High-order finite element methods for three-dimensional multicomponent convection-diffusion

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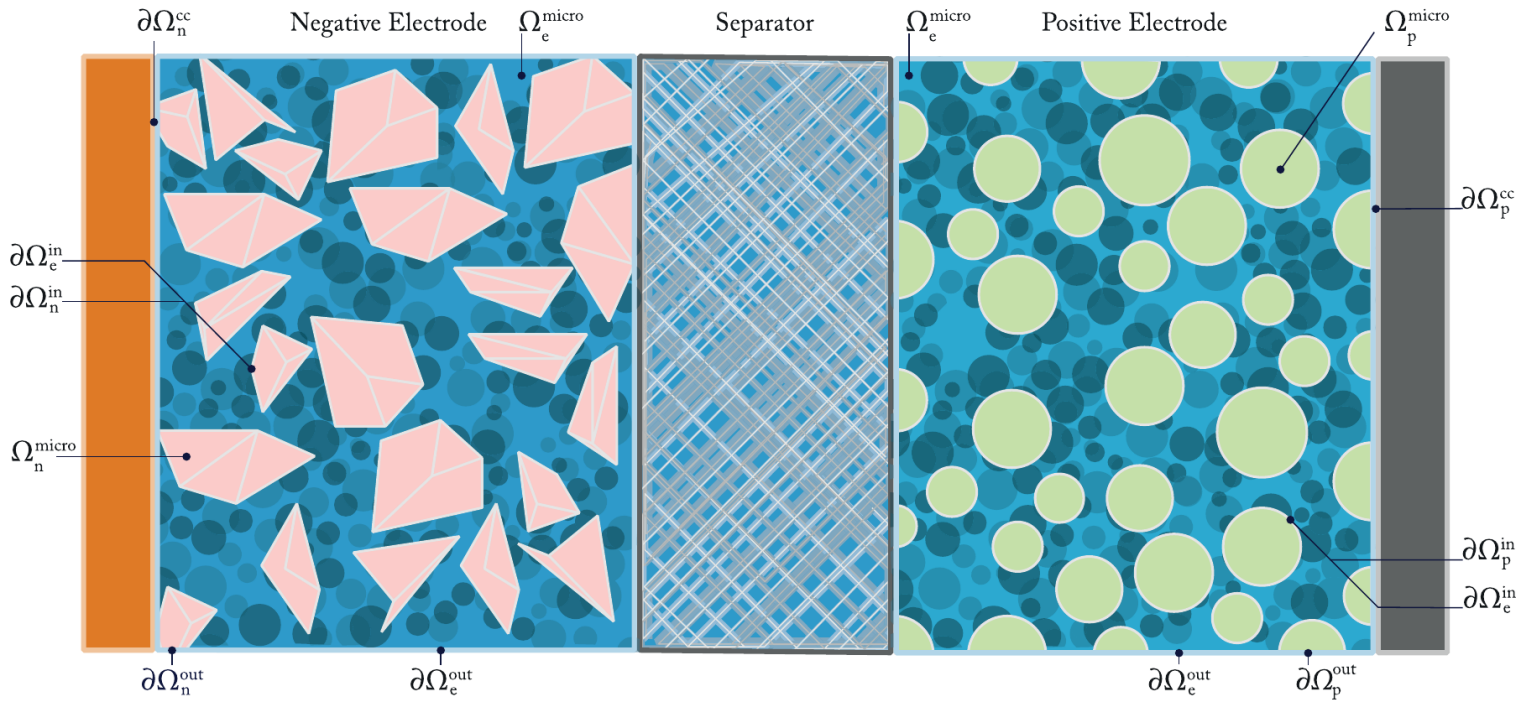
Multicomponent flows: motivating example



How to model chemical flow in liquid battery electrolytes?

- Multiple chemical species (e.g. EMC, EC, Li^+, PF_6^-).
- Each species has its own concentration and velocity field.
- Need to capture convection, diffusion and electrical effects.

