Coupled Transport, Poisson and gFBV Model for 1D Double Layer Description of RFB Electrode-Electrolyte Interface

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1. Context & Motivation

The electrode–electrolyte interface in electrochemical systems is a region of fundamental physical and engineering relevance. Within the first few nanometers inside the electrolyte phase, state variables — ionic concentrations, electric potential, and mechanical pressure — undergo sharp spatial variations. Electron-transfer reactions localized at the interface are strongly influenced by this highly structured double-layer (DL) region.

Classical continuum DL models, typically based on dilute-solution Poisson–Nernst–Planck formulations coupled to Butler–Volmer kinetics, neglect finite-size effects, pressure–electrostatics coupling, and full thermodynamic consistency. As a consequence, their predictive capability is limited, particularly at high concentrations and large applied potential.[1]

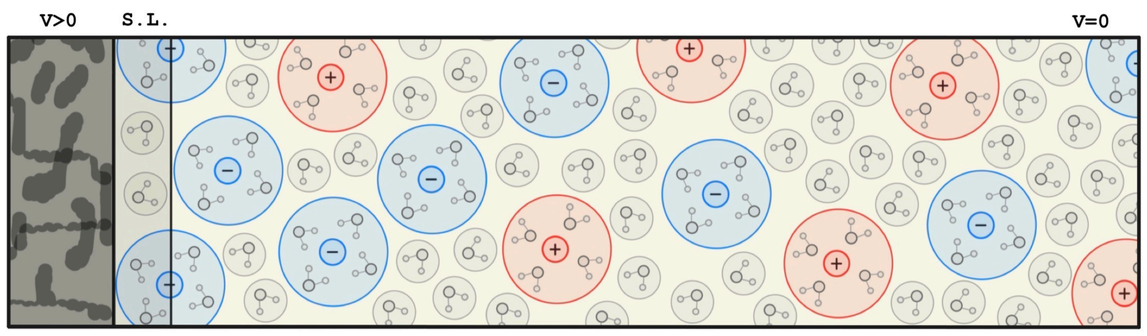

Figure 1. *Double layer schematics with solvated ions, water molecules and Stern Layer (SL).*

2. Thermodynamically Consistent Double Layer Model

The model describes the first nanometers of the electrolyte through a one-dimensional continuum formulation, where all state variables are expressed as functions of the distance from the solid–liquid interface.

The computational domain extends from the metal surface ($x = 0$) to a bulk reference position ($x = L$).

A Stern layer of thickness x_r is introduced to represent the minimum approach distance of solvated ions to the metal surface. Beyond this region, the diffuse double layer develops following the governing equations.

The primary state variables are:

1. **electric potential** $\phi(x)$;
2. **concentrations** $c_i(x)$ for solvent and ionic species;
3. mechanical **pressure** $p(x)$.

Derived quantities include charge density, molar fractions y_i, and current density. The model is formulated within a thermodynamically consistent framework based on a free-energy density functional.[2] Transport, steric effects, solvation effects, and electrostatic interactions are derived from generalized chemical potentials, ensuring internal consistency of the constitutive relations.[1]

Some key features of the model are:

- **electrolyte compressibility**, pressure coupled with particle density;
- **generalized Frumkin–Butler–Volmer** (g-FBV) for a DL–consistent kinetics;[3]
- **Dirichlet boundary conditions** for $\phi(L)$, $\phi(0)$, $c_i(L)$, $p(L)$;
- **bulk electroneutrality** constraint;
- **multi-subdomain** formulation;
- **steady state formulation**, (i) time derivatives vanish and (ii) species flux is uniform.

Description	Equation
Flux balance	$\partial_x J_i(x) = 0 \qquad for \quad i = 1, \ldots, N-1$
Force balance	$\partial_x p(x) = -n^f(x)\ \partial_x \phi(x)$
Poisson equation	$\epsilon_0\ (1+\chi)\ \partial_x^2 \phi(x) = n^f(x)$
Flux for ionic species	$J_i(x) = -\frac{M_i}{T}\ [\partial_x(\mu_i(x) - \mu_N(x)) \ + \ \frac{e_0 z_i}{m_i}\ \partial_x \phi(x)]$
Chemical potential	$\mu_i(x) = g_i^{ref} \ + \ (k_i+1)\frac{K}{m_i\ n^{ref}}\ \ln(1+\frac{p(x)-p^{ref}}{K}) \ + \ \frac{k_B T}{m_i}\ \ln(y_i(x))$
Compressibility	$p(x) = p^{ref} \ + \ K\ (\frac{n(x)}{n^{ref}} - 1)$
g-FBV	$J_e(x_r) = k_R c_O(x_r)\ e^{\alpha_R n f\ (\phi(0)-\phi(x_r))} \ - \ k_O c_R(x_r)\ e^{-\alpha_O n f\ (\phi(0)-\phi(x_r))}$

The resulting nonlinear differential problem is discretized using a finite-volume method (VoronoiFVM) and implemented in Julia. The solver exhibits robust convergence, with computation times below 10 seconds for the reported parameter set.

