Update on Electrolyte Modeling with Emphasis on Low Temperature Performance

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This presentation does not contain proprietary or confidential information

Scope

Purpose

To gain further understanding of how performance of Li-ion batteries depends on molecular-scale behavior of electrolytes at cycling conditions, particularly at low temperatures. This is done to identify failure mechanisms related to the battery electrolyte.

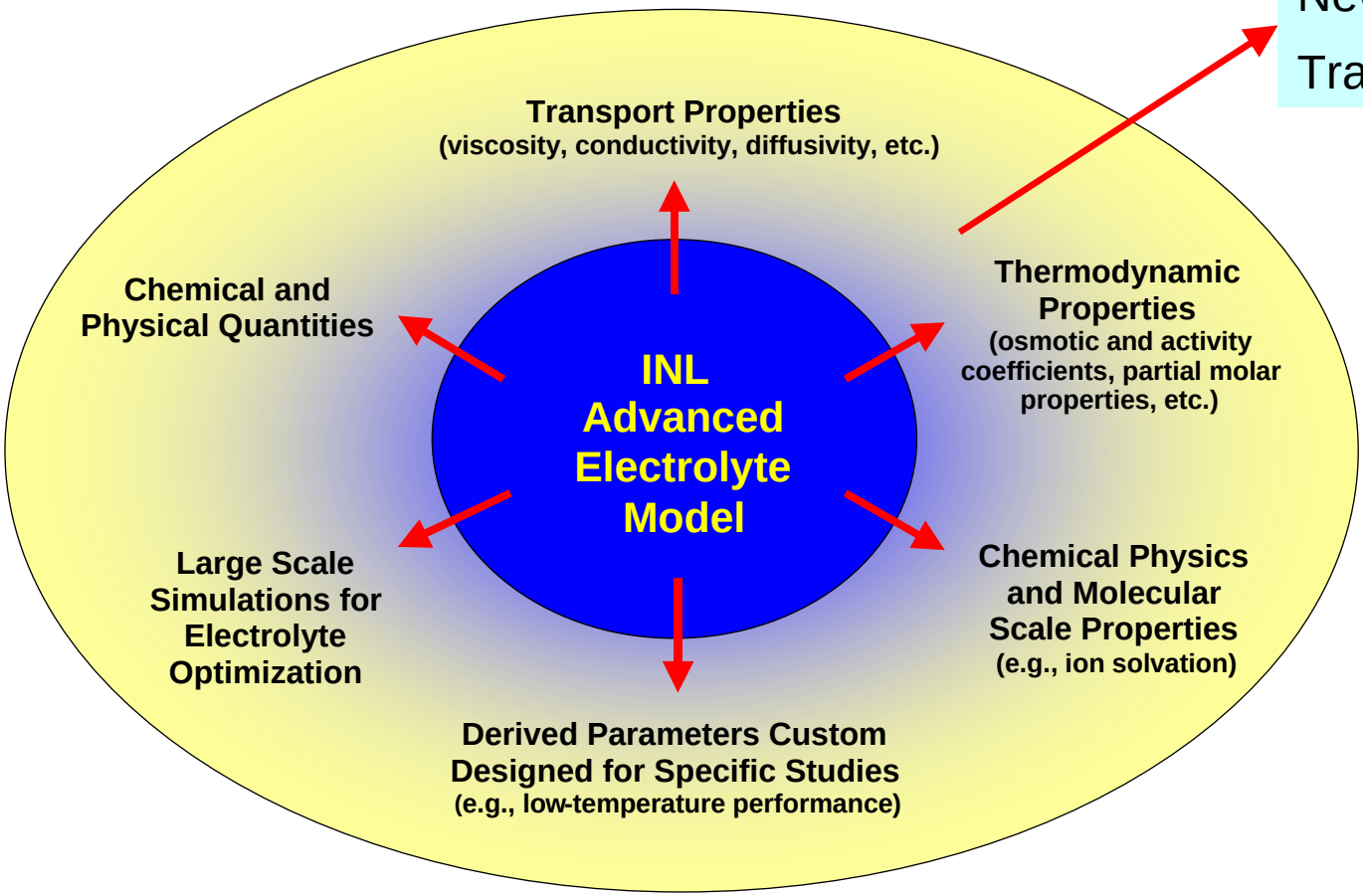
Barriers

Li-ion batteries generally undergo a marked decrease in performance at low temperatures, and the root causes have been difficult to pinpoint using conventional methods. This performance limitation prevents this technology from being fully deployed in HEV/PHEV applications for cold climate scenarios.

Approach

This work is based on the capabilities of the Advanced Electrolyte Model (AEM), developed under the DOE-ATD program. Foundations of the AEM include molecular-scale chemical physics, ion solvation, and accurate thermodynamics. The AEM delivers state-of-the-art predictions of numerous key properties useful for electrolyte characterization, screening, optimization, and transport modeling.

Summary of AEM Capabilities



New in 2007: used in Transport Modeling

Key properties are generally predicted to within 5-10 % of experimental values over wide ranges of T and composition.

Many predictions reach agreement to within 5 percent or less.

