Continuum scale electrolyte simulations based on finite volume methods

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Bridging Scales from Atomistic to Continuum in Electrochemical Systems

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Generalized Nernst-Planck-Poisson

- Transport of N charged species with molar concentration c_i, charge z_i in self-consistent electric field, dissolved in solvent with concentration c_0
- Driving forces for charged particle movement:
    - gradient of chemical potential of ideal dilute solvent $\mu_i^{\text{ideal}} = \mu^\circ + RT \ln \frac{c_i}{c^\circ}$
    - gradient of excess chemical potential μ_i^{ex} accounting for steric effects
    - gradient of electrostatic potential ϕ
    - barycentric mixture velocity $\vec{u}$

$$-\nabla\varepsilon\nabla\phi = F\sum_{i=1}^{N} z_i c_i \qquad \text{Poisson}$$

$$\partial_t c_i + \nabla\cdot(\vec{N}_i + c_i\vec{u}) = r_{bulk,i} \qquad (i = 1\dots N) \qquad \text{Continuity}$$

$$\vec{N}_i = -\frac{D_i}{RT}c_i\left(\nabla\mu_i^{\text{ideal}} + \nabla\mu_i^{\text{ex}} + z_i F\nabla\phi\right) \qquad (i = 1\dots N) \qquad \text{Nernst-Planck}$$

Alternative formulations of Nernst-Planck flux

- μ_i^{ideal} produces Fickian diffusion term: $\frac{c_i}{RT}\nabla\mu_i^{\text{ideal}} = D_i\nabla c_i$
- Activity coefficient: $\gamma_i = \exp\left(\frac{\mu_i^{\text{ex}}}{RT}\right)$
- No steric effects $\equiv$ infinitely small ions if $\mu_i^{\text{ex}} = 0, \quad \gamma_i = 1$

$$\begin{aligned}
\vec{N}_i &= -\frac{D_i}{RT}c_i\left(\nabla\mu_i^{\text{ideal}} + \nabla\mu_i^{\text{ex}} + z_iF\nabla\phi\right) && \text{(excess chemical potential form)}\\
&= -D_i\nabla c_i - c_i\frac{D_i}{RT}(\nabla\mu_i^{\text{ex}} + z_iF\nabla\phi) && \text{(drift-diffusion form)}\\
&= -D_ic_i\left(\nabla\log\left(\gamma_i\frac{c_i}{c^\circ}\right) + z_i\frac{F}{RT}\nabla\phi\right) && \text{(activity coefficent form)}
\end{aligned}$$

Steric effects with equally sized ions

- Solvent and ion molar volume $v = N_A a^3$ where a: lattice constant
- Incompressibility $\equiv$ volume filling $\equiv$ solvent and ions together fill up space
  - $c_0 + \sum_{i=1}^N c_i = \bar{c} = c^\circ = \frac{1}{v}$: constant summary concentration
  - Limitation if concentrations: $0 \leq c_i \leq \bar{c}$
- Chemical potentials including solvent ($i = 0 \dots N$):

$$\mu_i = \mu_i^\circ + RT \ln \frac{c_i}{\bar{c}} = \mu_i^{\text{ideal}}$$

- Excess chemical potential $\equiv$ negative chemical potential of solvent

$$\mu_i^{\text{ex}}(c_1 \dots c_N) = -\mu_0 = -\mu_0^\circ - RT \ln\left(1 - \sum_{j=1}^N \frac{c_j}{\bar{c}}\right)$$

$$\gamma_i(c_1 \dots c_N) = \frac{1}{vc_0} = \frac{1}{1 - v\sum_{j=1}^N c_j}$$

Bikerman, Phil. Mag. 1942; Freise, Z. Electrochem 1955; Borukhov/Andelman/Orland, PRL 1997 . . .

Steric effects with varying ion sizes, molar masses, solvation

Pressure dependent chemical potential

- Molar volumes v_i, molar masses M_i, relative molar masses $m_i = \frac{M_i}{M_0}$ $(i = 0 \dots N)$
- $\bar{c} = \sum_{i=0}^{N} c_i$: non-constant summary concentration
- Solvation: species i ions solvated with κ_i solvent molecules
- Incompressibility using solvated molar volume $\bar{v}_i = v_i + \kappa_i v_0 \Rightarrow c_0 = \frac{1}{v_0} - \sum_{i=1}^{N} \frac{\bar{v}_i}{v_0} c_i$

$$\mathbf{N}_i = -\frac{D_i}{RT} c_i \left(\nabla \mu_i - m_i \nabla \mu_0 + z_i F \nabla \phi \right) \qquad (i = 1 \dots N)$$

$$\mu_i = \mu_i^\circ + \bar{v}_i (p - p^\circ) + RT \ln \frac{c_i}{\bar{c}} \qquad (i = 0 \dots N)$$

$$\mu_i^{\text{ex}}(c_1 \dots c_N, p) = \mu_i - m_i \mu_0 - \mu_i^{\text{ideal}}$$

$$= (\bar{v}_i - m_i v_0)\, p - m_i RT \log \frac{c_0}{\bar{c}} - RT \log v_0 \bar{c} \qquad (i = 1 \dots N)$$

$$\gamma_i(c_1 \dots c_N, p) = \frac{1}{v_0 \bar{c}} \exp\left(\frac{\bar{v}_i - m_i v_0}{RT} p \right) \left(\frac{\bar{c}}{c_0} \right)^{m_i}$$

Dreyer/Guhlke/Müller, PCCP 2013, Dreyer/Guhlke/Landstorfer, Electrochem. Comm. 2014

Navier-Stokes equations

$$\partial_t(\rho\vec{u}) - \nu\Delta\vec{u} + \rho(\vec{u}\cdot\nabla)\vec{u} + \nabla p = q\nabla\phi$$
$$\nabla\cdot\rho\vec{u} = 0$$

- Constant density case (for coupling with some numerical solvers)
  - Density $\rho = M_0c_0 + \sum_{i=1}^N (M_i + \kappa_i M_0)c_i$ is constant if $m_i = \frac{M_i+\kappa_i M_0}{M_0} = \frac{\bar{v}_i}{v_0}$

$$\mu_i^{\mathrm{ex}} = -m_i RT\log\frac{c_0}{\bar{c}} - RT\log v_0\bar{c}, \quad \gamma_i = \frac{1}{v_0\bar{c}}\left(\frac{\bar{c}}{c_0}\right)^{\frac{\bar{v}_i}{v_0}}$$

- Mechanical equilibrium
  - Momentum balance with Coulomb force: $\nabla p = q\nabla\phi$
  - Assume $\nabla q || \nabla\phi$, take divergence: $\Delta p = \nabla\cdot q\nabla\phi$

Dreyer/Guhlke/Müller, PCCP 2013; JF, Comp. Phys. Comm 2015;
JF/Guhlke/Linke/Merdon/Müller, DOI 10.1007/978-3-030-33116-0_8, Springer 2020

