions such as growth of oxide and hydroxide films on surfaces: film thickness included as model variable

• Example: Kinetic expression for oxygen reduction and evolution

\[
i_{O_2} = i_{0,O_2} \left\{ \exp \left( -\frac{0.5F}{RT} \left( \phi_s - \phi_l - E_{eq,O_2} \right) \right) - \left( \frac{P_{O_2}}{P_{O_2,ref}} \right)^{0.25} \left( \frac{c_{H^+}}{c_{H^+,ref}} \right) \exp \left( \frac{0.5F}{RT} \left( \phi_s - \phi_l - E_{eq,O_2} \right) \right) \right\}
\]
Summary

• Descriptions in the Corrosion Module
  – Current and species conservation in electrolytes and solid structures
  – Charge conservation in the electrolyte
  – Shell interface for thin metal structures to account for ohmic losses in the metal
  – Competing charge transfer reactions at metal-electrolyte surface
  – Growth of oxide and hydroxide films and their influence on current an potential distribution
  – General surface reactions and homogeneous reactions in bulk solution

• The use in corrosion and corrosion protection:
  – Design metal structures to minimize corrosion
  – Control operating conditions to avoid corrosion
  – Optimize corrosion protection systems and estimate life
Electrochemistry Module
General Introduction
Contents

- Applications
- Key features
- Concluding remarks

Impedance spectroscopy tutorial done with the Electroanalysis interface in Electrochemistry Module
Applications
Electroanalysis

- **Fundamental methods in electroanalysis:**
  - Coulometry
  - Potentiometry
  - Voltammetry
  - Amperometry
  - Electrochemical impedance spectroscopy

- **Electrochemical sensors**
  - Glucose sensors
  - Gas sensors
  - Pressure sensors

- **Electrophoresis**
  - Separation of biomolecules and ions

Concentration profile in the electrolyte in microdisk voltammetry
Electrolysis

- Chlor-alkali process
- Chlorate process
- Water electrolysis
  - Hydrogen production
  - Oxygen production in submarines and space crafts

Secondary current density distribution in a chlor-alkali electrodes-membrane unit cell. Chlorine evolution and oxygen evolution kinetics may be applied at the anode and hydrogen evolution kinetics are used at the cathode.
Electrodialysis

- **Desalination**
  - Seawater to potable water
  - Removal of salts in effluents (waste water treatment)

- **Electrodeionization**
  - Ultra-pure water production

- **Control of pH**
  - Removal of acids from wine, juice and other "delicate" solutions

2D model of membrane electrolysis representative unit cell. The cross section of the flux of chloride is shown. The position of the cation selective membrane is shown in red while the anion selective membrane is shown in blue.
Bioelectrochemistry

- Ablation
  - Thermal
  - Chemical
- Biosensors

**Tutorial model of tumor ablation. The graph shows the selectivity of the anode for chlorine and oxygen evolution.**

pH as a function of distance from the anode at different times (s).
Key Features
Current Distribution

- Primary: Ohmic effects only

- Secondary: Both ohmic and activation (reaction kinetic) effects
  - Modeling of electrode kinetics for electrochemical reactions

- Tertiary: Ohmic, activation, and concentration overpotential effects
  - Transport modeling for the concentrations of all solute species
  - Use when mass transfer and electric field are both significant in an electrochemical system

Physics interfaces added or altered by Electrochemistry Module
Electroanalysis Interface

- Model electroanalytical experiments in the presence of excess supporting electrolyte
- Transport of chemical species by diffusion and convection
  - Full mass transfer description but no electric field
  - Can also include electrochemically inert species and follow-up reaction chemistry
- Automated multiphysics coupling of charge and mass transfer at electrode boundaries
  - Built-in electrode kinetic expressions such as Butler-Volmer equation
  - One interface: simplified model setup and computation

Dedicated interfaces for electroanalytical studies
Cyclic Voltammetry

- Sets up the typical experimental condition and allows for a simple specification of sweeps in electric potential between two electrodes

Cyclic voltammetry tutorial done with the Electroanalysis interface in Electrochemistry Module
Chemical Species Transport

- Diffusion-convection equation for electroanalysis
- Nernst-Planck for general applications
- Homogenous, heterogeneous and equilibrium reactions in solutions

Boundary layer elements around a representative unit cell of a coated DSA with a micromesh substrate
Other Capabilities in Transport Phenomena

- **Heat Transfer**
  - Heat sources due to Joule heating, activation losses, and other electrochemical phenomena.

- **Fluid Flow (Laminar and Porous Media)**
  - Allows for the modeling of electroosmotic flow
  - Couple to Electroanalysis to model hydrodynamic methods (e.g. channel electrode)

Flow field (arrows) and chloride concentration in the electrolyte surrounding a coated DSA on a micromesh substrate
Studies

- Stationary analysis (steady state)
- Dynamic simulation
  - Time-dependent analysis, for example sweeps
  - Cyclic voltammetry
  - Current interrupt analysis
- Electrochemical impedance spectroscopy (EIS)
  - Full phenomenological modeling in the frequency domain
  - Effects of Ohmic, activation, species transport, and adsorption (discharge and recharge) using high-fidelity physical models
  - Lends physical meaning to equivalent circuits
  - Uses a steady-state nonlinear model and adds a small linear potential
  - One physical model is applicable over a wide range of base polarizations

![Dedicated interfaces for EIS studies](Comsol.png)
Concluding Remarks

• Electrochemistry Module, the perfect tool for:
  – Electroanalytical chemistry
  – Applied electrochemistry
  – Electrochemical engineering
  – Bioelectrochemistry