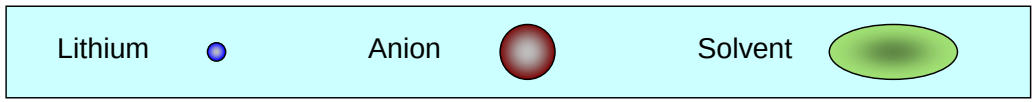
In concert, these elements provide a sound basis for electrolyte characterization, screening and optimization for numerous applications.

Technical Milestones in 2007

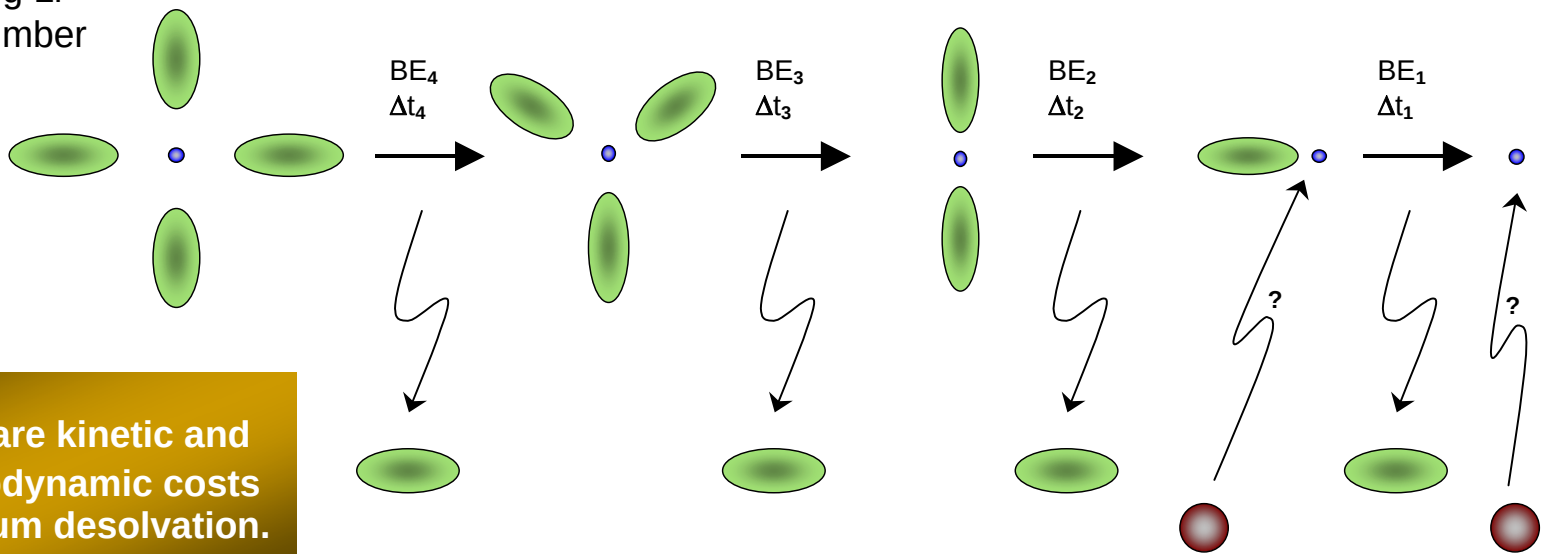
1. Developed self-consistent method for determination of net and ligand-wise lithium ion desolvation time and energy
2. Developed framework for modeling binary salt systems
3. Modeled electrolytes having a fluorinated solvent (mFEC)
4. Developed infrastructure for applying the AEM to cell-level transport modeling (e.g., double layer (DL) and separator regions)
5. Developed the theoretical framework for predicting how pulse conditions alter the effective transport properties of electrolyte species (ionic conductance, transference number, etc.)
6. Investigated how separator porosity affects colligative properties of the electrolyte during a pulse.

Lithium Desolvation
- *general process* -

Lithium desolvation involves the breaking of successive solvent-Li^+ ligands, resulting in ligand-specific binding energies and desolvation times.



For a starting Li^+ solvation number of four:



∴ **There are kinetic and thermodynamic costs to lithium desolvation.**

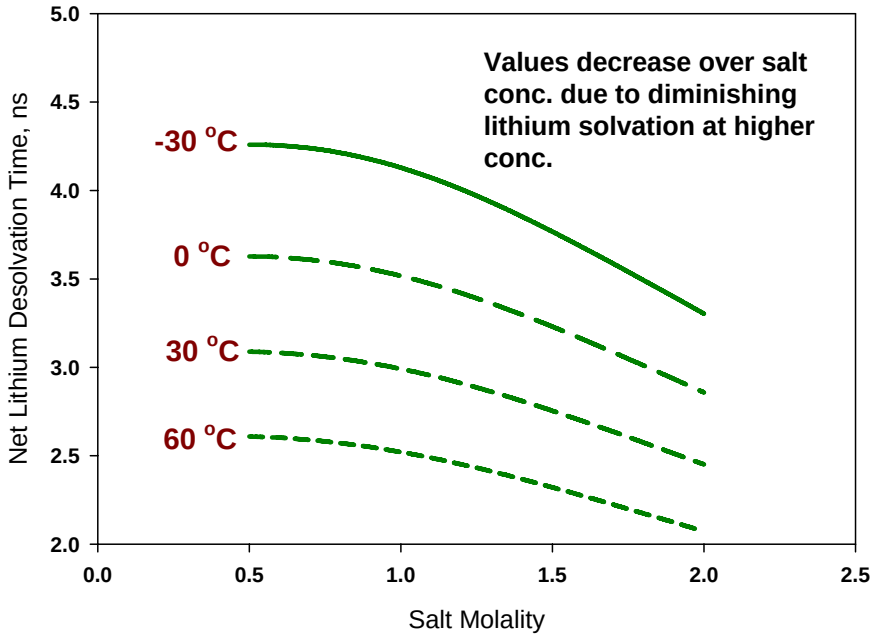
Net Energy Barrier = ΣBE_i , where $BE_4 < BE_3 < BE_2 < BE_1$