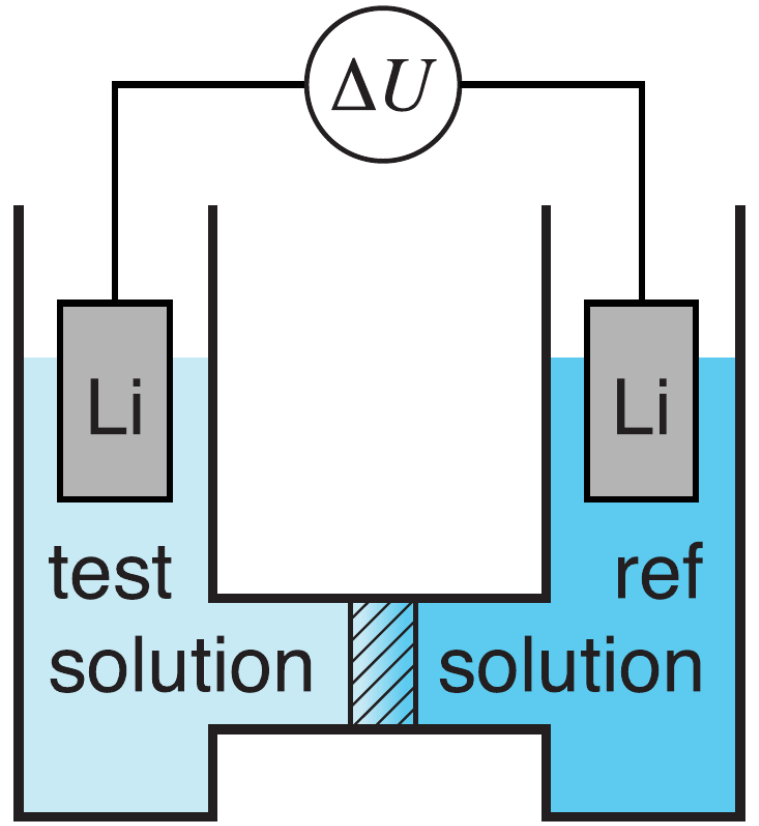
Image from *A continuum of physics-based lithium-ion battery models reviewed*, Brosa-Planella et al., 2022

Multicomponent flows: motivating example

Appreciable electrical potential, induced by a difference in the electrochemical potential of dissolved lithium cations, arises across a junction between two reservoirs of the same salt particle fraction but different EMC:EC ratios.

(...)

The portion of these overpotentials due to the solvent distribution is neglected by almost all state-of-the art P2D models.



Overpotential from cosolvent imbalance in battery electrolytes: $LiPF_6$ in EMC:EC, Jung et al., 2023.

Multicomponent flows

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  - Electrochemistry.
  - Combustion.
  - Separation processes.
  - Physiology.

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  - That diffusion and convection can be decoupled.

