

Electrochemical Engineering

電気化学工学

COMSOL Conference 2016

Henrik Ekström

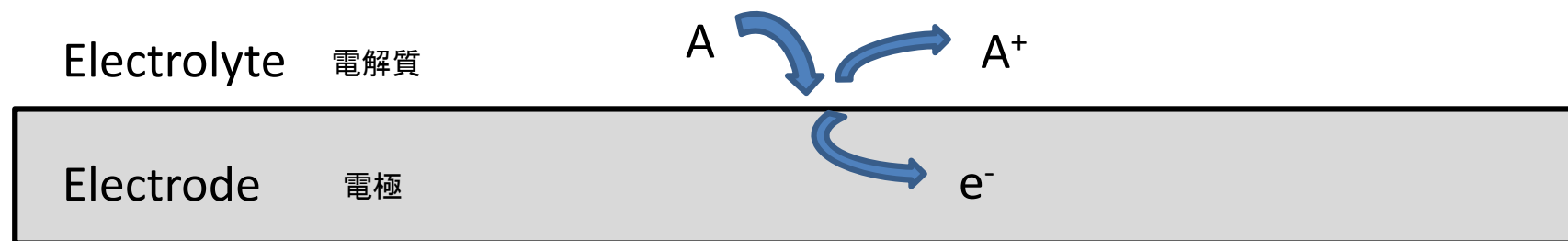
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Very Short Introduction to Electrochemistry

電気化学の簡単な紹介

- Electrochemical modeling usually boils down to describing the... 電気化学は以下をモデル化する
 - surface reactions at the interface between an electrode and an electrolyte 電極-電解液界面の表面反応
 - transport of ions, electrons, and uncharged species participating in the reactions イオン、電子の移動、反応に関与する電荷なし化学種の移動
- where...
 - the reaction rates depend on the potential difference between electrode and electrolyte 反応速度が電極-電解液間の電位差に依存する



Note: The current density at the interface is proportional to the surface reaction rate 界面の電極密度は表面反応速度に比例する

Current Distribution Modeling

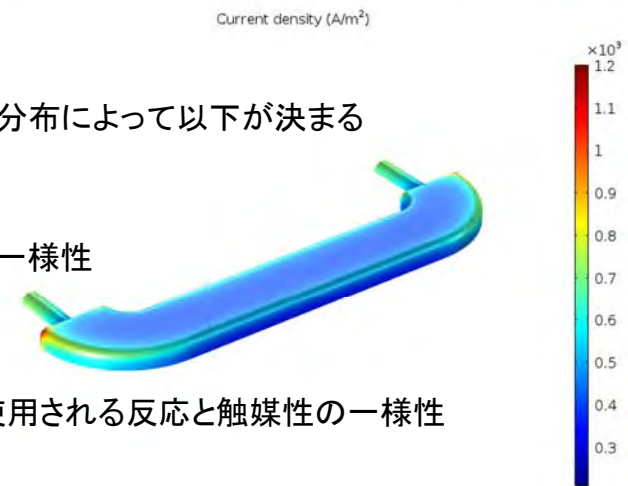
電流分布のモデリング

- The current distribution on an electrode surface or in a porous electrode determines 電極表面あるいは多孔質電極中の電流分布によって以下が決まる

- The magnitude of corrosion 腐食量
- The metal deposition rate and uniformity 金属析出速度と一様性
- The uniformity of reaction and catalyst utilization in electrolysis or in a fuel cell
- The local state-of-charge depletion/saturation rate in a battery

電池での局所的な枯渇/飽和速度

電解液/燃料電池に使用される反応と触媒性の一様性



Current distribution during electroplating

Current Distribution Types

電流分布のタイプ

- Primary: Only assuming Ohmic potential drops
一次: オームの法則による電圧降下のみを仮定
- Secondary: Adding effects of activation overpotential (Butler-Volmer kinetics or similar)
二次: 活性化過電圧の効果を追加 (バトラー-フォルマー反応あるいは類似のもの)
- Tertiary: Adding mass transport effects (concentration overpotential)
三次: 質量輸送効果の追加 (濃度過電圧)

