Battery Modelling with Cantera: Flexible and Robust Incorporation of Electrochemical Complexity

Earth • Energy • Environment — Colorado School of Mines

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https://github.com/decaluwe/OBMS_materials

CORES Research Group
Reacting Flows – Electrochemistry – Surface Science

cores-research.mines.edu

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Outline

- The Case for electrochemical complexity
- Cantera: object-oriented, generalized chemical kinetics software
- Case study: Tabulated thermodynamics of lithium intercalation
- Case study: Intermediate polysulfide chemistry in Li-S
- Case study: Detailed chemistry of SEI growth and evolution
- Concluding remarks: Future directions and community input

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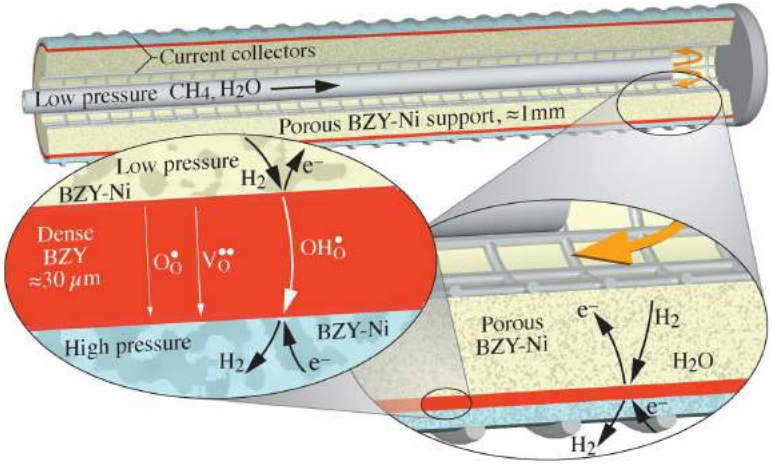
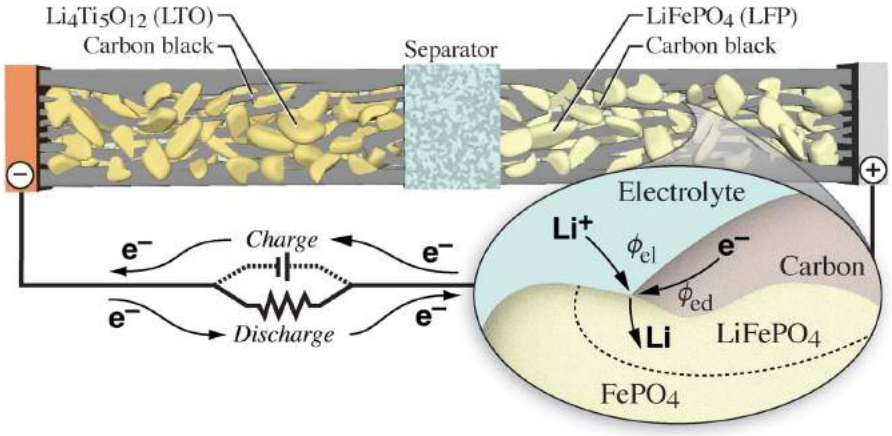
- **Next steps: Future development, community input**