Net Desolation Time = $\Sigma \Delta t_i$, where $\Delta t_4 < \Delta t_3 < \Delta t_2 < \Delta t_1$

Is Li^+ more susceptible to forming ion pairs as it becomes desolvated? Yes, if counter-transport of the anion is hampered by poor mass transport conditions (e.g., low temperature). This could further impact performance.

Lithium Desolvation
- *sample results from AEM* -

Net Time Required for Step-wise Lithium Desolvation
Gen2 Electrolyte EC:EMC (3:7) + 1.2M $LiPF_6$
(Chemical Kinetics Basis = 1st Order)



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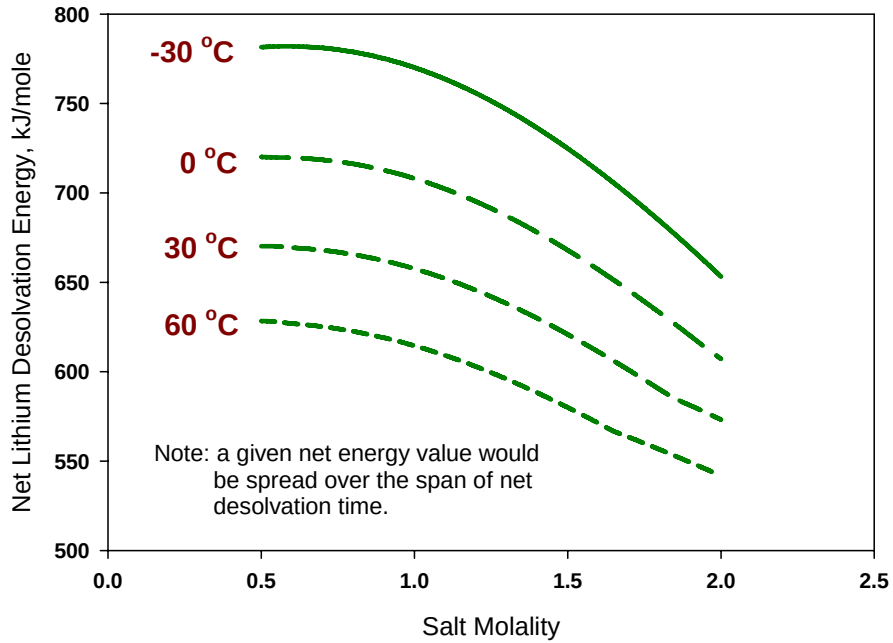
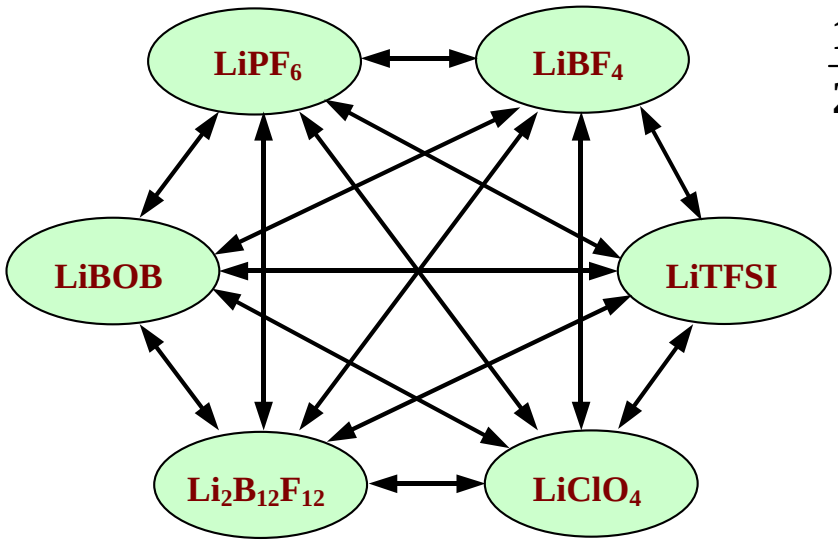


Li^+ desolvation time and energy show similar trends over temperature and salt concentration, although they are obtained independently. These results indicate that *step-wise lithium desolvation becomes more problematic at low temperatures and lower salt concentrations.*

Mixed-Salt Electrolytes
- *new modeling capability* -

Benefits in transport properties and SEI formation can be realized by using mixed salt electrolytes, just as mixed solvents are seen as necessary for contemporary electrolyte systems.