Tertiary Current Distribution Cases

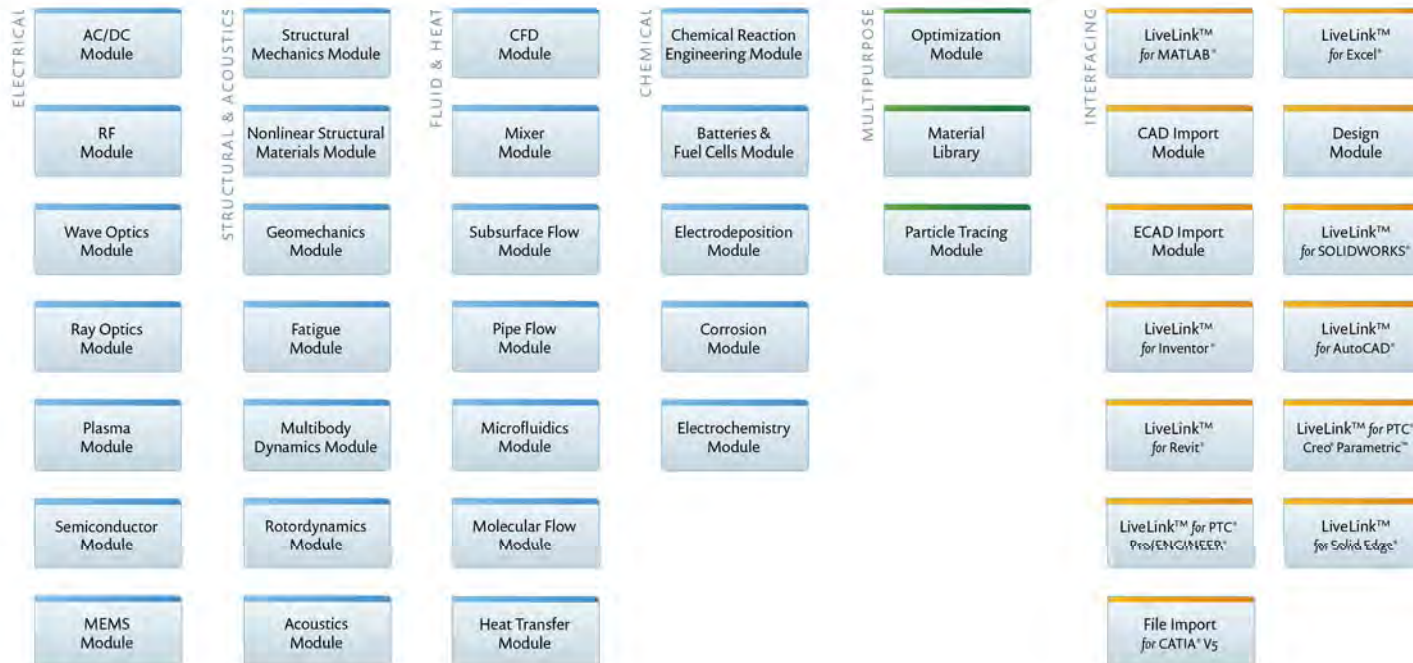
三次電流分布ケース

- Nernst-Planck with electroneutrality ネルンスト-プランク（電気的中性）
 - If mass transport = charge transport 質量輸送 = 電荷輸送の条件下
 - Use *Tertiary Current Distribution, Nernst-Planck* Interface
- Nernst-Planck-Poisson ネルンスト-プランク-ポアソン
 - If local charge neutrality cannot be assumed 局所電荷中性を仮定できない条件下
 - Use *Nernst-Planck-Poisson Equations* Interface
- Concentrated electrolyte theory 高濃度電解液理論
 - When the charged species interact in the solution (binary diffusion coefficients)
 - Implemented in Battery Interfaces 荷電化学種は溶液における相互作用(両極性拡散係数)
- Supporting electrolyte assumption 支持電解液の仮定
 - If conductivity not affected by reactions 導電率が反応によって影響されない条件下
 - Use *Secondary Current Distribution* + Chemical Species Transport interfaces
- Electroanalysis 電気分析
 - Excess electrolyte and small current densities – neglecting the electrolyte ohmic drop
電解液が多く微小電流密度 オーム電圧降下を無視の条件下

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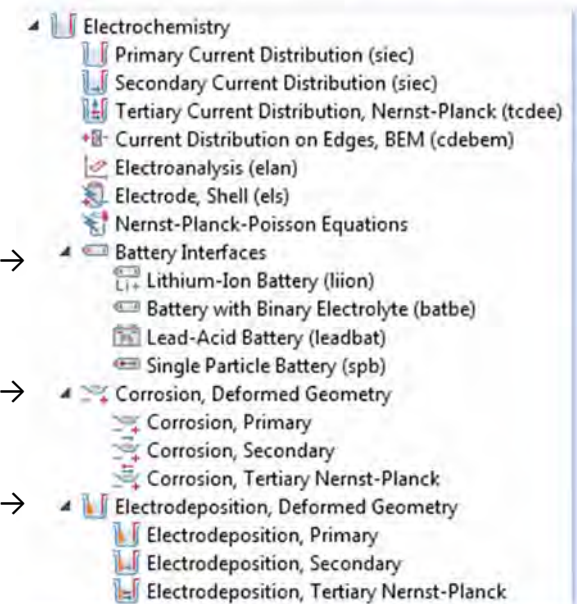


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The Electrochemistry Interfaces

電気化学インターフェース

- *Current Distribution* interfaces 電流分布インターフェース
 - Generic electrochemical cell modeling 一般的な電気化学モデリング
 - Nernst-Planck equations ネルンスト・プランクの式
 - Flat or porous electrodes 平面/多孔質電極
 - Arbitrary number of reactions 任意数の反応
 - Double-layer effect 電気二重層の影響
- *Electroanalysis* 電気分析
- *Nernst-Planck-Poisson Equations* ネルンスト・プランク・ポアソンの式
- *Battery Interfaces* バッテリーインターフェース
- *Corrosion* interfaces 腐食解析インターフェース
- *Electrodeposition* interfaces 電気めっきインターフェース



The Battery Interfaces

バッテリーインターフェース

- Concentrated electrolyte theory used in all battery interfaces (except *Single Particle Battery*)
高濃度種電解液理論がバッテリーインターフェースに使用されている (単一粒子バッテリーは除く)
- *Lithium-Ion Battery* リチウム-イオンバッテリー
 - Charge balances in the electrodes and electrolyte
電極と電解質内の電荷均衡
 - Material balances for the salt 塩分の物質収支
 - Energy balance including electrochemical reactions
電気化学反応を含むエネルギー収支
 - Material balance of intercalating species in electrode particles
電極粒子中のインターカレート種の物質収支
 - Solid electrolyte interface (SEI) on electrode particles
電極粒子の固体電解質界面