Thermodynamic Equilibrium

- Zero flux $\vec{N}_i = 0$
- Given (bulk) reference values $\phi^b, p^b, c_i^b, \gamma_i^b = \gamma_i(c_1^b \dots c_N^b, p^b)$
- Integration of Nernst-Planck flux $\Rightarrow$

$$c_i = c_i^b \frac{\gamma_i^b}{\gamma_i(c_1 \dots c_n, p)} \exp\left(z_i \frac{F}{RT}(\phi^b - \phi)\right)$$

- algebraic system defining c_i
- Combine with Poisson equation, momentum balance:

$$-\nabla\varepsilon\nabla\phi = q = F\sum_{i=1}^{N} z_i c_i$$

$$\Delta p = \nabla \cdot q\nabla\phi$$

(Modified) Poisson-Boltzmann

- Let $a_i = \frac{\gamma_i c_i}{\gamma_i^b c_i^b} = \exp\left(z_i \frac{F}{RT}(\phi^b - \phi)\right)$: activity
  Then $c_i = c_i^b \gamma_i^b \frac{a_i}{\gamma_i}$
- If $\gamma_i = \frac{1}{1 - v\sum_{i=1}^N c_j}$, one can explicitely express the activity coefficient in activities:

$$\gamma_i = 1 + \sum_{j=1}^{N} v a_j$$

- “Collapse” to Generalized Poisson Boltzmann independent of p

$$-\nabla\varepsilon\nabla\phi = q = F\sum_{i=1}^{N} z_i c_i = F\sum_{i=1}^{N} z_i \frac{\exp\left(z_i \frac{F}{RT}(\phi^b - \phi)\right)}{1 + v\sum_{j=1}^N \exp\left(z_j \frac{F}{RT}(\phi^b - \phi)\right)}$$

- $\gamma_i = 1 \Rightarrow$ original Poisson-Boltzmann/Gouy-Chapman model

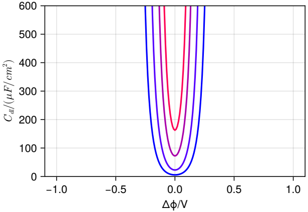
Double layer capacitance of ideally polarizable working electrode

- Computational domain: $\Omega = (0, L) = (x_{WE}, x_{bulk})$
- Half-cell boundary conditions:

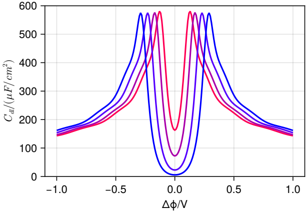
$$\phi|_{x_{WE}} = \phi_{WE} \qquad \phi|_{x_{bulk}} = \phi^b = 0$$

$$(\nabla p - q\nabla\phi)\cdot\vec{n}|_{x_{WE}} = 0 \qquad p|_{x_{bulk}} = p^b = 0$$

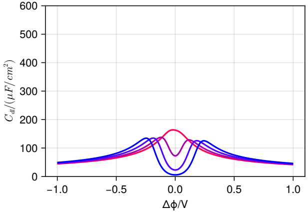
Poisson-Boltzmann



Ideal Mixture/Bikerman

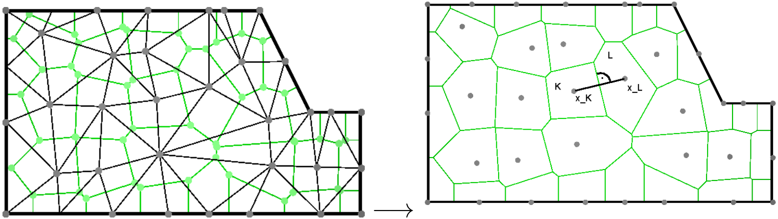


Solvation Mixture/DGML



Finite volume discretization method

- Subdivide computational domain into control volumes aka “representative elementary volumes” (REV)
- Use Gauss theorem to derive balance laws for REV’s from PDE
- “admissible” REV generation: start with triangulation,
  create Voronoi cells by joining triangle cirumcenters as REVs

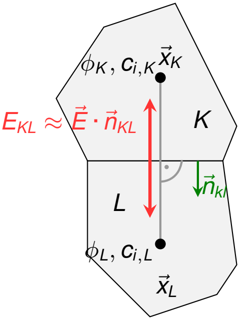


- Orthogonality between interface $\partial K \cap \partial L$ and line $x_K x_L$ between neigboring collocation points $\Rightarrow$ calculate fluxes between REVs by standard two-point finite difference formulas

R. H. Macneal, Quart. Math. Appl., 11:295–310, 1953

Discrete Poisson equation

$$\int_K (-\nabla\cdot\varepsilon\nabla\phi - q)d\omega = 0$$



Gauss theorem:

$$\int_{\partial K} \varepsilon\nabla\phi\cdot\vec{n}d\gamma - \int_K q d\omega = 0$$

Quadrature:

$$\sum_{L \text{ neighbor of } K} |\partial K \cap \partial L| E^n_{KL} - |K| F \sum_{i=1}^{N} z_i c_{i,K} = 0$$

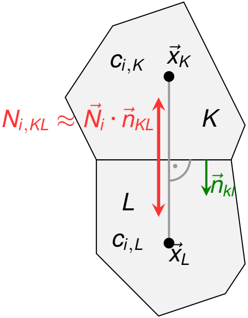
Finite difference approximation:

$$E^n_{KL} = \varepsilon \frac{\phi^n_K - \phi^n_L}{|\vec{x}_K - \vec{x}_L|}$$

Discrete Nernst-Planck flux via modified Scharfetter-Gummel ansatz

Modify implicit Euler “Scharfetter-Gummel” exponential fitting upwinding ansatz from semiconductor simulation by introducing μ^{ex} along with ϕ in the appropriate places.

$$\partial_t c_i - D_i \nabla c_i - c_i \frac{D_i}{RT}\left(\nabla \mu_i^{\text{ex}} + z_i \nabla \phi\right) = 0$$



- Subdivide time: $0 = t^0 < t^1 < \cdots < t^k = T$

$$\frac{|K|}{\Delta t}\left(c_{i,K}^n - c_{i,K}^{n-1}\right) = - \sum_{L \text{ neighbor of } K} |\partial K \cap \partial L| N_{i,KL}^n$$

$$\delta\phi_{KL}^n := \frac{F}{D_i RT}\left(\phi_K^n - \phi_L^n\right), \quad \delta\mu_{i,KL}^{\text{ex},n} := \frac{1}{D_i RT}\left(\mu_{i,K}^{\text{ex},n} - \mu_{i,L}^{\text{ex},n}\right)$$

$$N_{i,KL}^n = D_i \frac{B\left(-\delta\mu_{i,KL}^{\text{ex},n} - z_i \delta\phi_{KL}^n\right) c_{i,K}^n - B\left(\delta\mu_{i,KL}^{\text{ex},n} + z_i \delta\phi_{KL}^n\right) c_{i,L}^n}{|\vec{x}_K - \vec{x}_L|}$$

$B(x) = \frac{x}{e^x - 1}$: Bernoulli function

Allen/Southwell, Quart. J. Mech. and Appl. Math. 1955; Ilin, Mat. Zametki 1969; Scharfetter/Gummel 1969; Yu/Dutton 1988; Liu/Eisenberg, J. Chem. Phys. 2014

Qualitative properties of excess chemical potential scheme
Pressure independent case