The AEM now has the capability to characterize and optimize mixed-salt (binary), multi-solvent electrolytes. Taking six of the salts from the AEM library:



$$\frac{1}{2}\left(n(n-1)\right) = 15 \text{ pair combinations}$$

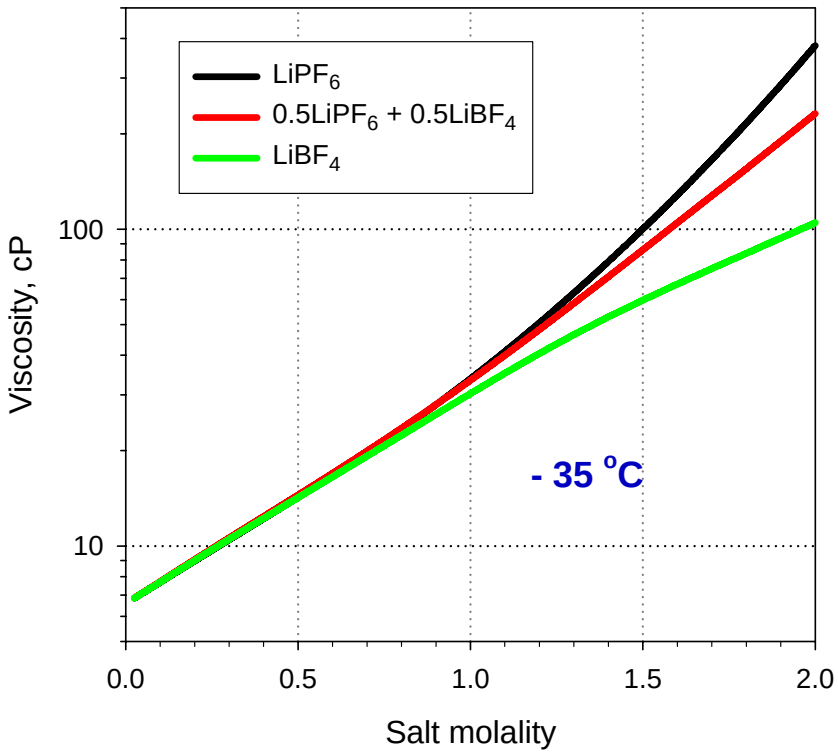
The approach is based on molar averaging of key molecular-scale quantities.

This new capability opens up a new frontier in electrolyte development and screening.

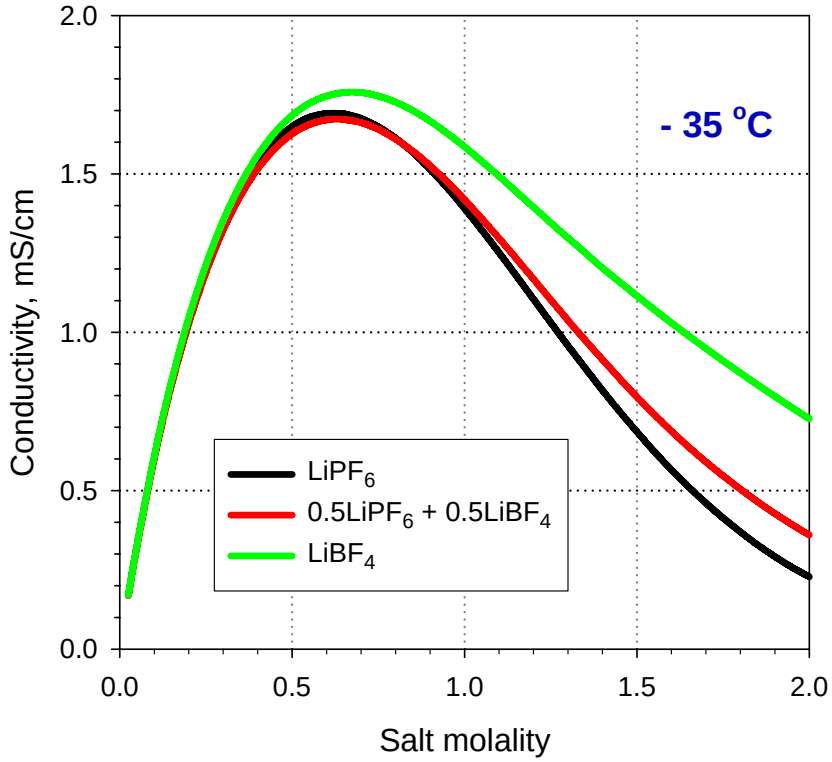
Mixed-Salt Electrolytes
- *sample results from AEM* -

Comparison of Single and Mixed-Salt Electrolytes (Solvent = GBL)

Viscosity Comparison (log scale)



Conductivity Comparison



Lithium Desolvation

- mono-fluoroEC vs EC Systems -

System	Lithium Solvation Number	Solvent-Lithium Binding Energy (kJ/mole)	Activation Energy for lithium desolvation (kJ/mole)	Net Lithium Desolvation Time (ns)
EC + 1 M $LiPF_6$	3.90	477.5	30.0	1.6
mFEC + 1 M $LiPF_6$	3.43	426.0	24.5	1.0
Difference	-12.0%	-10.8%	-18.3%	-37.5%

These AEM results at 30 °C clearly show an advantage using mFEC regarding lithium solvation quantities. Such advantages will impact charge transfer resistances at critical interfacial regions. In practice, mFEC would be added in small amounts (5-20%) to conventional electrolytes.