Electrode Kinetics

Kinetics expression type:
Lithium insertion

Anodic transfer coefficient:
 α_a 0.5 1

Cathodic transfer coefficient:
 α_c 0.5 1

Anodic rate constant:
 k_a k_neg m/s

Cathodic rate constant:
 k_c k_neg m/s

Electrolyte reference concentration:
 $c_{l,ref}$ 1[mol/m^3] mol/m^3

$$i_{loc} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta}{RT}\right) \right)$$

$$i_0 = F(k_c)^{\alpha_a} (k_a)^{\alpha_c} (c_{s,max} - c_s)^{\alpha_a} (c_s)^{\alpha_c} \left(\frac{c_l}{c_{l,ref}}\right)^{\alpha_a}$$

Limiting current density

Active Specific Surface Area

Active specific surface area:
 a_v (3*liion.epss)/liion.rp 1/m

$i_{v,m} = a_v i_{loc}$

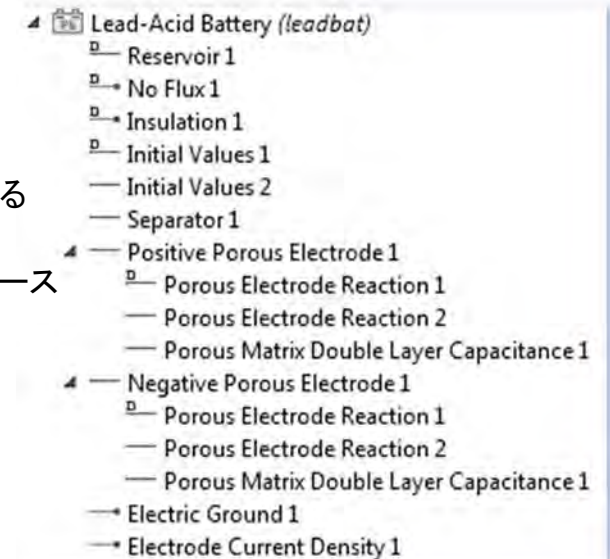
Stoichiometric Coefficients

ν_{Li+}	-1	1
ν_{An-}	0	1
ν_{Li0}	1	1

Settings for
electrode reactions
in the lithium-ion
battery interface

The Battery Interfaces

- *Battery with Binary Electrolyte* バイナリー電解液利用のバッテリー
 - Similar to the *Lithium-Ion Battery* interface
リチウム-イオンバッテリーインターフェースに似ている
 - Generic interface for batteries with concentrated binary electrolytes 高濃度バイナリー電解液利用のバッテリーの共通のインターフェース
- *Lead-Acid Battery* 鉛酸バッテリー
 - Porosity variation within electrodes coupled to electrode reactions and material balances
 - Material balance for the salt in the electrolyte
- *Single Particle Battery* 単一粒子バッテリー
 - Simplified generic battery interface 簡単化されたバッテリーの共通のインターフェース
 - Each electrode is treated as a single "particle" 電極は単一粒子で扱われる
 - For larger geometries, battery packs, or shorter simulation times 大きなジオメトリがあるバッテリーパック、或いはシミュレーション時間を減らす

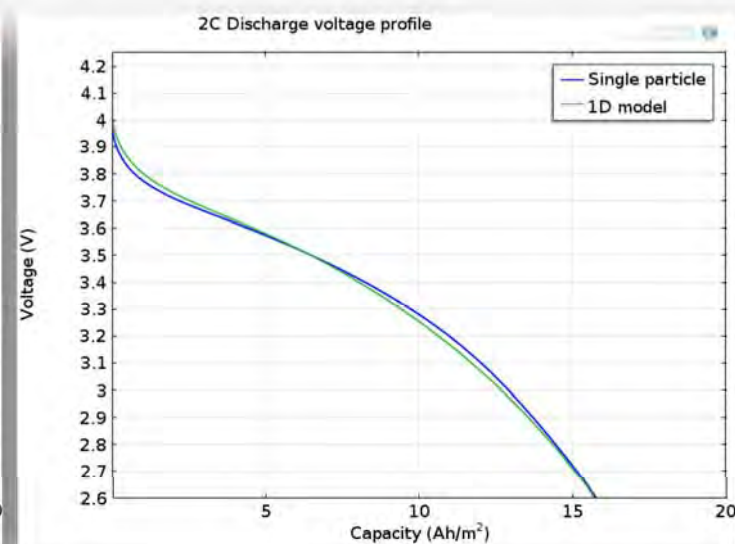
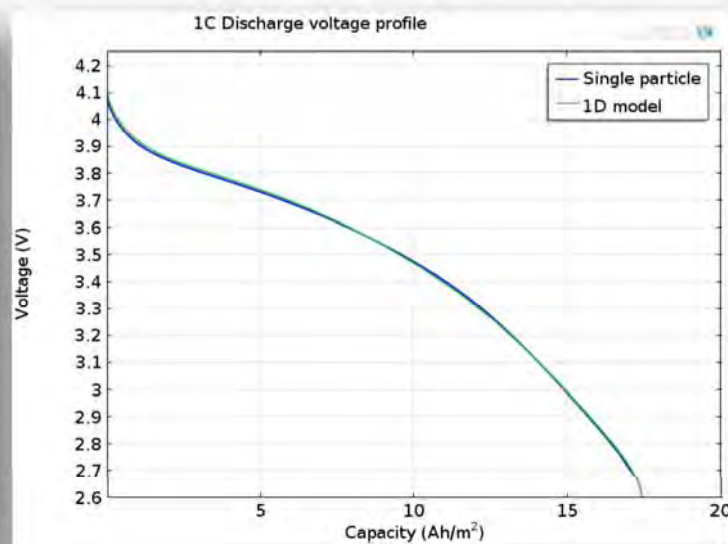
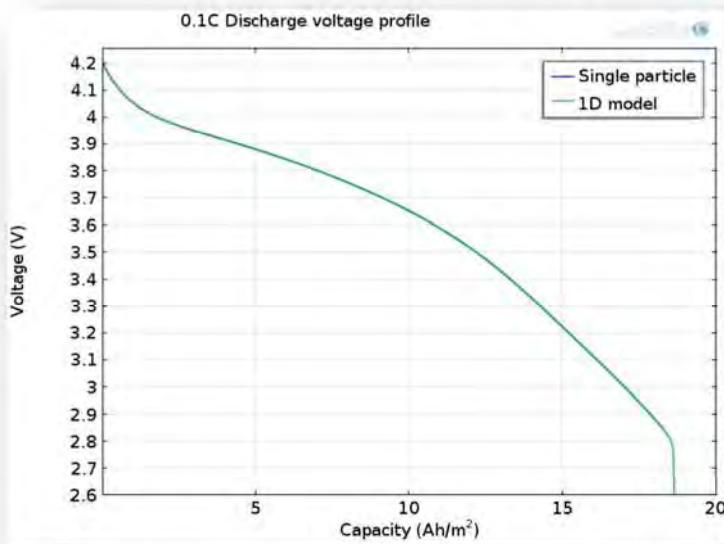