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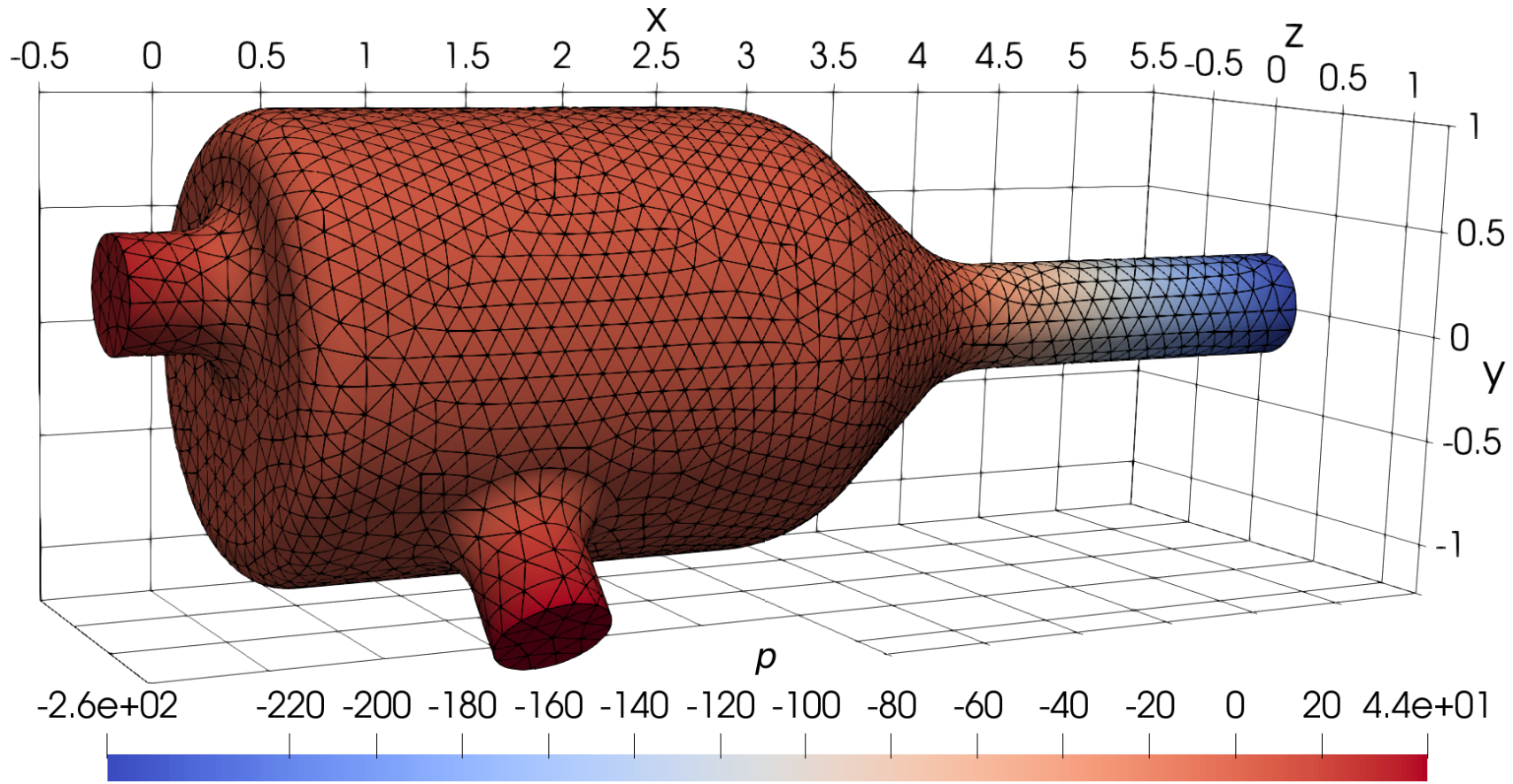
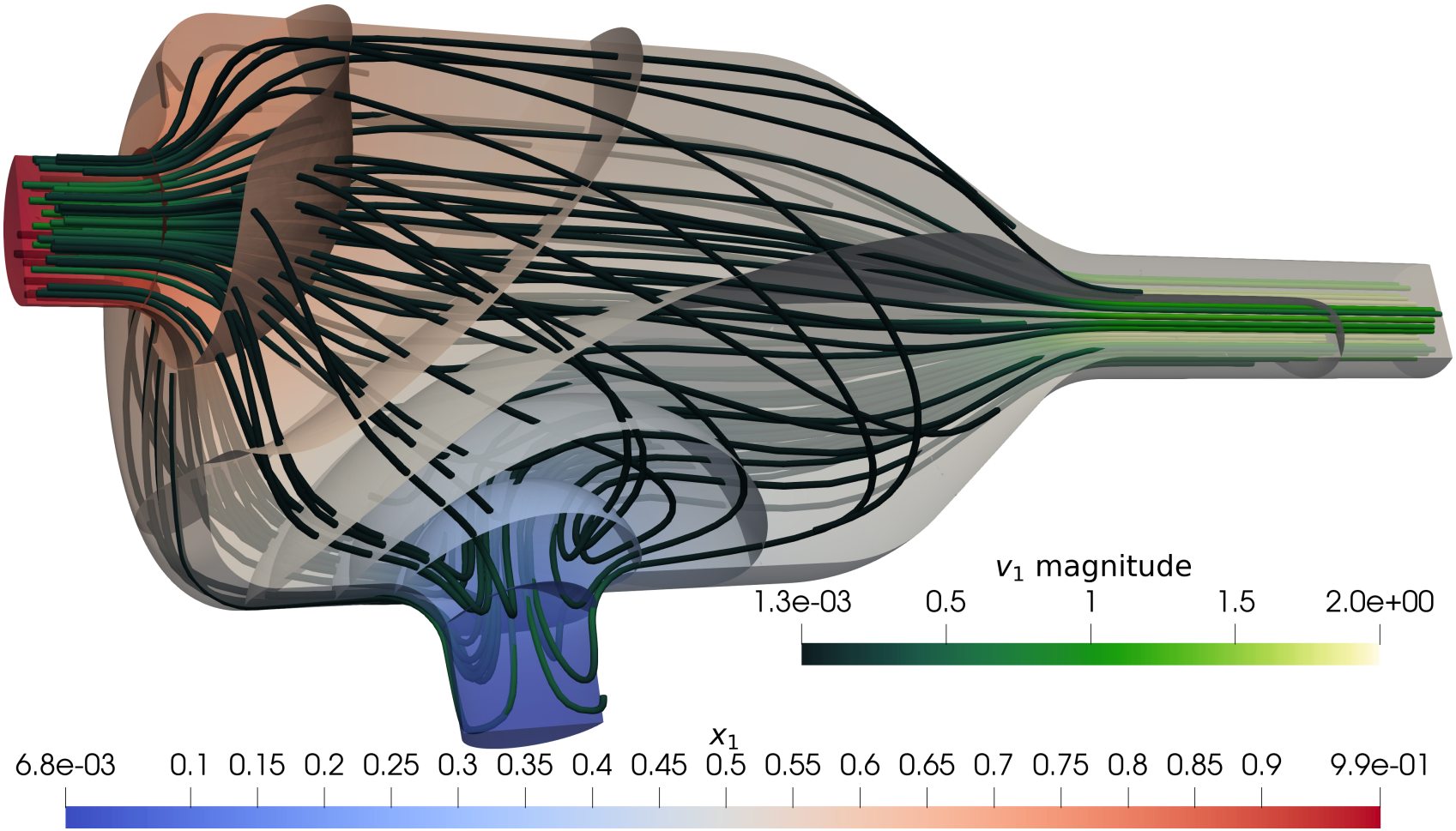
We devise finite element schemes that do not rely on these assumptions. Of particular interest: lithium-ion battery electrolyte modelling.