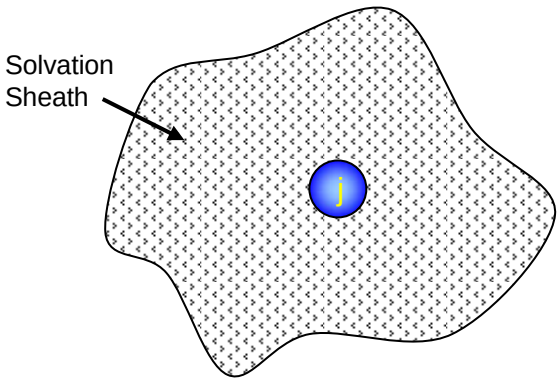
Transport Modeling of Electrolytes

The AEM accounts for:

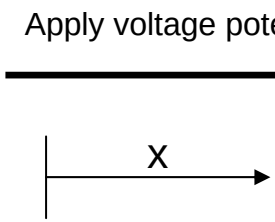
- Continuity expressions for all mobile species in a given electrolyte (single cations and anions, solvent, ion pairs, and triple ions (ABA,BAB)) over (x,t).
- Diffusion of all electrolyte species,
- Diffusion potential,
- The effects of ion solvation on solvent co-transport, and how this changes with species velocities,
- Explicit consideration of intrinsic lithium desolvation kinetics,
- Electrolyte properties for conditions of non-electroneutrality,
- Limiting packing fractions of electrolyte species,
- Considers a fine matrix of spatial dimension in x versus pulse time,
- Calculates current, resistance, net charge delivered, etc. over (x,t).
- Pulse type:
  - constant potential or constant current
  - charge or discharge
  - duration and magnitude.
- *And More*

Faradaic transport of ions results in alterations to their solvation environment, which will affect key transport properties linked to battery performance.

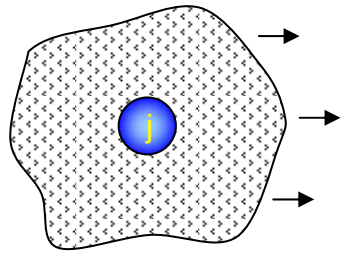
At thermodynamic equilibrium



Apply voltage potential



Under pulse conditions



Solvation region around ion is at maximum value, and

$$v_{j,x} = v^{o}_{j,x} = 0$$
$$n_{s,j} = n^{o}_{s,j}$$
$$\lambda_j = \lambda^{o}_j$$
$$t_j = t^{o}_j$$

The AEM determines the shift in transport properties due to the Faradaic transport of all charged species.

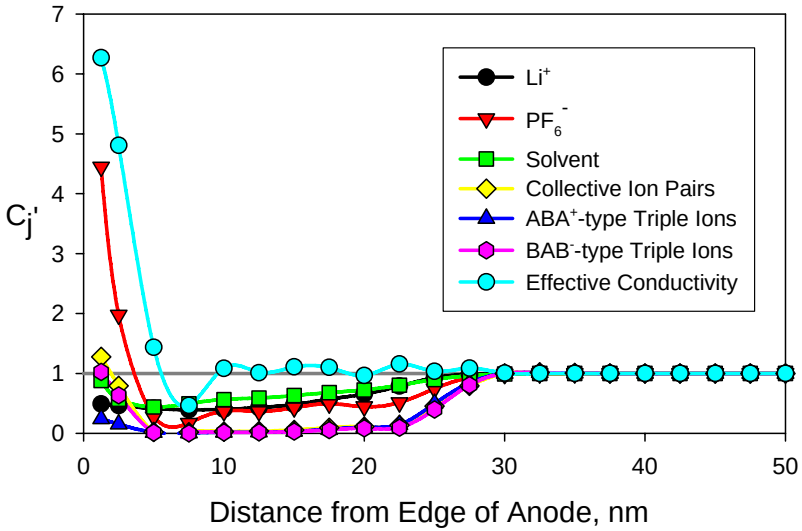
Solvation region diminishes under transport conditions, and