Typical set of nodes of the Lead-Acid Battery interface for creating a model

Single Particle Battery Model Accuracy

単一粒子バッテリーモデルの精度

- Comparing the discharge profiles at 0.1C, 1C and 2C from the single particle and 1D formulations 単一粒子バッテリーと1Dモデルの0.1C、1Cおよび2Cの放電曲線の比較



The Batteries and Fuel Cells Material Library

バッテリー & 燃料電池材料ライブラリ

- Included library based on literature data for the most common electrode and electrolyte materials for lithium-ion, NiMH, and lead-acid batteries:

リチウム-イオン、NiMHおよび鉛酸バッテリー用の最も多い電極・電解質材料の文献データを含む

– Electrolyte conductivities	電解質導電率
– Equilibrium potentials	平衡電位
– Diffusion coefficients	拡散係数
– Activity coefficients	活量係数
– Transport numbers	輸率
– Densities	密度
– Heat capacities*	熱容量

*All listed properties not available for all listed materials

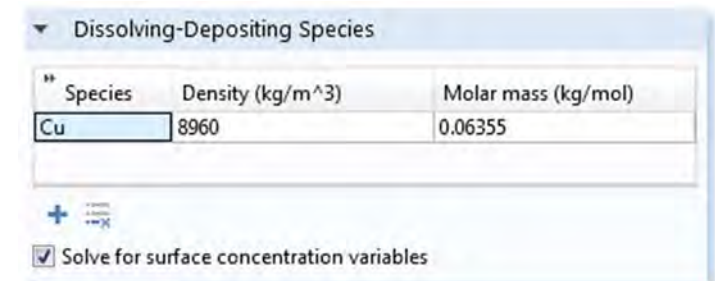


The Corrosion/Electrodeposition Interfaces

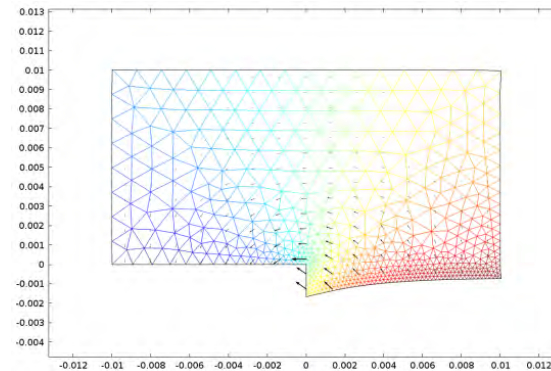
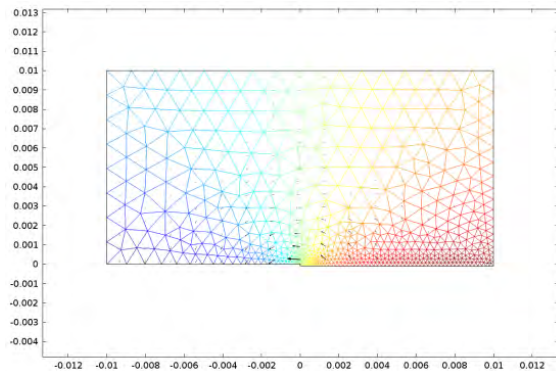
腐食解析/電気めっきインターフェース

溶解・析出電極の化学種

- Dissolving/Depositing Electrode Species
 - Keep track of reacted material per m^2 of electrode surface in time-dependent simulations
時間依存シミュレーションにおける電極表面で平方メートルあたりの反応材料を追跡
- Predefined couplings to geometry deformations
幾何形状変形との連成を用意している



Specifying the deposition of copper on an electrode surface in the user interface



Initial and corroded geometry due to galvanic corrosion of a magnesium alloy. Modeled using a deforming geometry (moving mesh/ale).