Example: mixing of benzene and cyclohexane



- Governing PDEs are discretized using order 5 finite elements.
- Discretized problem has 6 million unknowns – the need for efficient numerical methods quickly arises, especially in 3D.

Example: mixing of benzene and cyclohexane (cont'd)



Mole fraction x_1 of benzene and streamlines of its velocity v_1.

The numerical schemes

We derive, for the first time, FEM schemes for this model that are:

- High-order in space.
- Applicable on complicated three-dimensional spatial domains.
- Are provably convergent for a linearized version of the governing PDEs.

Modelling multicomponent diffusion

Suppose we have n chemical species labelled by $i \in \{1, \ldots, n\}$.

Modelling multicomponent diffusion

Suppose we have n chemical species labelled by $i \in \{1, \dots, n\}$. The **Onsager–Stefan–Maxwell (OSM) equations** express the *diffusional driving force* d_i acting on species i in two ways:

$$\underbrace{-c_i \nabla \mu_i}_{\substack{\text{thermodynamic} \\ \text{“forcing”}}} = d_i = \underbrace{RT \sum_{j=1}^{n} \frac{c_i c_j}{c_T \mathscr{D}_{ij}} (v_i - v_j)}_{\substack{\text{drag forces} \\ \text{due to relative motion}}} .$$

- c_i is the molar concentration of species i.
- $c_T = \sum_{i=1}^{n} c_i$ is the total concentration.
- μ_i is the (electro)chemical potential of species i.
- $\mathscr{D}_{ij}$ are diffusion coefficients.
- R the ideal gas constant and T the temperature.
- v_i is the velocity of species i.

Why OSM equations?

$$-c_i \nabla \mu_i = RT \sum_{j=1}^{n} \frac{c_i c_j}{c_T \mathscr{D}_{ij}} (v_i - v_j) \qquad \text{(OSM)}$$

$$c_i v_i = \underbrace{-z_i u_i F c_i \nabla \Phi}_{\text{migration}} - \underbrace{D_i \nabla c_i}_{\substack{\text{Fickian} \\ \text{diffusion}}} + \underbrace{c_i v_{\text{ref}}}_{\text{convection}} \qquad \text{(Nernst–Planck)}$$

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- Can be generalised to account for non-isobaric and non-isothermal effects.

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The mere notion of Φ is on shaky ground. We use μ_i instead!