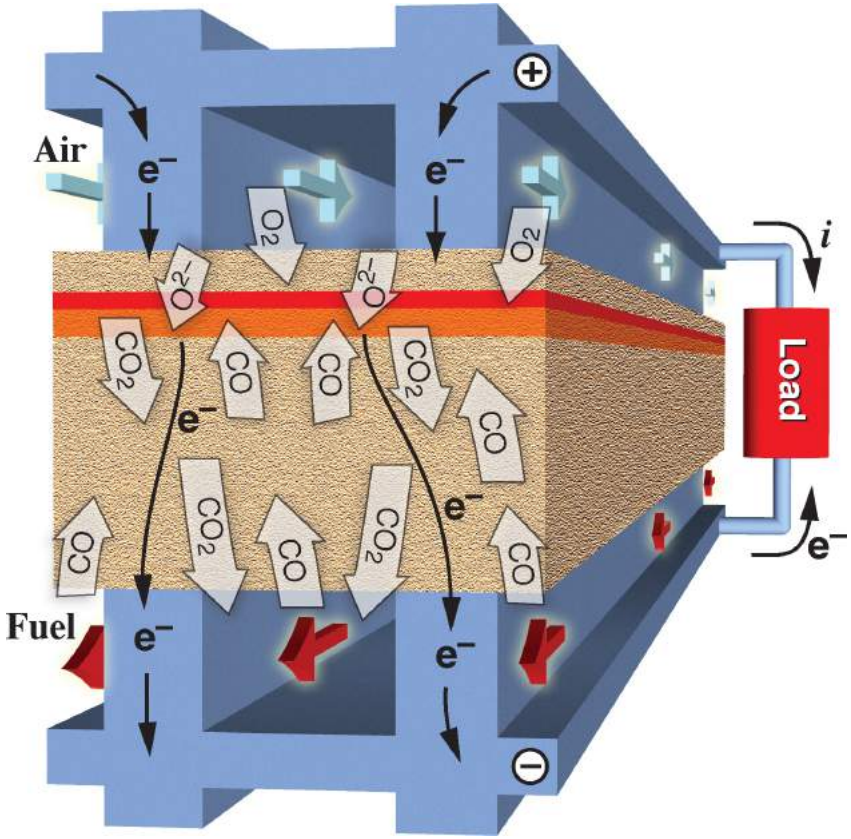
Thermo-chemical complexity is common throughout electrochemical applications



Multiple charge carriers in protonic ceramics



Phase-change thermodynamics in LFP cathode



Catalytic reforming in SOFC anode

Figures courtesy Robert J. Kee, CSM

See also: DeCaluwe, et al., J. Electrochem. Soc., 165 (2018)

Current electrochemical and battery models under-represent electrochemical complexity

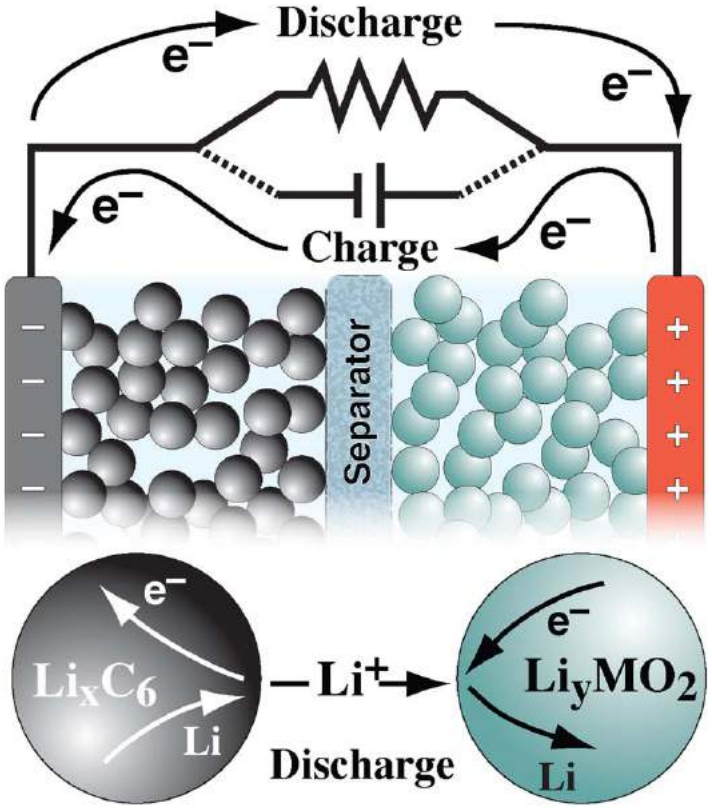
"Complex" mechanisms commonly limited to a handful of species, reactions.

- **Generally okay for intercalation**
- **Covers "standard" operation**
- **Poorly suited for degradation, new materials, solution-phase processes.**

Barriers to complex battery models:

- **Rapidly evolving material sets**
- **Lack of physical validation data**
- **No commonly adopted software tool sets**
- **Norms for software valuation not fully developed.**

See also: DeCaluwe, S.C. "Open Software for Chemical and Electrochemical Modeling: Opportunities and Challenges" *ECS Interface,* Spring 2019.



DeCaluwe, et al., J. Electrochem. Soc., 165 (2018)

Incorporating electro-chemical complexity requires robust, flexible software tools.