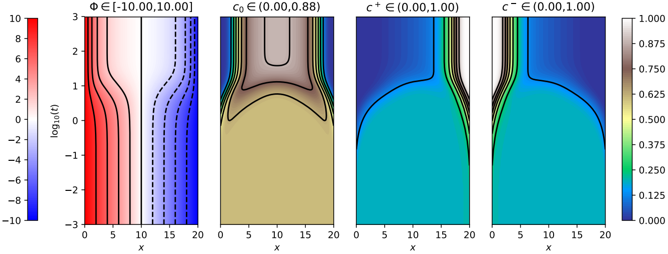
- Exact local and global **charge conservation**
- **Consistency to thermodynamic equilibrium** aka “well posedness”: Stationary solution $c_1 \dots c_N, \phi$ obtained from discrete Nernst-Planck-Poisson system coincides with the solution of the discretized generalized Poisson-Boltzmann problem
- Concentrations stay within **limits from natural constraints**
- Discrete counterpart of free energy $\int_\Omega (c_i \log c_i - \bar{c} \log \bar{c}) + (\nabla\phi)^2 \, d\omega$:

$$\sum_K |K| \sum_{i=0}^{N} c_{i,K} \log c_{i,K} - \bar{c}_{i,K} \log \bar{c}_{i,K} + \sum_{KL} |K \cap L| E_{KL}^2$$

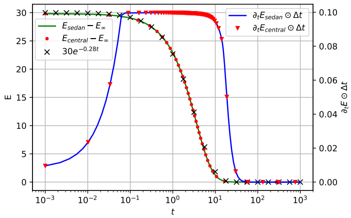
- **Decay of relative free energy** along solution trajectories on approach to equilibrium
- **Existence** of solutions of discretized system
- weak **Convergence** of discrete solution to continuous solution (proven so far for electrolyte case)

Gaudeul/JF, Numerische Mathematik 151, 99–149 (2022)
Abdel/Chainais-Hillairet/Farrell/Herda, IMAJNA 44, 1090-1129 (2024)

Applied potential jump in closed 1D electrochemical cell with ideally polarizing electrodes Symmetric binary electrolyte with equal sizes of solvent molecules, anions and cations.



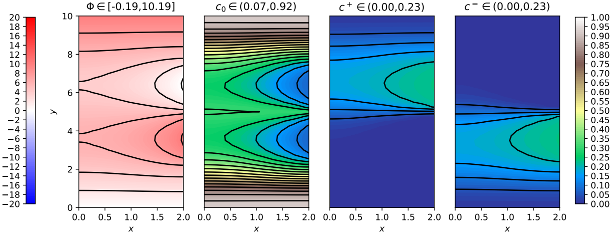
- x-t plots of potential, solvent, anion, cation concentrations
- Concentrations stay within natural bounds



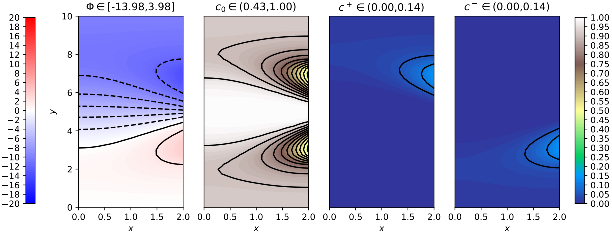
- Evolution of relative free energy and energy dissipation per time step.
- Energy dissipation per time step als step size control criterion

Gaudeul/JF: Numerische Mathematik 2022

Electrolytic diode, domain $\Omega = (0,2) \times (0,10)$
Rectification via surface charges of opposite signs



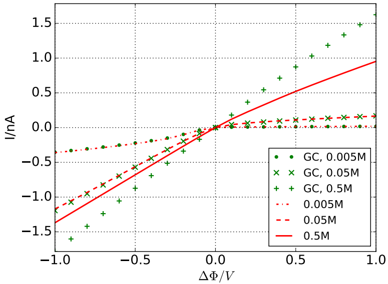
- Forward bias
- High ion concentration
- High ionic current



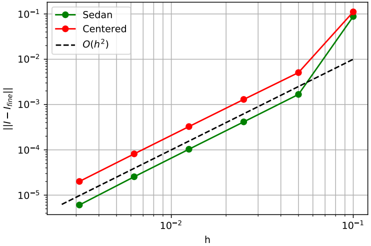
- Reverse bias
- Low ion concentration
- Low ionic current

Gaudeul/JF: Numerische Mathematik 2022

IV curve for electrolytic diode: convergence



IV curve for electrolytic diode



Second order grid convergence of calculated IV curve. “SEDAN” $\equiv$ excess chemical potential scheme

Gaudeul/JF: Numerische Mathematik 2022

Coupling with electro-osmotic flow

- Nernst-Planck-Poisson-Stokes system on triangular/tetrahedral meshes
- Finite ion size via pressure dependency of chemical potentials and solvent chemical potential gradient as counterforce for ion transport
- Solvation via increased effective ion volumes

Flow solver:

- Pressure robust FEM via local correction to classical FEM
- Pointwise divergence free discrete velocity
- Velocity error independent of pressure

Nernst-Planck-Poisson solver:

- Voronoi box based finite volume method
- Exponentially fitted upwind fluxes
- Consistency to thermodynamic equilibrium

Coupling:

- Divergence free projection of FEM velocity to FVM
- Fix point iteration
- WIP: re-implementation in Julia environment

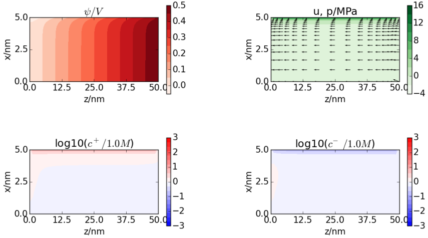
Linke, CMAME 2014; John/Linke/Merdon/Neilan/Rebholz, SIAM Review 2017
JF/Guhlke/Linke/Merdon/Müller, Electrochimica Acta, vol. 317, pp. 778–785, 2019

Electro-osmotic flow through straight nano pore Velocity, concentration and electrostatic potential

- Inlet/outlet concentrations

  $c_+ = c_- = 1M$
- Surface charge

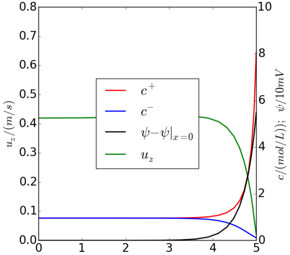
  $\varepsilon \nabla \phi \cdot \vec{n} = \sigma = -10 \mu As/cm^2$
- Potential drop $\Delta \phi = 0.01\,V/nm$
- Simulated half channel due to symmetry



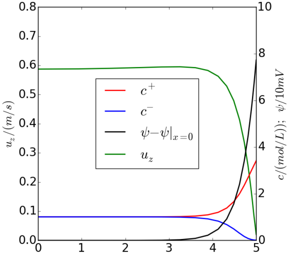
Top left: distribution of the electrostatic potential. Top right: velocity field (arrows) and pressure (color). Bottom row: positive resp. negative ion concentration.