The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities. It is therefore a conception which has no physical significance. (Guggenheim, 1929)

The consideration of the electrical potential in the electrolyte, and especially the consideration of the difference of potential in electrolyte and electrode, involve the consideration of quantities of which we have no apparent means of physical measurement. (Gibbs, 1899)

Modelling multicomponent convection

Convective flow of the chemical mixture is modelled using the so-called **mass-average velocity** v:

$$v := \sum_{j=1}^{n} \omega_j v_j \qquad \text{“mass-average constraint”}$$

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We assume that v satisfies the Cauchy momentum equation:

$$-\operatorname{div}\tau + \nabla p + \underbrace{\operatorname{div}(\rho v \otimes v)}_{\approx 0} = \rho f,$$

where τ is the *viscous stress tensor*. We use the usual Newtonian constitutive law to relate τ and the symmetric gradient of v.

The Stokes–Onsager–Stefan–Maxwell (SOSM) equations

Putting all of this together we get the (steady) **SOSM equations**:

$$-c_i \nabla \mu_i + \omega_i \nabla p = \sum_j \boldsymbol{M}_{ij}(v_j - v_i), \tag{1a}$$

$$-\operatorname{div} \tau + \nabla p = \rho f, \tag{1b}$$

$$\operatorname{div}(c_i v_i) = r_i, \tag{1c}$$

$$v = \sum_j \omega_j v_j. \tag{1d}$$

- An additional "thermodynamic constitutive law" must be supplied that algebraically relates the chemical potentials to temperature, pressure and composition.
- The thermodynamic framework of Van-Brunt et al. allows for the model to incorporate charged species and electroneutrality.

Structural electroneutrality in Onsager–Stefan–Maxwell transport with charged species, Van-Brunt et al., 2023.

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Finite element methods for multicomponent convection-diffusion, Aznaran et al., 2024.

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- Since there are so many unknowns, numerics will be expensive.

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A novel class of high-order discretizations

We have derived a large class of finite element schemes for the SOSM equations, through the following ideas:

1. Suitably rewrite the equations in terms of the $(2n+2)$ unknown fields $(v, p, \{J_i\}_{i=1}^n, \{\mu_i\}_{i=1}^n)$ where $J_i := M_i c_i v_i$ is the *mass-flux* of species i. Discretize these using high-order FEM spaces that satisfy certain stability conditions.