Modelling electro-chemical complexity at the continuum level yields important insights:

- **Guide device design**
- **Identify operation and control strategies**
- **Feedback for materials design and selection**

Each new species, process, or reaction requires handling new parameters:

- **Phase behaviors: *p-v-T***
- **Species thermodynamics**
- **Kinetic rate constants**
- **Transport parameters**

New phenomena change the dimensions of model equations and data structures (solution vectors, stoichiometric coefficient matrices, etc.).

Managing inter-dependent physical parameters (e.g., thermodynamic consistency) can also pose challenges.

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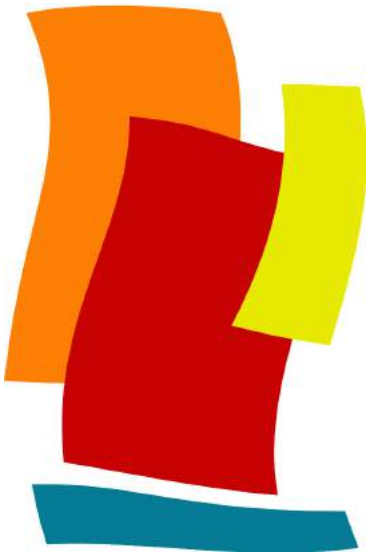
Cantera offers an object-oriented framework to model thermodynamics, kinetics, transport



Cantera

- Thermodynamics
- Chemical kinetics
- Transport

Cantera objects/classes represent:

- **Phases of matter (solids, liquids, vapors, interfaces).**
- **Functions to calculate properties and processes.**
- **Selected applications relevant to combustion**

Object-oriented code:

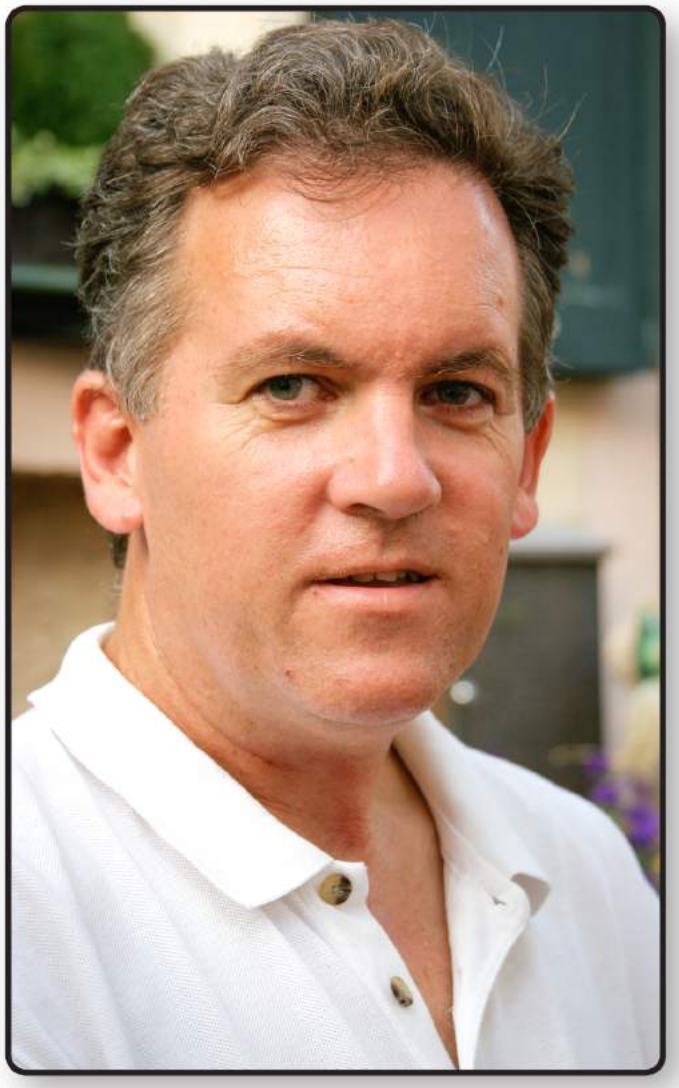
- **Easily extensible**
- **Flexible**
- **Significant learning curve**

Cantera is designed for incorporating:

- **Community-developed input files and property databases.**
- **User-developed simulations and CFD code,**
- **Thermodynamic and kinetic information from atomistic simulations**

Cantera library is vetted by active user & developer communities, to automate and generalize calculations.