The Chemical Species Transport Interfaces

化学種輸送インターフェース

- *Transport of Diluted Species* 希釈種輸送
 - Diffusion, migration, and convection 拡散、マイグレーション、対流
 - Fick's law/Nernst-Planck equations フィックの法則/ネルンスト・プランクの式
 - Multiple species マルチ種
- *Transport of Diluted Species in Porous Media*
- Batteries & Fuel Cells: 多孔質中の希釈種輸送
 - *Transport of Concentrated Species*
 - Maxwell-Stefan equations
 - Typically used for gas phase diffusion
 - *Reacting flow* interfaces
- Use *Surface Reactions* to model intermediate species on electrode surfaces 電極表面近傍の化学種をモデル化する表面反応の利用が可能
- Coupling features to electrochemistry 電気化学との連成機能
 - Flat electrodes (molar fluxes) 平面電極(モル流束)
 - Porous electrodes (molar sources/sinks) 多孔質電極(モルソース/シンク)

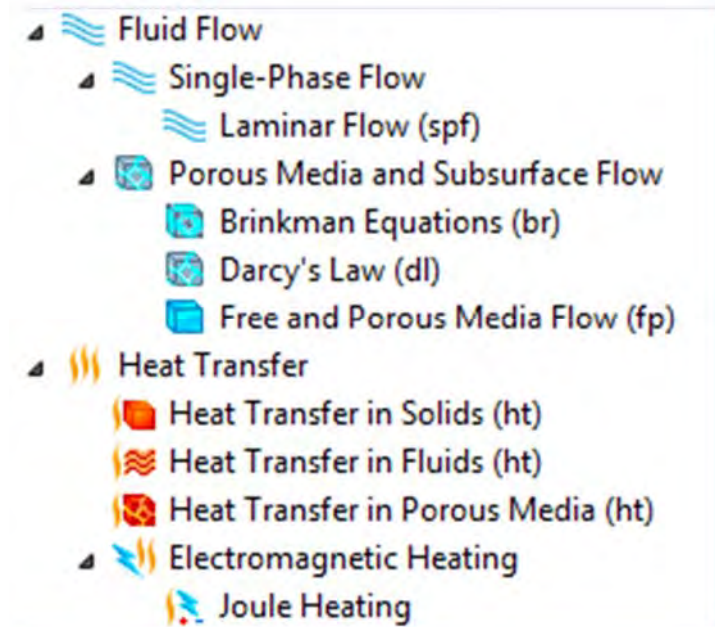


Heat Transfer and Fluid Flow

伝熱と流体の流れ

- Laminar flow 層流
- Porous media flow 多孔質媒体内流れ
- Heat transfer 伝熱 固体、流体、多孔質媒体
 - Solids, fluids, and porous media
- Coupling features 連成機能
 - Joule heating and heat from electrochemical reactions ジュール加熱/電気化学反応熱
 - All *Electrochemistry* interfaces contain predefined heat source variables to be used for coupling to *Heat Transfer* interfaces
 - Predefined mass sources and fluxes for coupling *Electrochemistry* to *Fluid Flow*

流体の流れと連成するための質量ソースと流束を用意

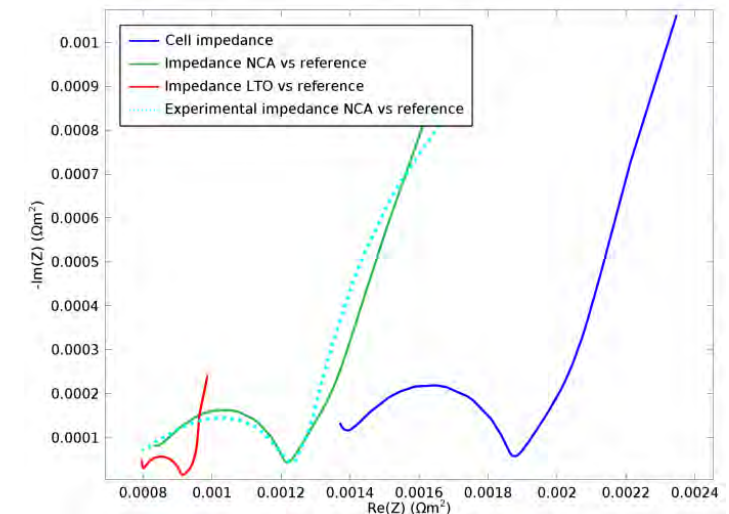


電気化学の全インターフェースは伝熱連成用の熱源を用意

Studies

スタディの種類

- Stationary analysis (steady state) 定常分析 (定常状態)
 - Steady-state current distributions 定常状態の電流分布
 - Steady-state polarization curves 定常状態の分極曲線
- Dynamic simulation 動的シミュレーション
 - Time-dependent analysis 過渡分析
 - Cyclic voltammetry サイクリックボルタンメトリ
 - Current interrupt analysis 故障電流分析
- Current Distribution Initialization study step 電流密度初期化スタディステップ
 - Valuable tool for deriving suitable initial potential values for the highly nonlinear kinetics
- Electrochemical impedance spectroscopy (EIS) 電気化学インピーダンス法
 - Full phenomenological modeling in the frequency domain 周波数域での現象の完全モデル
 - Effects of Ohmic, activation, species transport, and adsorption (double-layer discharge and charge) using high-fidelity physical models 高忠実度の物理モデルに基づくオーム性の影響、活性化、化学種の輸送及び吸着(電気二重層充放電)
 - Lends physical meaning to equivalent circuits
 - Uses a steady-state nonlinear model and adds a small linear perturbation in potential/current 定常状態の非線形モデルを利用する上で電位/電流の小さな線形摂動を追加
 - One physical model is applicable over a wide range of base polarizations 一つの物理モデルは広いベース分極範囲に適用



Impedance spectroscopy study, Nyquist plot. Model fitted to experimental data.