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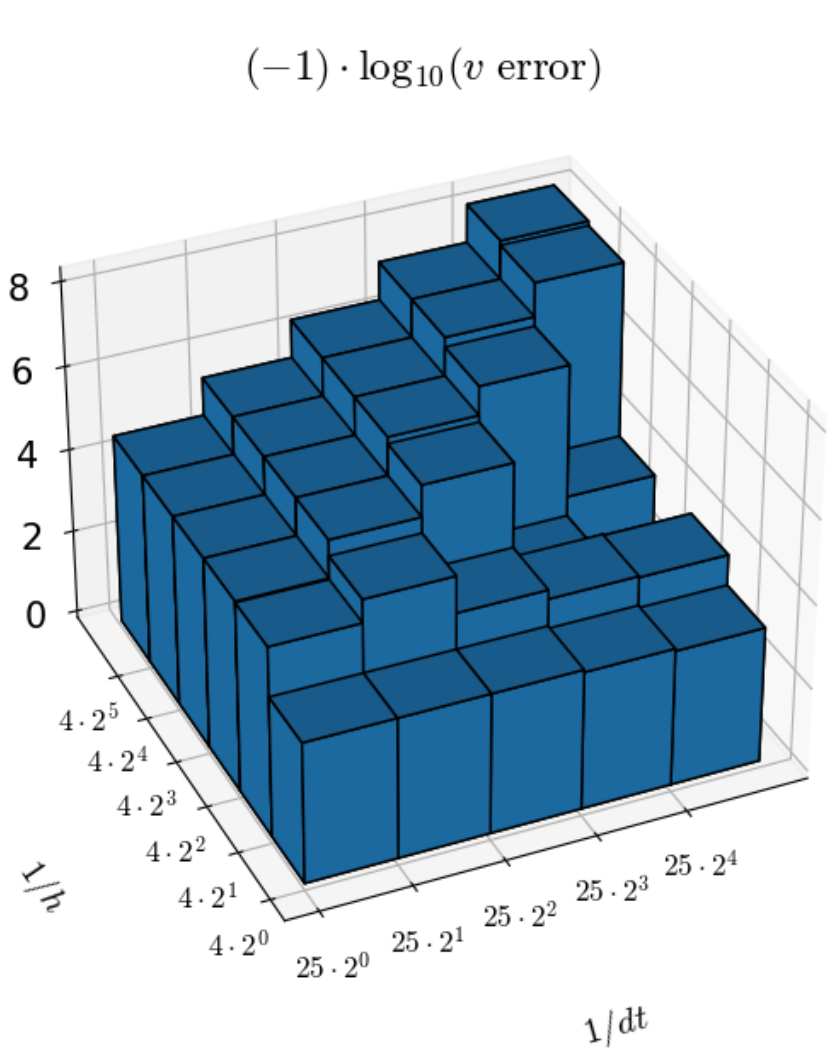
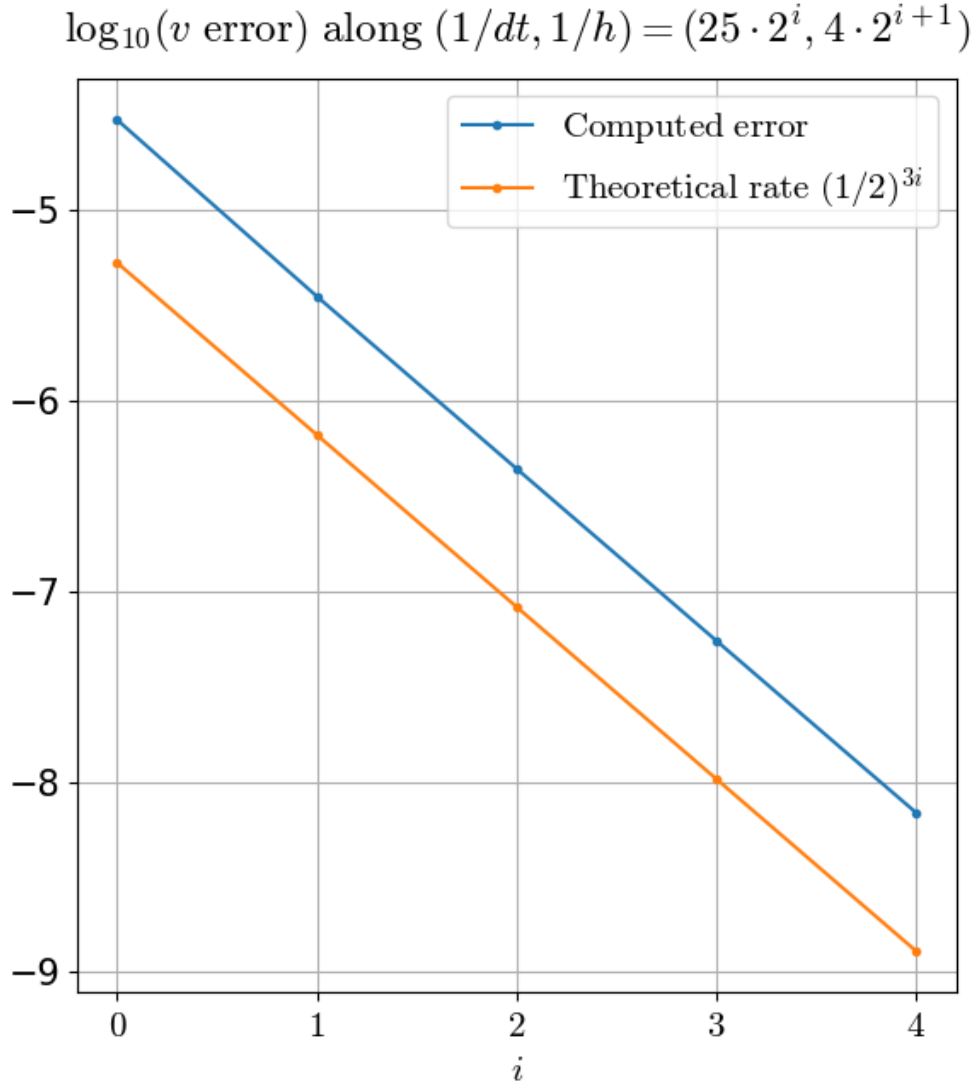
When applied to a Picard linearization of the SOSM problem, our schemes are *provably* convergent and quasi-optimal. The schemes are high-order, applicable in two and three spatial dimensions, and straightforward to implement.