JF/Guhlke/Linke/Merdon/Müller, DOI 10.1007/978-3-030-33116-0_8, Springer 2020

Electro-osmotic flow through straight nano pore
Velocity, concentration and electrostatic potential profiles



Classical Nernst-Planck (Dilute)



Improved (DGML) model, $\kappa = 10$

- Body force $q\nabla\phi$ acts only in EDL
- Electro-neutral region with constant velocity $\Rightarrow$ plug flow
- Velocity, ζ-potential increase with solvation number due to wider double layer

JF/Guhlke/Linke/Merdon/Müller, DOI 10.1007/978-3-030-33116-0_8, Springer 2020

Towards simple redox reaction
Boundary conditions for Faradaic reactions

- Solvent and metal inert with respect to reaction – only ions and electrons react
- Constant e^- concentration in electrode material (metal)
- Applied potential difference ϕ_{WE}
  $\Rightarrow$ Dirichlet BC for the electrostatic potential and bulk concentrations
- **Postulate: Reaction rates depend solely on chemical potentials at surface**

$$
\begin{aligned}
\phi|_{x_{WE}} &= \phi_{WE}, & \phi|_{x_{bulk}} &= 0\\
(\nabla p - q\nabla\phi)\cdot\vec{n}|_{x_{WE}} &= 0 & p|_{x_{bulk}} &= 0\\
(N_i\cdot\vec{n})|_{x_{WE}} &= J_i(\mu_{WE,1}0\dots\mu_{WE,N}) & c_i|_{x_{bulk}} &= c_i^b
\end{aligned}
$$

- Fast adsorption $\Rightarrow$ equal bulk and surface chemical potentials $\mu_{WE,i} = \mu_i(x_{WE})$

Guhlke, PhD Thesis TU Berlin, 2015
Dreyer/Guhlke/Müller PCCP 2015

Surface reaction equation

- Let $C_0 \dots C_N$ be the reacting species, $\mathcal{R}_\nu$ $(\nu = 1 \dots n_R)$ reactions
- C_{-1}: electrons on the metal side, $(b_{\nu,-1} - a_{\nu,-1}) = n_\nu$: number of electrons
- ν-th chemical reaction equation $\mathcal{R}_\nu$:

$$\sum_{i=-1}^{N} a_{k,i} C_i \underset{k_\nu^-}{\overset{k_\nu^+}{\leftrightharpoons}} \sum_{i=-1}^{N} b_{\nu,i} C_i$$

- Affinity:

$$\mathcal{A}_\nu = \frac{1}{RT} \sum_{i=-1}^{N} (b_{\nu,i} - a_{\nu,i}) \mu_i$$

- Rate expression:

$$\mathcal{R}_\nu(\mu_0 \dots \mu_N) = k_\nu \Big(\exp(-\beta_\nu \mathcal{A}_\nu) - \exp((1-\beta_\nu)\mathcal{A}_\nu) \Big)$$

Dreyer/Guhlke/Müller PCCP 2016; Landstorfer, JES 2017

Redox reaction

- Aqeuous solution with reacting species $O = C_1, R = C_2$ with $z_O = z_R + n$
- Chemical equation:

$$O + ne^- \rightleftharpoons R$$

- Affinity: $\mathcal{A} = \frac{1}{RT}\left(\Delta g + \mu_R - \mu_O\right)$
- $\Delta g = n\mu_{-1}$ – chemical potential of electrons == work function
- Surface rate expression:

$$\mathcal{R}(\mu_R, \mu_O) = k\Big(\exp(-\beta_1 \mathcal{A}) - \exp((1-\beta_1)\mathcal{A})\Big)$$

$$J_O = \mathcal{R}, J_R = -\mathcal{R}$$

- Inert background electrolyte $S = C_3, X = C_4$ with $z_S = -1$, $z_X = 1$, $J_S = J_X = 0$

Local electroneutrality & dilute solution assumption outside of double layer

$$\underbrace{\nabla\varepsilon\nabla\phi +}_{=0} F\sum_{i=1}^{N} z_i c_i = 0$$

- Sum over Nernst-Planck equations multiplied by z_i $\Rightarrow$

$$\underbrace{-\sum_{i=1}^{N}\nabla\cdot D_i(z_i\nabla c_i)}_{\text{assumed small}} - \nabla\cdot\underbrace{\left(\sum_{i=1}^{N} z_i^2 D_i c_i \frac{F}{RT}\right)}_{=:\sigma\ \text{conductivity}}\nabla\phi = 0$$

- $\Rightarrow$ Ohm’s law $-\nabla\cdot\sigma\nabla\phi = 0$. Often mistaken for Poisson equation ...
- Large background electrolyte concentration c_S dominates σ
- $\Rightarrow$ Species transport reduces to convective diffusion equation $\partial_t c_i - \nabla\cdot(D_i\nabla c_i + c_i\vec{u}) = 0$

Equilibrium in the polarization boundary layer

- Motivated by asymptotic analysis, one can assume equilibrium in the polarzation boundary layer (x_{WE}, x_{DL})

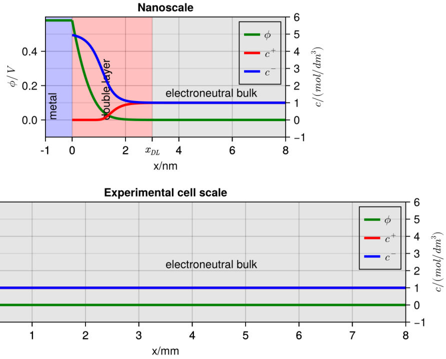
$$\mu_i + z_i F\phi = \text{constant}$$

- $\Rightarrow$ chemical potentials at the surface:

$$\begin{aligned} \mu_i(x_{WE}) + z_i F\phi(x_{WE}) &= \mu_i(x_{DL}) + z_i F\phi(x_{DL}) \\ \mu_{WE,i} = \mu_i(x_{WE}) &= \mu_i(x_{DL}) + z_i F(\phi(x_{DL}) - \phi(x_{WE})) \end{aligned}$$

Dreyer/Guhlke/Müller, PCCP 2015

Nanoscale vs “Device scale”



- Orders of magnitude between cell size and nanometer scale
- Replace domain $\Omega_{nano} = (x_{WE}, L)$ by $\Omega_{device} = (x_{DL}, L_{device})$
- Lump processes in (x_{WE}, x_{DL}) into boundary condition in Ω_{device}

Assuming $\Omega_{device} \approx (0, L_{device})$, one has for $U = \phi_{WE}^{solute} - \phi_{WE}^{metal}$:

$$\mu_{WE,i} = \mu_i(x_{DL}) + z_i F U$$

Towards Butler-Volmer like rate expression at device scale

$$\mathcal{A} = \frac{1}{RT}\left(\Delta g + \mu_R - \mu_O + nF(\phi - U)\right)$$

$$\mathcal{R}(\mu_O, \mu_R, \phi) = k\left(\exp\left(-\beta\frac{\mu_R - \mu_O - nF(\phi - U)}{RT}\right) - \exp\left((1-\beta)\frac{\mu_R - \mu_O - nF(\phi - U)}{RT}\right)\right).$$