Dave Goodwin conceived Cantera and began software implementation around 1998



Dave Goodwin (1957-2012)

Logical extension of CHEMKIN
- Modern object-oriented structure
- Written in C++
- Higher-level interfaces (Python, MATLAB,…)
- New physics and chemistry

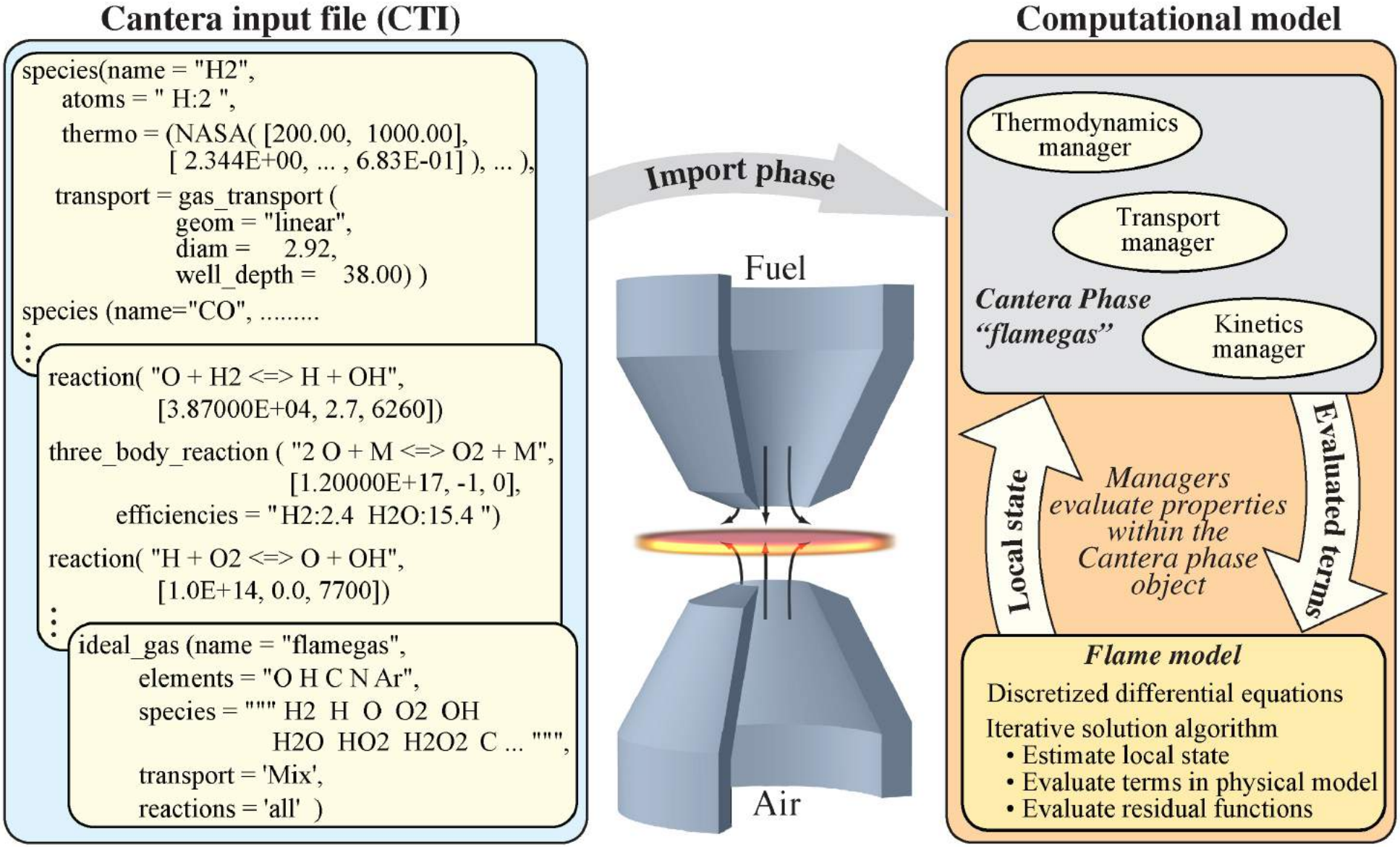
"Cantera" means a quarry of building blocks
- Molecules built from atoms
- Reactions built from molecules
- Processes built from reactions