Electrochemical Modules: Physics Summary

電気化学モジュール、フィジックスまとめ

In the Electrochemistry Module and the modules below:

- *Current Distribution* interfaces 電流分布
- *Electroanalysis* 電気分析
- *Heat Transfer* 伝熱
- *Fluid Flow* (Laminar and Porous Media) 流体流れ(層流および多孔質媒体内流れ)
- *Chemical Species Transport* 化学種輸送

電気めっきモジュール

Electrodeposition Module:

- *Electrodeposition* interfaces
- *Deforming Electrodes* 電極変形

バッテリー&燃料電池モジュール

Batteries & Fuel Cells Module:

- *Battery Interfaces*
- *Reacting Flow* interfaces 反応流
- *Transport of Concentrated Species*

高濃度種輸送

腐食モジュール

Corrosion Module:

- *Corrosion* interfaces
- *Deforming Electrodes* 電極変形
- *Sacrificial Edge Electrodes* 犠牲エッジ電極
- *Infinite Electrolyte* feature 無限界電解質



The Application Libraries

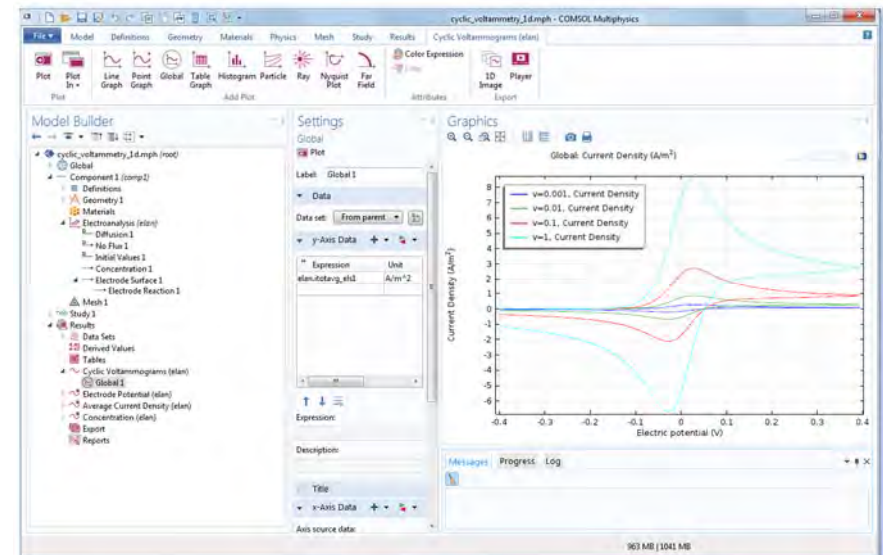
アプリケーションライブラリ

Generic Electrochemistry Applications

一般的な電気化学アプリケーション

チュートリアル

- Tutorials shared by all four modules:
 - Cyclic voltammetry サイクリックボルタンメトリー
 - Electrochemical impedance spectroscopy 電気化学インピーダンス法
 - Diffuse double layer 拡散二重層
 - Current distributions in an orange battery オレンジバッテリーの電流分布



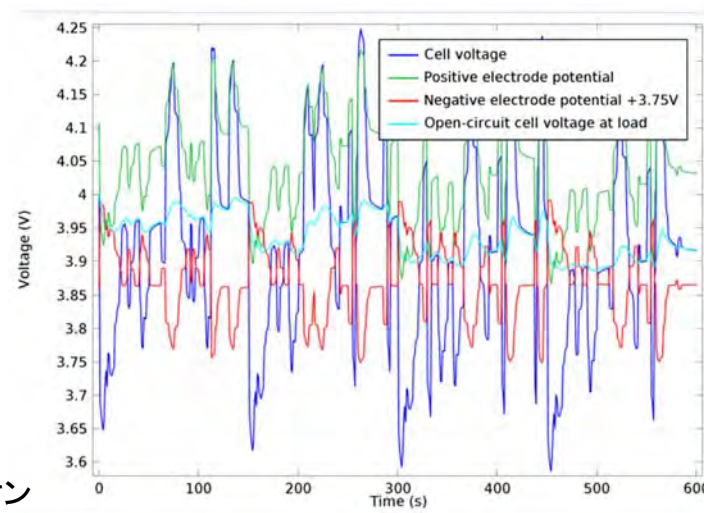
Cyclic voltammetry tutorial created with the Electroanalysis interface

The Batteries & Fuel Cells Application Library

バッテリー&燃料電池のアプリケーションライブラリ

● Batteries

- Lithium-ion リチウムイオン
 - Rate capability Cレート
 - Load cycling 負荷サイクリング
 - Internal resistance 内部抵抗
 - Capacity fade 劣化
 - Thermal management 熱管理
 - Internal short circuit 内部短路
- All-solid-state lithium-ion 全固体リチウム-イオン
- Nickel-metal hydride ニッケル金属水素化物
- Lead-acid 鉛酸