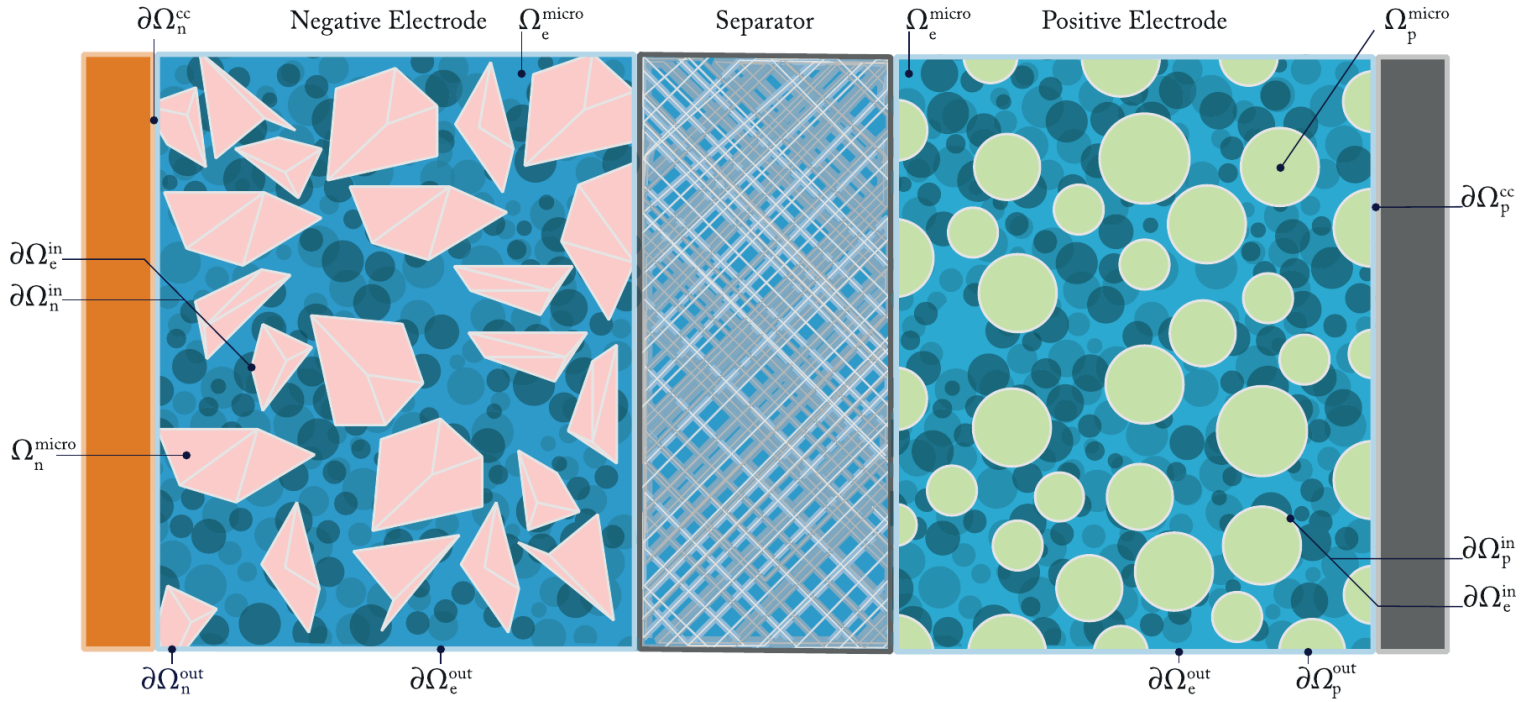
Time-stepping





For the transient problem we seem to need $\delta t \geq C \cdot h$ for stability, but only when coupling to Stokes!

Conclusions



See the manuscript on arXiv: *High-order finite element methods for three-dimensional multicomponent convection-diffusion*.

Next step is to simulate liquid battery electrolytes.

- Capturing the complex geometry may be a challenge.
- The number of parameters is $\mathcal{O}(n^2)$. E.g. for $n = 4$ there are 12 parameters. Can use experimental measurements, or solve inverse problems.