Strong conceptual foundation
- Ongoing development retains basic structure

Early work supported by
- NSF/DARPA; Intelligent Materials Processing
- ONR/MURI: Solid-oxide fuel cells

Always intended to be open source
- A vibrant user/developer community is growing

Cantera's object-oriented architecture enables efficient development of new models



Jupyter Notebook Demonstration

https://github.com/decaluwe/OBMS_materials/blob/master/OBMS_2020_CanteraOverview.ipynb

There is an active, robust, and growing Cantera user and developer community

Cantera Workshop
- National Combustion meeting
- Pasadena, March 2019
- Speth, Weber, DeCaluwe
- 95 Paid attendees

Active community support
- Lead roles by Speth and Weber

Cantera-users group
- 1396 current members
- Overall, 2232 topics/threads
- In 2019:
  - 234 threads, 1044 posts
  - 10,300 total views.

Cantera is used heavily in academia: will form basis of example in next Ed. of Stephen Turns' combustion text.

Cantera 2.4.0 has been downloaded > 24,527 times via Conda over ~1 year.

Developed on GitHub (https://github.com/cantera/cantera).

NSF has awarded a new community-driven, extensible, chemical-kinetics software initiative

NSF: Cyberinfrastructure for Sustained Scientific Innovation (CSSI)

- **Selected for 3-year award (start January 2020)**

Three Primary objectives:

1. ***Extend*** **Cantera's capabilities:**
   Support tech development in energy storage & conversion, Chemicals processing, and atmospheric chemistry.

2. ***Expand*** **Cantera's user base**
   Outreach to critical fields including electrochemistry, heterogeneous catalysis, and atmospheric chemistry.

3. ***Broaden*** **participation in the software's development and management**
   Improve Cantera's sustainability and usability.

While NSF's explicit interest is high-impact sustainable software, not scientific computing capabilities, the two are of course strongly coupled.

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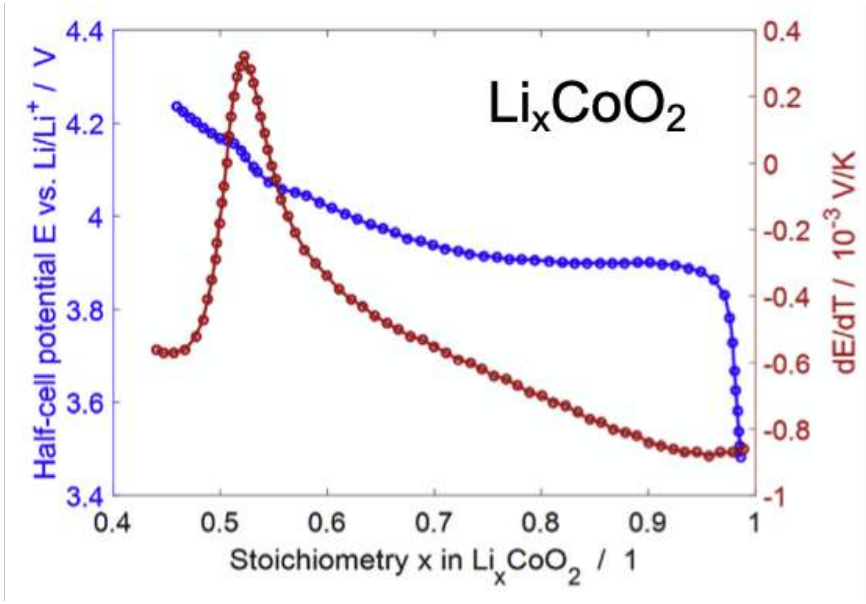
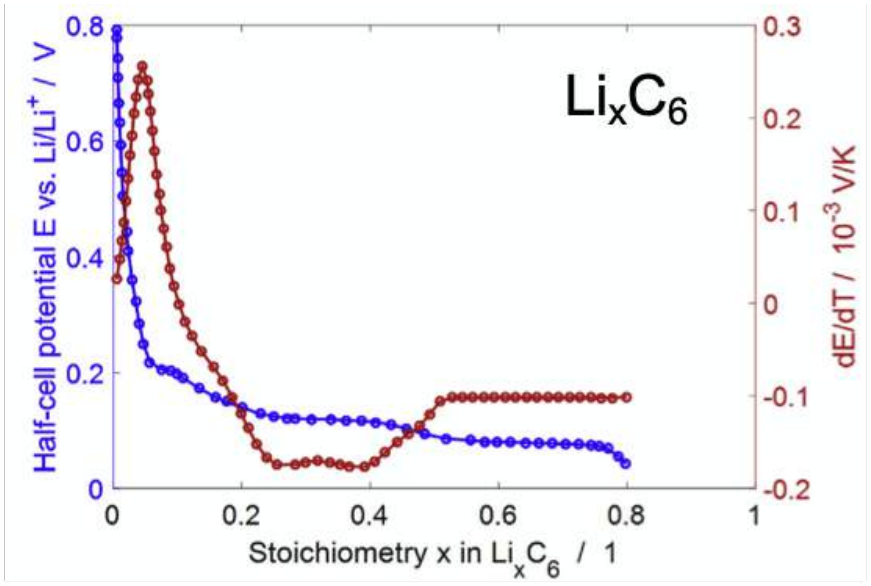
Thermodynamics of common intercalation materials do not facilitate convenient EoS