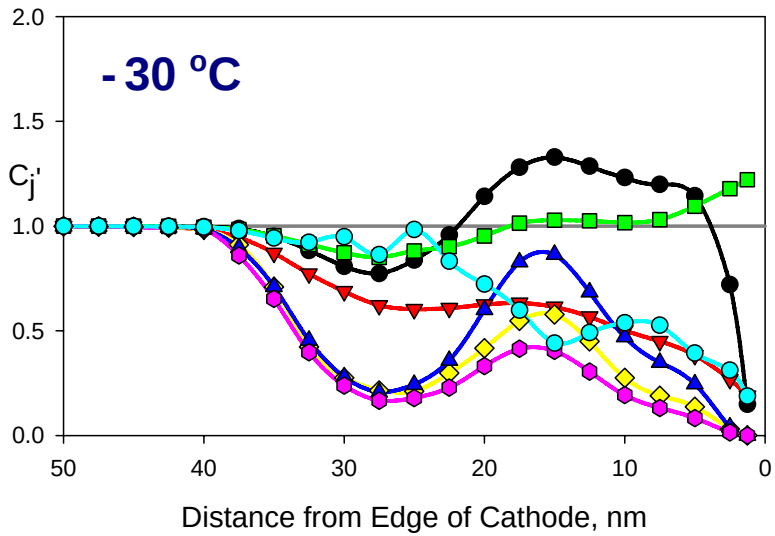
$$v_{j,x} = v^{eff}_{j,x} \neq v^{o}_{j,x}$$
$$n_{s,j} = n^{eff}_{s,j} \neq n^{o}_{s,j}$$
$$\lambda_j = \lambda^{eff}_j \neq \lambda^{o}_j$$
$$t_j = t^{eff}_j \neq t^{o}_j$$

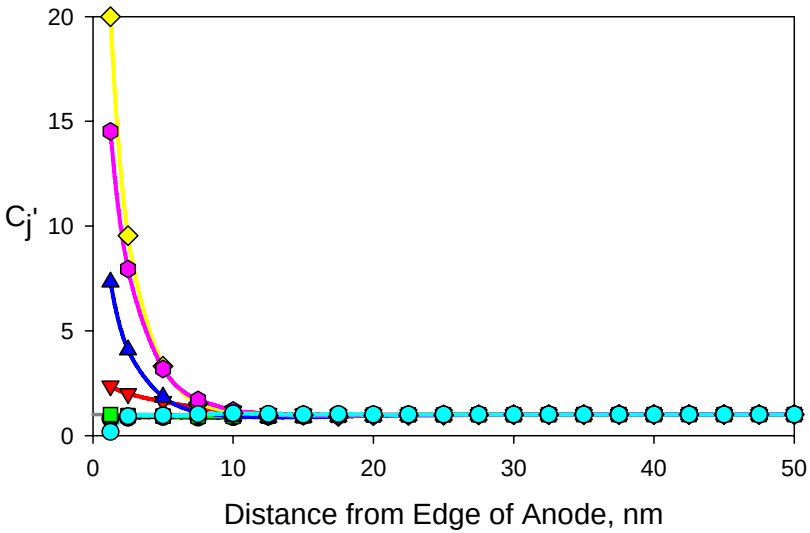
Concentration Profiles (normalized to time zero values)

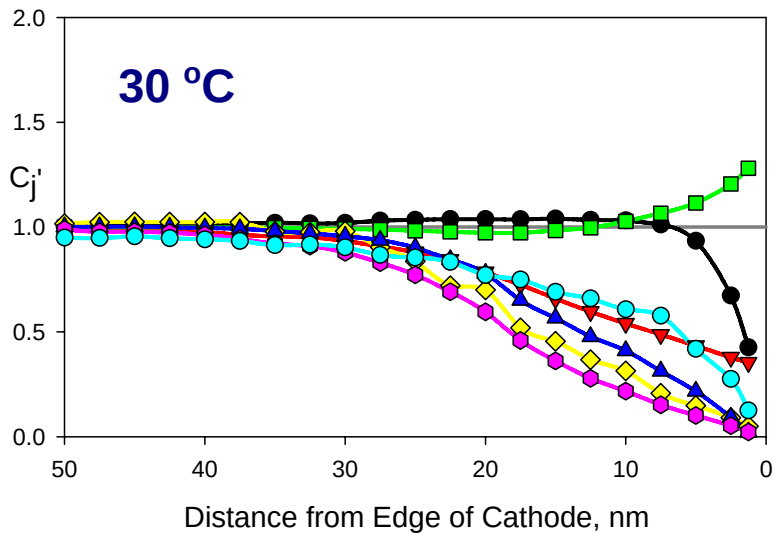
After 1-second Constant Current Discharge Pulse (0.1 mA/cm^2)