Expressed in concentrations, one yields (setting $\beta = \frac{1}{2}$)

$$\begin{aligned}\mathcal{R}(c_O, c_R, \phi) &= k\left(\left(\frac{c_O}{c_R}\right)^{\frac{1}{2}}\exp\left(\frac{zF(\phi - U)}{2RT}\right) - \left(\frac{c_R}{c_O}\right)^{\frac{1}{2}}\exp\left(-\frac{zF(\phi - U)}{2RT}\right)\right)\\ &= \frac{\bar{c}R_0}{(c_O c_R)^{\frac{1}{2}}}\left(\frac{c_O}{\bar{c}}\exp\left(\frac{zF(\phi - U)}{2RT}\right) - \frac{c_R}{\bar{c}}\exp\left(\frac{-zF(\phi - U)}{2RT}\right)\right).\end{aligned}$$

Replacing $\frac{\bar{c}k}{(c_O c_R)^{\frac{1}{2}}}$ by $i_0 = \frac{\bar{c}k}{(c_O^{\text{bulk}} c_R^{\text{bulk}})^{\frac{1}{2}}}$ yields a Butler-Volmer like equation

Experimentalist’s approach

- Convective diffusion equations for R, O

$$\partial_t c_i + \nabla\cdot(\vec{N}_i + c_i\nabla\vec{u}) = 0 \quad \vec{N}_i = -D_i\nabla c_i$$

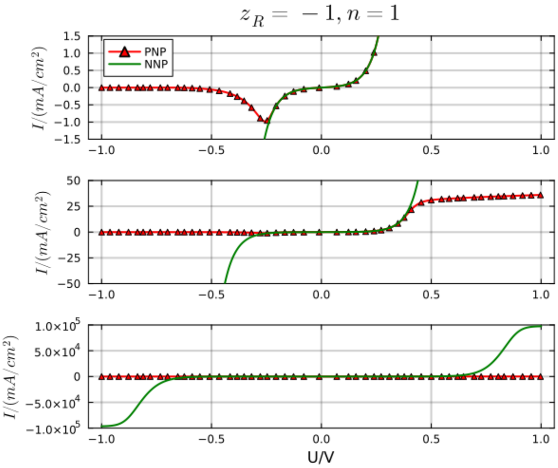
$$(\vec{N}_i + c_i\nabla\vec{u})\cdot\vec{n}|_{WE} = J_i \quad + \text{bulk boundary conditions}$$

- Potentiostat controls counter electrode in order to maintain a well defined potential difference $\phi_{WE}^{metal} - \phi_{RE}$ between metal side of working electrode and high impedance reference electrode
- Background electrolyte concentration is large enough $\Rightarrow \phi_{WE}^{solute} \approx \phi_{RE}$
- Butler-Volmer rate equation dependent on potential difference $U = \phi_{WE}^{solute} - \phi_{WE}^{metal}$

$$\mathcal{R}_{BV} = k^+ c_O \exp\left(-\alpha n\frac{F}{RT}U\right) - k^- c_R \exp\left((1-\alpha)n\frac{F}{RT}U\right)$$

$$J_O = \mathcal{R}, J_R = -\mathcal{R}_{BV}$$

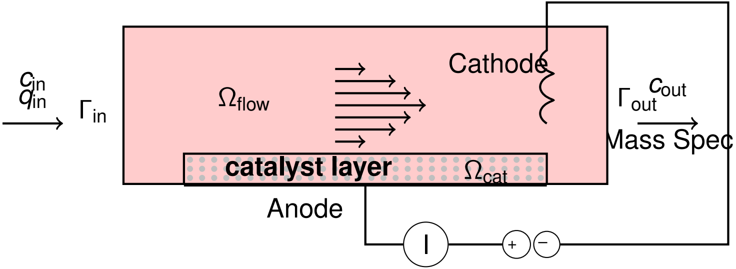
Comparison: NP + local electroneutrality (NNP) vs. NP+ Poisson (PNP)
Half cell with $L = 20nm$



- Good match between results for asymptotic expression and resolved boundry layer for small voltages
- “Levich exclusion” for larger negative voltages
- Displacement by X^- accumulated due to electrostatic attraction for larger positive voltages

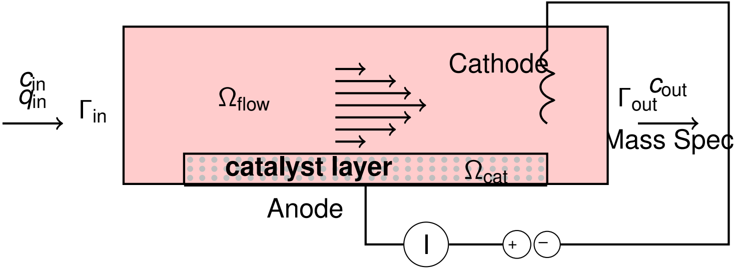
V. Levich, Dokl. Akad. Nauk SSSR 67 (1949) 309–312

Rotating disk electrode



- Solution containing electrolyte and reactant is injected at given rate
- Oxidation reaction (creating electrons) at the anode
- Reduction reaction (consuming electrons) at cathode
- Reaction rate can be measured as anodic current
- Product composition can be measured at outlet

Rotating disk electrode



- Solution containing electrolyte H_2SO_4 and reactant H_2 is injected at given rate
- Oxidation reaction (creating electrons) at the anode $H_2 \rightarrow 2H^+ + 2e^-$
- Reduction reaction (consuming electrons) at cathode $2H^+ + 2e^- \rightarrow H_2$
- Reaction rate can be measured as anodic current
- Product composition can be measured at outlet

Limiting current experiment

- Stationary, incompressible Navier-Stokes equations for fluid flow
- Stationary transport of species

$$\nabla \cdot \vec{q} = 0, \quad \vec{q} = -(D\nabla c - c\vec{v})$$

$$\begin{array}{lrcl rl}
\text{anode: fast reaction} & c & = & 0 & \vec{v} & = 0 \\
\text{outlet:} & \vec{q}\cdot\vec{n} & = & -c\vec{v}\cdot\vec{n} & p & = 0 \\
\text{inlet:} & c & = & c_I & \vec{v}\cdot\vec{n} & = v(x) \\
\text{impermeable walls:} & \vec{q}\cdot\vec{n} & = & 0 & \vec{v} & = 0
\end{array}$$

- $\vec{v}$: Hagen-Poiseuille flow with parabolic velocity profile
- Limiting current: $I_{lim} = 2F \int_{anode} \vec{q}\cdot\vec{n}ds$ F: Faraday constant

Asymptotics for 3D cell with circular electrode
Asymptotics work if boundary layer is small compared to cell height

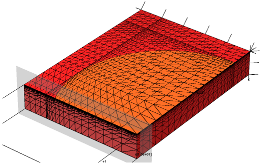
Average velocity: $\bar{v}$

Poiseuille flow: $\vec{v} = 6\bar{v}\left(\frac{z}{H}(1-\frac{z}{H}), 0, 0\right)^T$

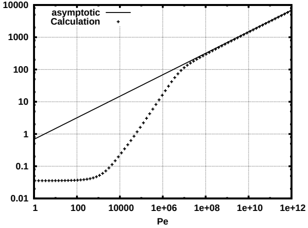
Shear rate based Peclet number $Pe = 6\frac{\bar{v}R^2}{DH}$