Battery drive-cycle analysis

The Batteries & Fuel Cells Application Library

バッテリー&燃料電池のアプリケーションライブラリ

- Flow batteries 流れバッテリー
 - Vanadium redox バラジウムレドックス
 - Soluble lead-acid 可溶性鉛酸
- Fuel cells 燃料電池
 - Proton exchange membrane, high and low temperature プロトン交換膜 高温、低温
 - Solid oxide 固体酸化物
 - Molten carbonate モルテンカーボナイト

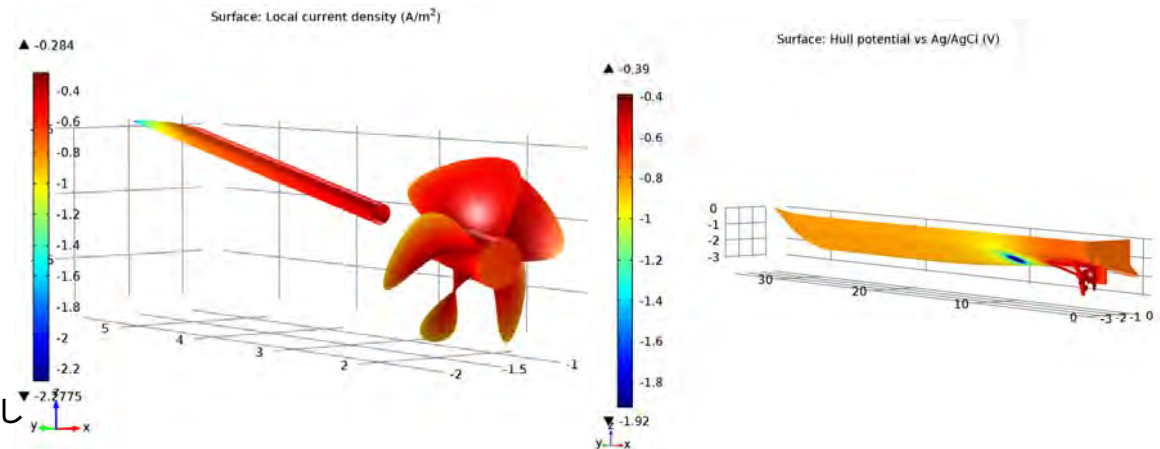


Oxygen concentration in a fuel cell flow plate

The Corrosion Module Application Library

腐食解析モジュールのアプリケーションライブラリ

- Cathodic protection カソード防食
 - Ship hull ICCP 船体ICCP
 - Off-shore structures 海洋構造物
 - Buildup of anode hydroxide films
 - Depletion of sacrificial anodes
 - Rebar in concrete コンクリート中の鉄筋
- Galvanic corrosion ガルバニ腐食
 - With or without deformation 変形有り無し
 - Atmospheric corrosion 大気腐食
 - Localized corrosion 局部腐食
 - CO₂ corrosion CO₂腐食
- Crevice corrosion すきま腐食
 - With or without deformation 変形有り無し
 - Similar to pitting corrosion 孔食に似ている

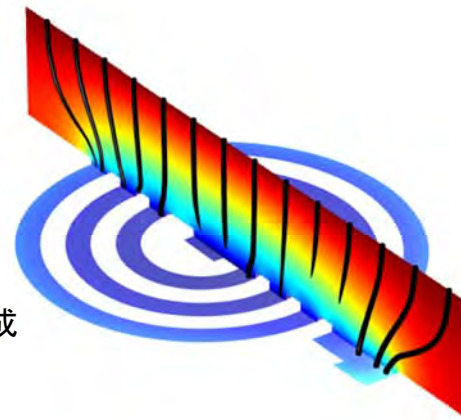


Current density on propeller and shaft (left) and potential of the ship hull surface when protected by an ICCP system (right)

The Electrodeposition Module Application Library

電気めっきモジュールのアプリケーションライブラリ

- Electrodeposition 電気めっき
 - Electronic components 電子部品
 - Trench deposition トレンチ内の成膜
 - On wafers ウエハー上
 - Deformation effects 変形影響
 - Coupled diffusive-convective transport 拡散・対流の輸送との連成
- Decorative plating 装飾めっき
- Electrophoretic painting 電気泳動塗装
- Electrochemical machining 電解加工
- Electrowinning 電解採取