3. Results

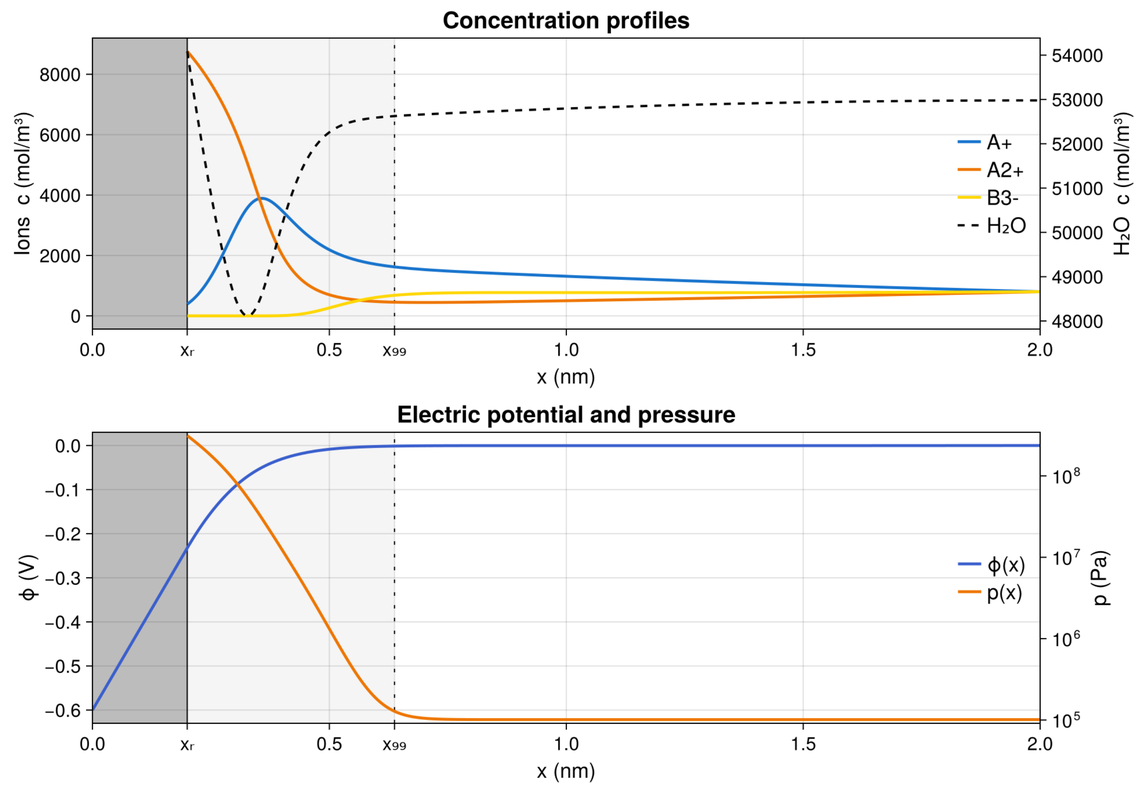

Figure 2. *DL profiles for the parameters in the table below.*

Parameter	Value	Parameter	Value
Domain length L	2 nm	Stern thickness x_r	0.2 nm
Bulk potential ϕ_0	0 V	Electrode potential ϕ_L	-0.6 V
Bulk pressure p_L	1.01325×10^5 Pa	Temperature T	293.75 K
Dielectric susceptibility χ	20	Bulk modulus K	2.2×10^9 Pa
Bulk number density n_L	3.335×10^{28} m^{-3}	Grid points N	2000
Reference n_{ref}	3.335×10^{28} m^{-3}	Reference p_{ref}	1.01325×10^5 Pa
Reference L_{ref}	20 nm	Transfer coeffs $\alpha_O = \alpha_R$	0.5
Rate constants $k_O = k_R$	2×10^{-4} m s^{-1}	Species mass m_i	2.99×10^{-26} kg
Mobility coeff. M_i	2×10^{-10} kg K s m^{-3}	Bulk conc. c_i^{bulk}	$c_{A^+} = c_{A^{2+}} = 800$ mol m^{-3}

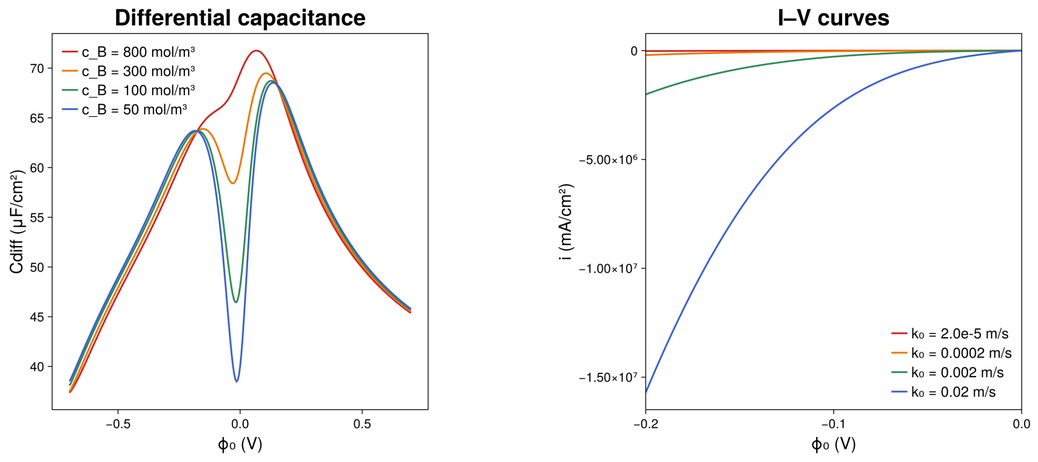

Figure 3. *Differential capacitance and current density as functions of the electrode potential.*

4. Conclusions & Outlook

1. Electrochemical Impedance Spectroscopy (EIS):[4]
   used both for model validation and for parameter estimation through comparison between simulated and experimental impedance spectra.
2. Adsorption and advanced reaction kinetics:
   inclusion of adsorption phenomena and reaction mechanisms described by Marcus–Hush theory, providing a smaller-scale physical description.
3. Coupling with porous-electrode models:
   integration of the double-layer model with porous-scale transport models to enable simulations of full redox flow battery (RFB) systems.

Acknowledgments

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