Asymptotic scaling law: $Sh = \frac{3^{\frac{4}{3}}2^{\frac{2}{3}}}{5\sqrt{\pi}\Gamma(\frac{5}{6})}Pe^{\frac{1}{3}} \approx 0.68658 Pe^{\frac{1}{3}}$

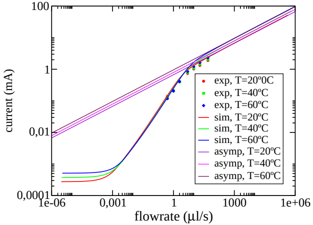
Limiting current $I_{lim} = 2FDc_l\frac{\pi}{R}Sh \sim \bar{v}^{\frac{1}{3}}$



Flow-aligned 3D grid



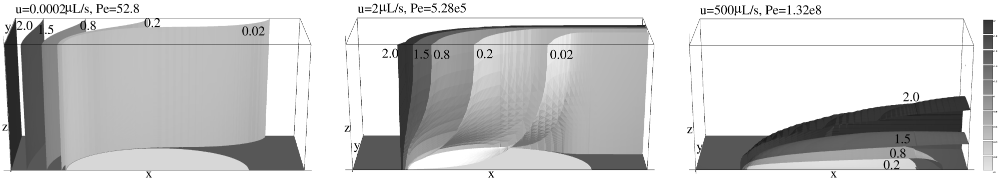
Sh vs. *Pe*



vs Experiment

Lévêque, Ann. des Mines 1928
JF/Zhao/Holzbecher/Langmach/Chojak/Jusys/Halseid/Behm PCCP (2008)

Limiting current simulation using 3D convective diffusion in Hagen Poiseulle flow Isolevels



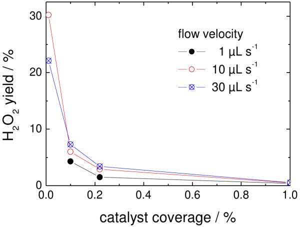
0.000283 $\mu L/s$ 2.83 $\mu L/s$ 567 $\mu L/s$

Concentration isolevels at different Peclet numbers. At low flow rates, the behaviour is purely diffusive. The assumptions for asymptotic theory are true only for higher flow rates.

JF/Zhao/Holzbecher/Langmach/Chojak/Jusys/Halseid/Behm PCCP (2008)

H_2O_2 yield in catalytic oxygen reduction

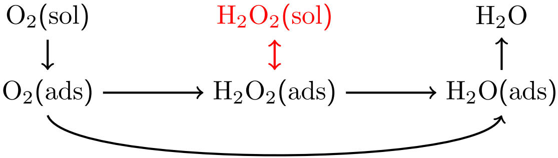
$$\begin{tikzcd}
O_2(\mathrm{sol}) \arrow[d] & H_2O_2(\mathrm{sol}) \arrow[d, leftrightarrow] & H_2O \\
O_2(\mathrm{ads}) \arrow[r] \arrow[rr, bend right] & H_2O_2(\mathrm{ads}) \arrow[r] & H_2O(\mathrm{ads}) \arrow[u]
\end{tikzcd}$$



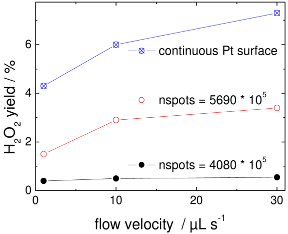
H_2O_2 yield decreases with increasing coverage of active Pt nanodisks on planar glassy carbon substrate (nanostructured Pt/GC model electrodes)

Y. E. Seidel, A. Schneider, Z. Jusys, B. Wickman, B. Kasemo, and R. J. Behm, Faraday Discussions **140**, 167(2008).

H_2O_2 yield in catalytic oxygen reduction



$$\begin{tikzcd}
O_2(\mathrm{sol}) \arrow[d] & H_2O_2(\mathrm{sol}) \arrow[d, leftrightarrow] & H_2O \\
O_2(\mathrm{ads}) \arrow[r] \arrow[rr, bend right] & H_2O_2(\mathrm{ads}) \arrow[r] & H_2O(\mathrm{ads}) \arrow[u]
\end{tikzcd}$$



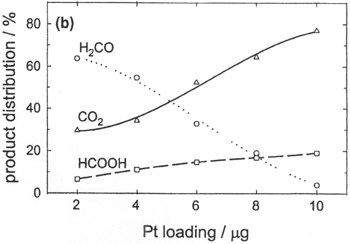
H_2O_2 yield increases with increasing electrolyte flow velocity for

- two different densities of similarly sized Pt nanodisks
- fully Pt covered electrode.

Y. E. Seidel, A. Schneider, Z. Jusys, B. Wickman, B. Kasemo, and R. J. Behm, Faraday Discussions **140**, 167(2008).

Potentiostatic Electrooxidation of Methanol

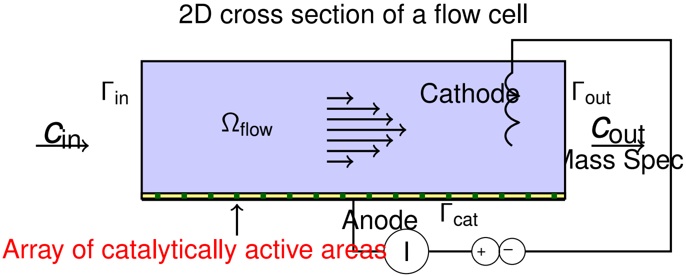
$$\begin{tikzcd}
\mathrm{CH_3OH(sol)} \arrow[d] & \mathrm{H_2CO(sol)} \arrow[d, leftrightarrow] & \mathrm{HCOOH(sol)} & \mathrm{CO_2(sol)} \\
\mathrm{CH_3OH(ads)} \arrow[r] \arrow[dr, bend right] & \mathrm{H_2CO(ads)} \arrow[r] \arrow[d] & \mathrm{HCOOH(ads)} \arrow[r] \arrow[u] & \mathrm{CO_2(ads)} \arrow[u] \\
 & \mathrm{CO(ads)} \arrow[urr, bend right] & &
\end{tikzcd}$$



Fraction of formaldehyde in product distribution decreases with increasing Pt loading of carbon-supported Pt/C catalysts

Z. Jusys, J. Kaiser, and R. J. Behm, Langmuir **19**, 6759(2003).

Principle of a flow cell with array of Pt nanospots as electrode



Model assumptions:

- Hagen-Poiseuille flow
- Stationarity
- Langmuir assumption: sorption reactions involved follow mass action law
- Constant temperature and potential

Solute transport coupled with surface reaction

- Stationary diffusion and transport of species $X = A, B, C$ in velocity field $\vec{v}$:

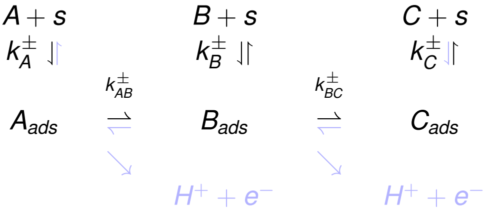
$$\frac{\partial c_X}{\partial t} - \operatorname{div}(D_X \vec{\nabla} c_X - \vec{v} c_X) = 0$$