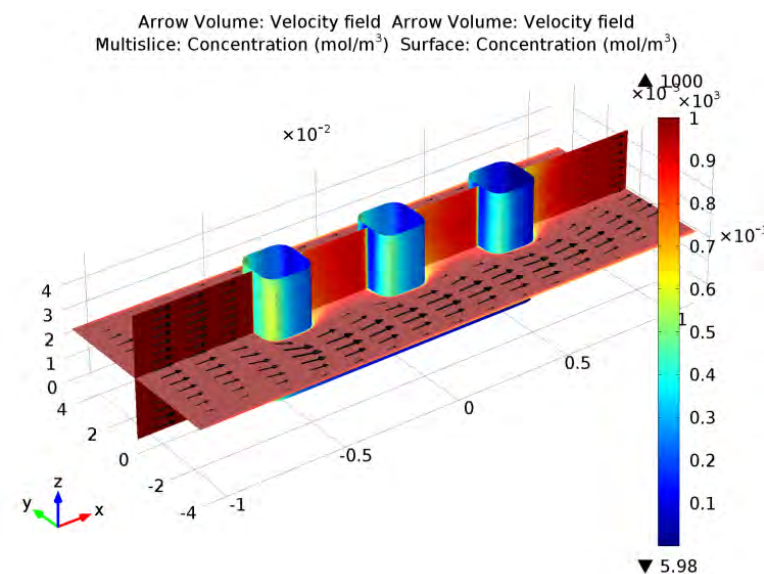
Deposition of an inductor coil

The Electrochemistry Module Application Library

電気化学モジュールのアプリケーションライブラリ

- Electrochemical engineering 電気化学工学
 - Wire electrode ワイヤ電極
 - Chlor-alkali electrolysis 塩素アルカリの電気分解
 - Electrodialysis 電気透析
- Electroanalysis 電気分析
 - Microdisk voltammetry マイクロディスク電極のボルタンメトリー
 - Chronoamperometry クロノアンペロメトリー
 - Glucose sensor グルコースセンサー

Note: Any application from the Electrochemistry Module Application Library can be solved using any of the other electrochemical modules

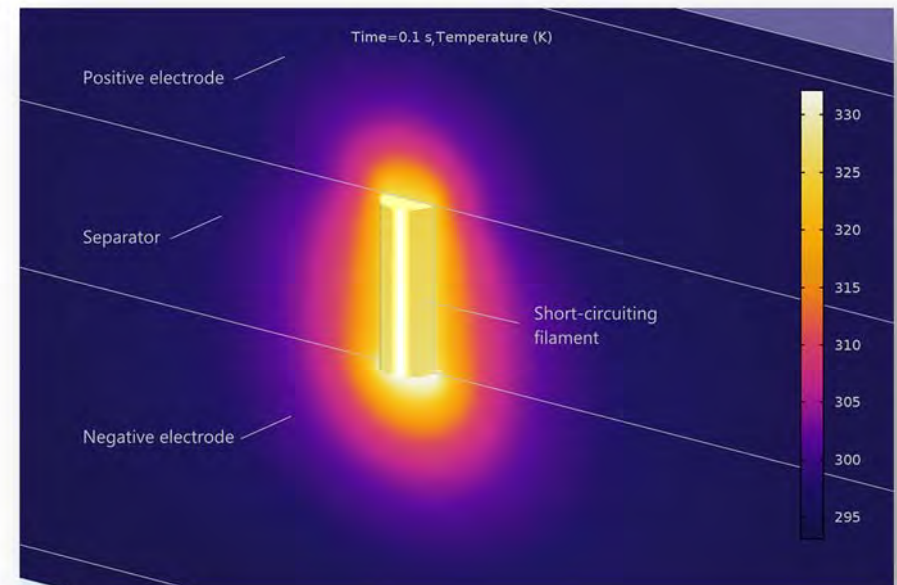


Flow field (arrows) and chloride concentration in the electrolyte surrounding a coated DSA on a micromesh substrate

News in 5.2a

5. 2aでの新機能

- Nernst-Planck-Poisson Equations ネルンスト-プランク-ポアソンの式
- External Short boundary condition 外部ショート境界条件
- Thermodynamic Equilibrium Kinetics type 熱力学平衡の反応モデル
- Generic Film Resistance and Dissolving-Depositing Species for Porous Electrodes 多孔性電極の共通のフィルム抵抗と溶解・析出種
- Batteries & Fuel Cells: バッテリー&燃料電池モジュール
 - Porous Media Transport in Transport of Concentrated Species
 - Single Particle Battery Interface
 - Fast Assembly for lithium intercalation
 - Improved solver defaults for battery interfaces in 2D and 3D
 - Improved numerical stability for high and low SOCs in battery interfaces
 - Internal short-circuit tutorial model in the Application Library
 - Updated capacity fade model in the Application Library
- Corrosion Module: 腐食解析モジュール
 - New Sacrificial Edge Anode feature and monopile tutorial model
新しい犠牲エッジアノード機能およびモノパイルチュートリアルモデル
- See also www.comsol.com/release/5.2a



A cross section of the temperature distribution in a lithium-ion battery around a small penetrating filament and the temperature at the surface of the filament.



Additional Material

追加資料

Electrolyte Transport

- Nernst-Planck transport

- Flux = diff. + conv. + migration
 - Valid for diluted electrolytes

流束=拡散+対流+泳動 希釈電解液で成立

- Current density 電流密度

$$\mathbf{j} = F \sum_i z_i \mathbf{N}_i$$

- Assuming electroneutrality, sum of charges = 0
電気的中性を仮定

- A perfectly mixed electrolyte results in Ohm's law

- Primary/secondary and supporting electrolyte case

完全混合の電解液ではオームの法則が成立

電解液電位

濃度
拡散

Concentration
Diffusivity

流速

Flow velocity

Charge
Mobility

荷電数
移動度

$$\mathbf{N}_i = -D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_l$$

Faraday's constant Ionic potential

$$\mathbf{j} = F \left(\sum_i -z_i D_i \nabla c_i + \mathbf{u} \overbrace{\sum_i z_i c_i}^{\text{sum of charges}} - \nabla \phi_l \sum_i (z_i)^2 m_i F c_i \right)$$

$$\mathbf{j} = F \left(\sum_i -z_i D_i \nabla c_i - \nabla \phi_l \sum_i (z_i)^2 m_i F c_i \right)$$

$$\mathbf{j} = - \left(F \sum_i (z_i)^2 m_i F c_i \right) \nabla \phi_l$$

$\kappa = \text{conductivity}$ 導電率