• Find more information about the use of COMSOL in electrochemistry:

• Contact your local COMSOL representative for more information about the Electrochemistry Module

• Browse the list of events for webinars, courses, and workshops near you:
The Electrodeposition Module

- Moving geometry effects in 3D
- Surface catalytic effects
- Coupled diffusion-convection
- Current conduction in thin deposited layers

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Electrodeposited Layers, Typical Applications Targeted by the Module

• Fabrication of electrical and thermal conductors
  – Printed circuit boards, electrical contacts, and cooling devices

• Protection of metal parts
  – Corrosion protection of nuts, bolts, and other components
  – Wear resistance coatings on bearings and shafts

• Decoration of metals and plastics
  – Chromium coatings of automotive parts
  – Nobel metals on jewelry and tableware

• Electroforming of parts with thin complex shapes
  – Manufacturing of thin screens and shaver heads
  – Manufacturing of MEMS devices

The shaver cap in a Philips shaver is manufactured using electroforming, from COMSOL News 2008
Why Modeling and Simulations?

• Cost effective way of understanding, optimizing, and controlling electrodeposition through...

• ...investigating the influence of the parameters below on the thickness and composition of deposited layers:
  – Cell geometry
  – Electrolyte composition and mixing
  – Electrode kinetics
  – Operating potential and average current density
  – Temperature

Thickness of the decorative deposited layer in a furniture fitting modeled using simulations based on secondary current distribution
Electrochemical Reactions

- The Electrodeposition Module is able to model arbitrary reaction mechanisms:
  - Electrode kinetics using Butler-Volmer or by just typing in arbitrary expressions
  - Multiple competing reactions
  - Adsorption reactions including diffusion of adsorbed species at the electrode surface
The Deposited Layer and its Composition

• Material balances are defined for the deposited species

• Surface diffusion and active site density can be accounted for in the model

• The deposited layer’s thickness:
  – Calculated on a fixed geometry or...
  – ...modeled using moving boundaries based on the ALE method

Settings windows for the deposited species. The concentration, density and molar mass determine the thickness of the layer.
Transport of Charged and Neutral Species

- Flux = diffusion + convection + migration

\[ \mathbf{N}_i = -D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_i \]

- Concentration
- Diffusivity
- Flow velocity
- Charge
- Mobility
- Faraday’s constant
- Electrolyte potential
Transport of Charged and Neutral Species

- **Current density**

\[
j = F \sum_i z_i N_i \quad \Rightarrow \quad j = F \left( \sum_i -z_i D_i \nabla c_i + \sum_i \nabla \phi_i \sum_i (z_i)^2 m_i F c_i \right)
\]

- **Electroneutrality, charge conservation** \( \text{sum of charges} = 0 \)

\[
j = F \left( \sum_i -z_i D_i \nabla c_i - \nabla \phi_i \sum_i (z_i)^2 m_i F c_i \right)
\]

- **Perfectly mixed primary and secondary current distribution**

\[
j = - \left( F \sum_i (z_i)^2 m_i F c_i \right) \nabla \phi_i \quad \kappa = \text{conductivity}
\]
Conservation of Species, Current, and Charge

- Conservation of species
  n-1 species, n:th through current and charge conservation (electroneutrality)

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot \left( -D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_c \right) + R_i \]

- Conservation of current, net current is not accumulated, produced or consumed in the bulk electrolyte

\[ \nabla \cdot \left( F \left( \sum_i -z_i D_i \nabla c_i - \nabla \phi_c \sum_i (z_i)^2 m_i F c_i \right) \right) = 0 \]

- For primary and secondary cases

\[ \nabla \cdot \left( -\kappa \nabla \phi_i \right) = 0 \]
Tutorial from The Model Library

• Copper deposition
  – Copper sulfate electrolyte
  – Copper dissolution at the anode
  – Copper deposition at the cathode

• Dependent variables
  – Copper concentration
  – Sulfate ion concentration
  – Potential in the electrolyte

• Electrode kinetics
  – Butler-Volmer expression including concentration overpotential
Tutorial from The Model Library, continued

• Original boundary position
  – Gray colored line
  – Updated boundary position with automatic remeshing
  – Four automatic remeshing steps

Copper ion concentration [mol/m3], current density (streamlines), and potential (contours) after 11 s of deposition
Model Library Examples

- Via Superfilling
  - Surface catalyst-enhanced deposition

- Microconnector Bump
  - Mass transfer by coupled convection-diffusion
Model Library Examples, continued

- **Inductor Coil**
  - Mass transfer and moving geometry effects in 3D

- **Resistive Wafer**
  - Current distribution with changing lateral electric conductivity in a depositing layer
Model Library Examples, continued

• Electrochemical Machining
  – Removal of material with moving geometry effects

• Electrophoretic Painting (Ecoating)
  – Dynamic current distribution due to a resistive paint layer
Model Library Examples, continued

- Fountain Flow Effects on Rotating Wafer
  - Mass transfer due to convection and diffusion
  - Current conduction in the electrolyte
  - Potential drop in thin wafer
  - Swirl Flow used to calculate 2D-axisymmetrical flow profile
  - Note: CFD Module needed for Swirl Flow

Electrode reaction current density on wafer

Concentration of ions in boundary layer

Flow profile
The Electrodeposition Module Interfaces

• Current and potential distribution based on:
  – Charge and current balances
  – Material transport
  – Fluid flow
  – Heat transfer

• Deposited layer thickness and composition through:
  – Electrode reactions coupled to surface species balances
  – Fixed and moving boundaries coupled to surface species balances

Physics interfaces as listed in the GUI of the Electrodeposition Module