Electroneutrality in Onsager–Stefan–Maxwell models with charged species

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Isobaric, isothermal, reaction-free OSM + continuity equations

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\begin{aligned}
-\nabla \mu_i &= \sum_{j=1}^{n} \mathbf{M}_{ij} \mathbf{N}_j, \quad && i = 1, \dots, n, \\
\partial_t c_i &= -\nabla \cdot \mathbf{N}_i, && i = 1, \dots, n,
\end{aligned}
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- n is the number of species;
- μ_i and c_i are the electrochemical potential and molarity of species i;
- $\mathbf{M}$ is the (symmetric positive semidefinite) Onsager transport matrix;
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The equations are closed …

…with a convective velocity and thermodynamic constitutive laws.

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Challenge

How do we reconcile this constraint/equation with the Onsager–Stefan–Maxwell equations?

Newman et al., through careful/complicated manipulation, worked out

- ✓ binary electrolytes (e.g. $LiPF_6$ in ethyl methyl carbonate),
- ✓ molten salts that share a common ion (e.g. Li_2CO_3 and K_2CO_3).

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But this manual approach is cumbersome: not yet carried out for important systems like

- ✗ electrolytes with cosolvents (e.g. what's used in lithium ion batteries);
- ✗ electrolytes with additives, contaminants, or products of side reactions;
- ✗ flow batteries (e.g. vanadium flow battery, 8 distinct species);
- ✗ Nafion membranes with cation contaminants (H^+, ${SO_3}^-$, H_2O, Fe^{3+}) for hydrogen electrolysers and fuel cells.

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This talk

A general, elegant formulation, using linear algebra.

Section 2

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This idea dates back at least to Guggenheim in 1928; we merely systematise it and phrase it in the language of linear algebra.

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We postulate a minimal set of $n - 1$ independent hypothetical equilibrium reactions:

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\mathrm{H_2O} &\leftrightharpoons \mathrm{H_2O} \\
\mathrm{Na^+} + \mathrm{Cl^-} &\leftrightharpoons \mathrm{NaCl} \\
\mathrm{Mg^{2+}} + 2\mathrm{Cl^-} &\leftrightharpoons \mathrm{MgCl_2} \\
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The choice of reactions is not unique, but any neutral component not defined can always be recovered from those chosen, e.g. the last possible binary salt $MgSO_4$:

$$\mathrm{MgCl_2} + \mathrm{Na_2SO_4} \leftrightharpoons 2\mathrm{NaCl} + \mathrm{MgSO_4}.$$

In a matrix with n rows (species) and $n-1$ columns (equilibria), tabulate the stoichiometric coefficients:

$$\begin{aligned}
\mathrm{H_2O} &\leftrightharpoons \mathrm{H_2O} && \text{①}\\
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Call the columns $\boldsymbol{\nu}_i$, $i = 1, \ldots, n-1$.

If we define the species charges

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Since the stoichiometric coefficients are linearly independent by construction,

$$\{\boldsymbol{\nu}_1, \ldots, \boldsymbol{\nu}_{n-1}, \mathbf{z}\}$$

forms a basis for the entire n-dimensional composition space.

Encoding our basis in the transformation matrix

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The last entry μ_z encodes a solution voltage (the *salt-charge potential*).

Everything else follows by *thermodynamic structure preservation*.

The Euler equation defines volumetric Gibbs free energy $\tilde{G}$:

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$$c_z = \frac{\rho_e}{F\|\mathbf{z}\|} = 0 \text{ under electroneutrality.}$$

Applying the same principle to the dissipation function

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and expanding this shows that the last component is a renormalised current:

$$(\mathbf{N}_{\mathbf{Z}})_n = \frac{\vec{i}}{F\|\mathbf{z}\|}.$$

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The spectral structure of the Onsager transport matrix $\mathbf{M}$ is crucial for numerics.
Conveniently, the salt-charge transport matrix

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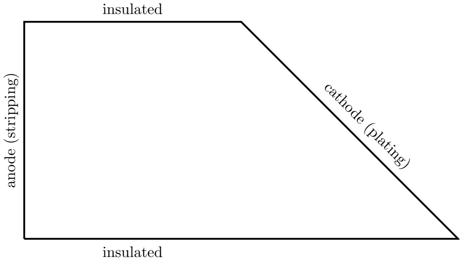
The thermodynamic constitutive relations between $\mathbf{c}_{\mathbf{Z}}$ and $\boldsymbol{\mu}_{\mathbf{Z}}$ also transform in a nice way.

Section 3

Example

We consider $LiPF_6$ in ethyl methyl carbonate and ethylene carbonate, with independent equilibrium reactions

$$\mathrm{EMC} \leftrightharpoons \mathrm{EMC}, \quad \mathrm{EC} \leftrightharpoons \mathrm{EC}, \quad \mathrm{Li}^{+} + \mathrm{PF_6}^{-} \leftrightharpoons \mathrm{LiPF_6}.$$



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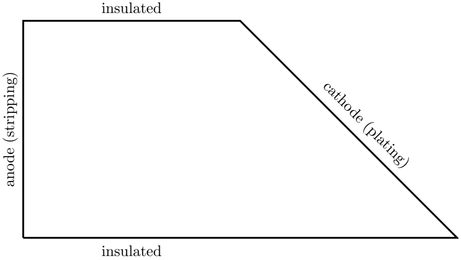

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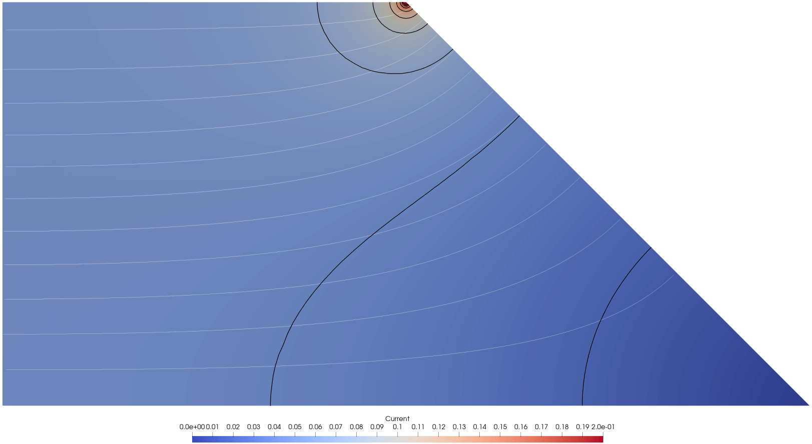
We (mostly) fit ionic conductivity, Stefan–Maxwell diffusivity, Darken factor, cation transference number, and density from experimental data reported by Wang et al.

Example



The current concentrates at the upper corner because it is closer to the anode.

Section 4

Conclusions

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A major obstacle is that experiments to measure the composition-dependent thermodynamic properties are expensive and slow.