Results for Gen2 Chemistry, Electrolyte = EC:EMC (3:7) + 1.2M $LiPF_6$

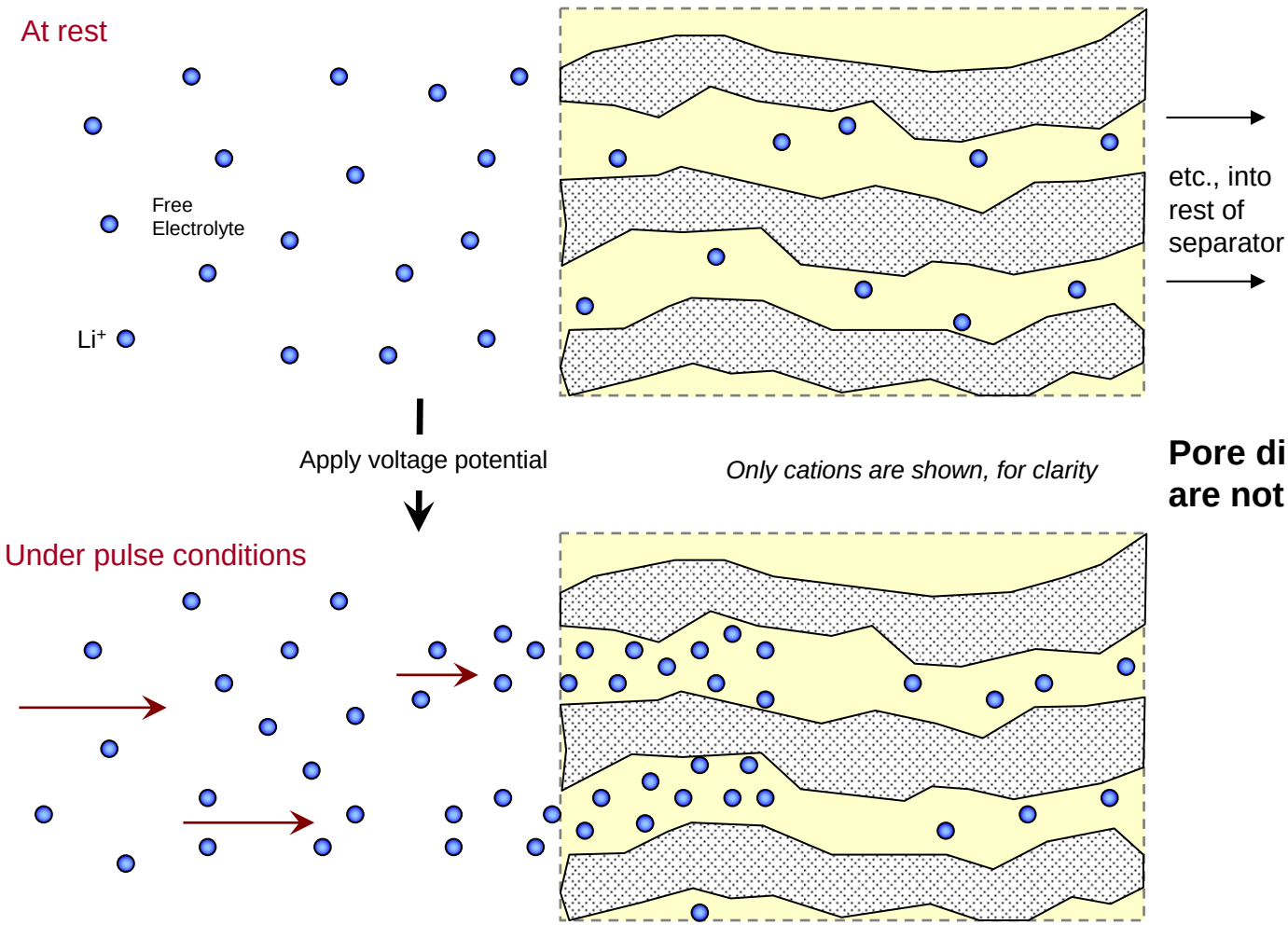








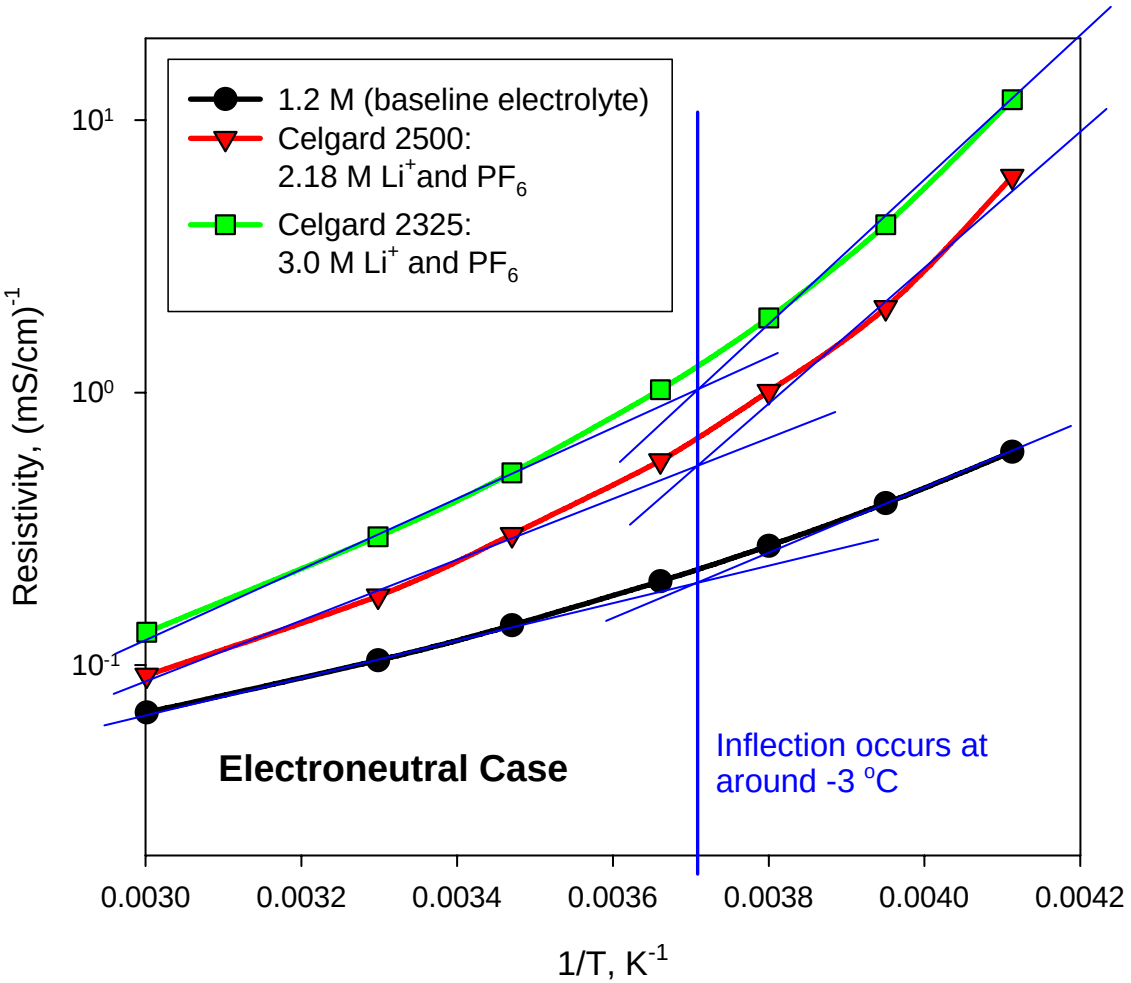
Looking at a small cross-section at one face of the separator