- Boundary conditions:

$c_X = c_{X,\text{in}}$	on Γ_{in}	Dirichlet
$(D_X \vec{\nabla} c_X - c_X \vec{v}) \cdot \vec{n} = -c_X \vec{v} \cdot \vec{n}$	on Γ_{out}	Outflow
$(D_X \vec{\nabla} c_X - c_X \vec{v}) \cdot \vec{n} = c_{cat}^{eff} \mathbf{r_X}$	on Γ_{cat}	Ad/Desorption at active areas
$\frac{\partial c_X}{\partial \vec{n}} = 0$	on $\Gamma \setminus (\Gamma_{\text{in}} \cup \Gamma_{\text{out}} \cup \Gamma_{\text{cat}})$	No flow

- Outflow of species X: $X_{\text{out}} = \int_{\Gamma_{\text{out}}} (D_X \vec{\nabla} c_X - c_X \vec{v}) \cdot \vec{n}\, ds$
- Relative amount of reaction intermediates: $\mathcal{I}_{out} = B_{out} / (B_{out} + C_{out})$

Model electrode reaction



Dissolved in fluid

Adsorption/Desorption

Adsorbed at catalyst surface

Released ions

Rate expressions:

$$\mathbf{r_A} = k_A^+ c_A \theta_f - k_A^- \theta_A$$

$$r_{AB} = k_{AB}^+ \theta_A - k_{AB}^- \theta_B$$

$$\mathbf{r_B} = k_B^+ c_B \theta_f - k_B^- \theta_B$$

$$r_{BC} = k_{BC}^+ \theta_B - k_{BC}^- \theta_C$$

$$\mathbf{r_C} = k_C^+ c_C \theta_f - k_C^- \theta_C$$

Algebraic conditions for adsorbed species:

$$d\theta_A/dt - r_A - r_{AB} = 0$$

$$d\theta_B/dt - r_B + r_{AB} - r_{BC} = 0$$

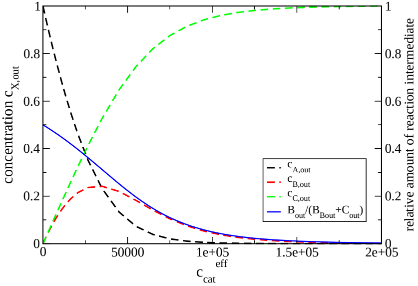
$$d\theta_C/dt - r_C + r_{BC} = 0$$

- θ_X – fraction of catalyst sites occupied by adsorbed species
- $\theta_f = 1 - \theta_A - \theta_B - \theta_C$ – fraction of free catalyst sites

JF/Zhao/Langmach/Seidel/Jusys/Behm, Fuel Cells (2011)

Influence of catalyst concentration

Relative amount of reaction intermediate decreases with increasing catalyst concentration.

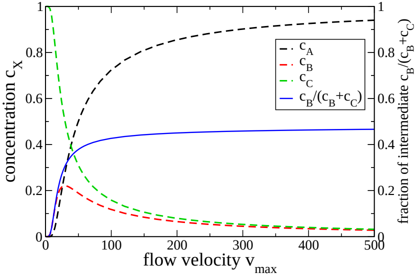


Outlet concentrations and relative amount of reaction intermediate for fixed active area geometry and flow velocity.

JF/Zhao/Langmach/Seidel/Jusys/Behm, Fuel Cells (2011)

Species concentration and fraction of intermediates vs. velocity

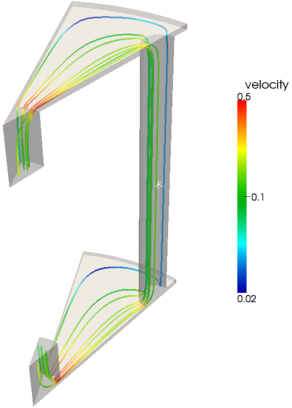
Relative amount of reaction intermediate increases with increasing flow velocity.

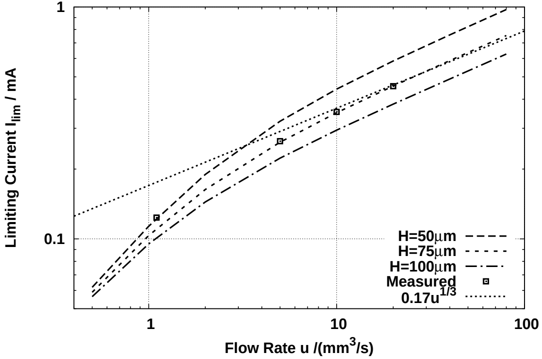


Species concentration and relative amount of reaction intermediate at the outlet depending on inflow velocity.

JF/Zhao/Langmach/Seidel/Jusys/Behm, Fuel Cells (2011)

Limiting current simulation in cylindrical flow cell





- Mass conservative coupling between finite volume transport solver and pressure robust FEM flow solver

JF/Linke/Langmach/Baltruschat, Electrochimica Acta 2008

Device scale simulations on the electroneutral scale

Rotating disk electrode

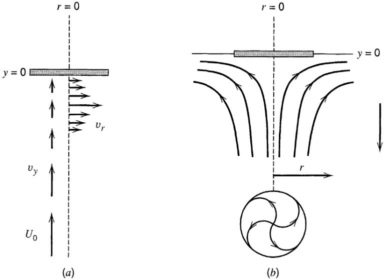


Image: Bard/Faulkner

- Based on asymptotic theory

- Levich equation:

$$I_{lim} = 0.62 nFAD^{\frac{2}{3}} \omega^{\frac{1}{2}} \eta^{-\frac{1}{6}} c_\infty$$

- Koutecký-Levich equation at rotating disk (for first order surface reactions $I_0 = kc_0$):

$$\frac{1}{i} = \frac{1}{FAkc_\infty} + \frac{1}{i_l} = \frac{1}{FAkc_\infty} + \frac{1}{0.62 nFAD^{\frac{2}{3}} \omega^{\frac{1}{2}} \eta^{-\frac{1}{6}} c_\infty}$$

V.G. Levich, Zhurnal Fizicheskoi Khimii, 18(1944)335

Deriving a software API for two-point flux finite volumes

Continuous:

n coupled PDEs in $\Omega \subset \mathbb{R}^d$:

$$\partial_t s(\vec{u}) - \nabla \cdot j(\vec{u}, \nabla \vec{u}) + r(\vec{u}) = 0$$

- “Storage” $s : \mathbb{R}^n \to \mathbb{R}^n$
- “Reaction” $r : \mathbb{R}^n \to \mathbb{R}^n$
- “Flux” $j : \mathbb{R}^n \times \mathbb{R}^{nd} \to \mathbb{R}^{nd}$

Problems in this class:

- Multiphase flow in porous media
- Ion transport in electrolytes
- Charge transport in semiconductors
- $\ldots$

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- Charge transport in semiconductors
- …

Discretized:

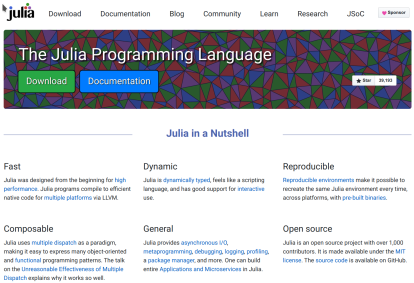
$$0 = |K| \frac{s(\vec{u}_k^n) - s(\vec{u}_k^{n-1})}{\Delta t} + \\ + \sum_{L \text{ neigbour of } K} |K \cap L| g(\vec{u}_k^n, \vec{u}_l^n) + |K| r(\vec{u}_k^n)$$

- “Storage” $s : \mathbb{R}^n \to \mathbb{R}^n$
- “Reaction” $r : \mathbb{R}^n \to \mathbb{R}^n$
- discrete edge flux $g : \mathbb{R}^n \times \mathbb{R}^n \to \mathbb{R}^n$

Solution methods:

- Delaunay mesh generation
- Implicit Euler time discretization
- Newton method with analytical Jacobians (+ damping, parameter embedding)
- Various direct and iterative linear solvers

Julia language and VoronoiFVM.jl



The Julia Programming Language

Julia in a Nutshell

Fast

Julia was designed from the beginning for high performance. Julia programs compile to efficient native code for multiple platforms via LLVM.

Dynamic

Julia is dynamically typed, feels like a scripting language, and has good support for interactive use.

Reproducible

Reproducible environments make it possible to recreate the same Julia environment every time, across platforms, with pre-built binaries.

Composable

Julia uses multiple dispatch as a paradigm, making it easy to express many object-oriented and functional programming patterns. The talk on the Unreasonable Effectiveness of Multiple Dispatch explains why it works so well.

General

Julia provides asynchronous I/O, metaprogramming, debugging, logging, profiling, a package manager, and more. One can build entire Applications and Microservices in Julia.

Open source

Julia is an open source project with over 1,000 contributors. It is made available under the MIT license. The source code is available on GitHub.

- Julia 1.0 (2018): new language for scientific computing & data science
- Just-in-time compilation ⇒ C-like performance
- Syntax level like python, matlab
- Best-in-class package manager supporting reproducibility
- Open source (MIT License)
- Easy access to automatic differentiation

VoronoiFVM.jl

- Solver for coupled nonlinear partial differential equations based on the Voronoi finite volume method.
- Implements the aforementioned API
- Use automatic differentiation to assemble Jacobians for complicated nonlinear problems
- 1/2/3D

https://julialang.org
JF et al: VoronoiFVM.jl, https://github.com/WIAS-PDELib/VoronoiFVM.jl

Example code for discrete fluxes
Derivatives for Jacobian calculated automatically from this code

```
function flux(f,u,edge,data)
    iphi=data.iphi
    f[iphi]=u[iphi,1]-u[iphi,2]
    sum_c1=0.0
    sum_c2=0.0
    for ic=1:data.nc
        sum_c1+=u[ic,1]
        sum_c2+=u[ic,2]
    end
    muex1=-log(1.0-sum_c1)
    muex2=-log(1.0-sum_c2)
    for ic=1:data.nc
        arg=data.z[ic]*(u[iphi,1]-u[iphi,2])+(muex1-muex2)
        bp,bm=fbernoulli_pm(arg)
        f[ic]=bm*u[ic,1]-bp*u[ic,2]
    end
end
```

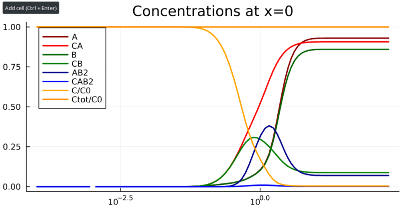
WIAS-PDELib: open source Julia packages for PDE simulation

- WIAS-PDELib: collection of Julia packages for supporting PDE simulations
  - Pre/postprocessing, mesh generation, visualization
  - finite volume solver VoronoiFVM.jl
  - finite element solver ExtendableFEM.jl
- ChargeTransport.jl: package for solid state drift-diffusion problems (semiconductors, perovskites) on top of VoronoiFVM.jl
- WIP: LiquidElectrolytes.jl: package for electrolyte calculations on top of VoronoiFVM.jl implements the aforementioned discretization methods for generalized PNP problems
- Integration with Julia SciML infrastructure (ODE solvers, linear solvers . . .)

https://github.com/WIAS-PDELib
C. Rackauckas et al: https://sciml.ai/

Julia symbolic tools for reaction modeling
ModelingToolkit.jl & Catalyst.jl

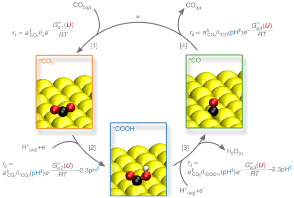
- ModelingToolkit.jl: modeling framework for symbolic-numeric computation. Automatically generate functions for model components like Jacobians and Hessians
- Catalyst.jl: symbolic modeling package for chemical reaction networks.
    - Create code for mass action reaction networks from chemical reaction equations written in Catalyst’s domain-specific language
    - Defines symbolic ReactionSystems, which can be created programmatically
- Reaction functions generated by Catalyst.jl can be used in bulk and boundary reaction callbacks of VoronoiFVM.jl

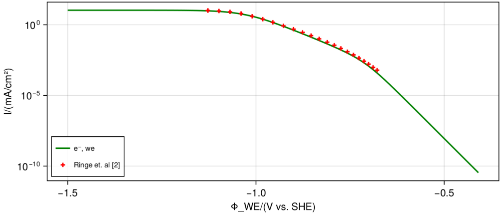


https://docs.sciml.ai/ModelingToolkit/stable/; https://docs.sciml.ai/Catalyst/stable/
https://wias-pdelib.github.io/VoronoiFVM.jl/stable/plutostatichtml_examples/heterogeneous-catalysis/

CatmapInterface
WIP, with Ringe Lab (Korea Univ.), S.Maaß (TU Berlin/AWI Bremen)

- CatMap: Python package for expressing and solving microkinetic models parametrized by relative energies of intermediate states obtained from ab-initio calculations by DFT
- CatInt: CatMAP coupled to a generalized PNP system realized in COMSOL
- CatMapInterface.jl
  - Generate electrode boundary condition functions from CatMAP data for LiquidElectrolytes.jl, leveraging Catalyst.jl
  - Use ModelingToolkit.jl to describe bulk buffer reactions





S. Ringe et al (2020). Nature communications, 11(1), 33, `https://catmap.readthedocs.io/en/latest/`
Chun/Maaß/Seol/JF/Ringe: IPAM ECHII workshop poster

Conclusions & outlook

- Thermodynamics informed generalized Poisson-Nernst-Planck models are able to reflect quite accurately experimental data (at least in equilibrium . . .)
- Mathematically consistent ways of upscaling to electroneutral scale
- Finite volume methods provide a provably thermodynamically consistent discretization approach for coupled nonlinear systems of PDEs
- Fluid dynamics, and coupling with reaction and transport are important to understand experimental systems
- The Julia language provides an open source environment for efficient and reproducible implementations of complicated nonlinear models, leveraging among others symbolic tools and automatic differentiation
- We try to leverage these possibilities with a focus on scientific computing for (bio)electrochemistry, semiconductor modeling, (mixture) flow in porous media . . .