Upon starting a pulse, there is an enrichment of ions along the face of the separator as the ion flux from the free electrolyte region enters the separator an encounters a restricted volume. The result is a funneling or bottleneck effect that increases the local concentration of ions, *which will have a profound effect on local properties such as viscosity and conductivity.*

Electrolyte Properties In Separator, per AEM

Gen2 Electrolyte Resistivity for Enrichment of *Bulk Salt* at Separator Edge at Start of Discharge



Gen2 Electrolyte:

EC:EMC (3:7) + 1.2M $LiPF_6$

Separators Studied:

Celgard 2500 (P = 0.55)
Celgard 2325 (P = 0.40)

Lower porosity separators result in higher electrolyte resistivity at their faces.

Note that electrolyte phase transitions are more likely at the higher molarities at low T.

Summary / Conclusions

1. Li-ion desolvation is a process whose kinetics and thermodynamics is modeled by the AEM and utilized in transport calculations.
2. In addition to mixed solvent systems, the AEM can now model mixed salts and was extended to include fluorinated solvents, which will allow many contemporary electrolytes to be screened and characterized.
3. The AEM transport model accounts for how ionic and bulk electrolyte properties are altered due to the effective ionic migration under the pulse conditions. More severe pulse conditions will intensify this effect.
4. It appears Faradaic co-transport of solvent with ions becomes more problematic for cell performance at low temperatures due to more stable Li^+-solvent interactions, slower Li^+ desolvation kinetics, and lowered solvent diffusivity.
5. Modeling of electrolyte properties in lower-porosity separators confirmed that high local impedance can exist at low T, due to ionic flux limitations and non-electroneutrality that can emerge at the separator faces. Higher-porosity separators can alleviate part of such limitations.
6. Thus, the AEM provides an advantage in that it produces accurate local electrolyte properties, spanning between the electrodes, without the need for oversimplifying assumptions that can render invisible the true root causes of performance limitations tied to the electrolyte.

Future Work

- Continue modeling novel candidate electrolytes of interest to ATD (e.g., explore mixed-salt systems and fluorinated solvents of potential benefit to ATD).
- Investigate the role of porosity and tortuosity within interfacial regions as it pertains to SEIs, double-layers, and the separator.
- Provide results and conclusions from AEM transport model for relevant test chemistries.
- Perform experiments that will confirm root causes of diminished cell performance at low temperatures, e.g., separator experiments.
- Publish.

Other

Response to Previous Review Comments

The previous merit review of this work occurred in FY 06. Relevant comments that followed the intent and scope of the work were considered and adopted as feasible (e. g., determine root causes, model transport at the interface).

Technology Transfer

DOE-ATD meetings provide some level of technology transfer between participants. AEM capabilities have served the private sector through the INL work-for-others program and ATD-relevant collaborations. Publication of this work will also serve as a technology transfer mechanism.

Publications / Patents / Presentations

Several peer-reviewed manuscripts are planned for this work, with some under preparation.

Presentations:

K. L. Gering, *Modeling the Thermodynamic and Kinetic Costs of Lithium Ion Desolvation*, ECS 2007 Fall Meeting.

K. L. Gering, *Molecular-Based Modeling of the Thermodynamic and Kinetic Costs of Ion Desolvation (Regarding The Commercial Application Of Lithium-Ion Batteries)*, AIChE 2007 Fall Meeting.

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Supplemental Information

This material will not be presented

For Reviewer Reference Only

AEM Approach and Overview