Bessler, W.G., Mayur, M. (Hoschule Offenburg); DeCaluwe, S.C., Kee, B.L. (CSM)

Half-cell potential varies non-monotonically with stoichiometry, temperature.

- **Challenging to represent via closed-form equation of state.**
- **Required for accurate cell voltage predictions.**
- **Required for accurate electrochemical kinetics: species activities.**

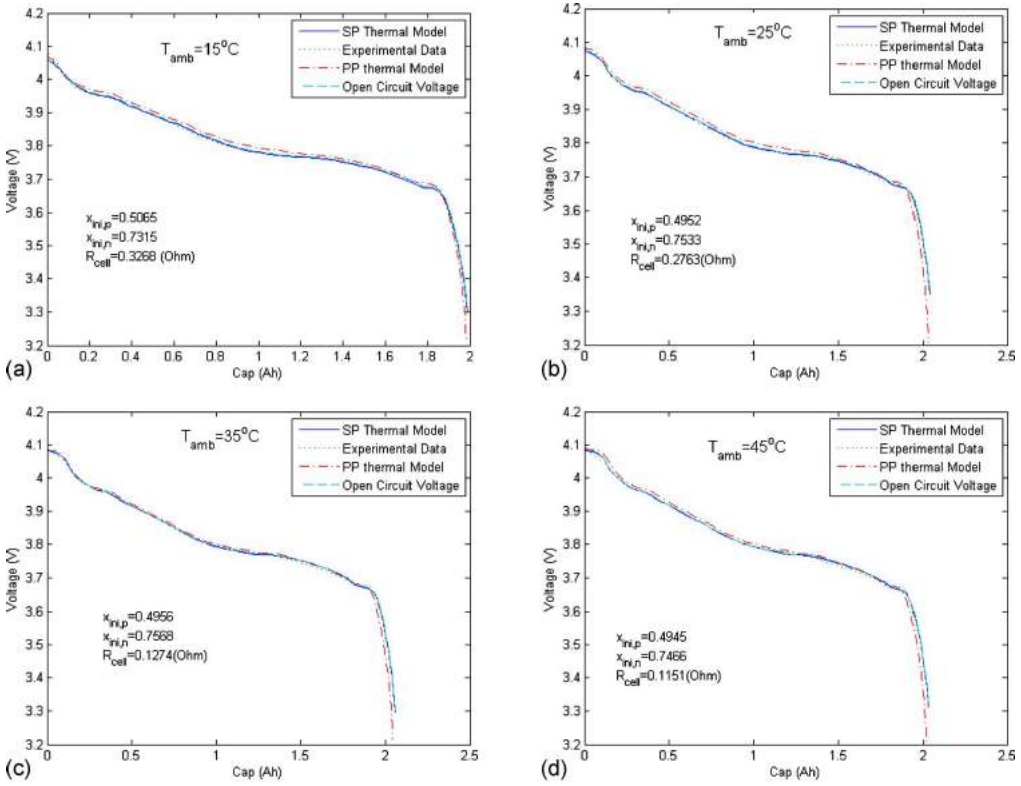




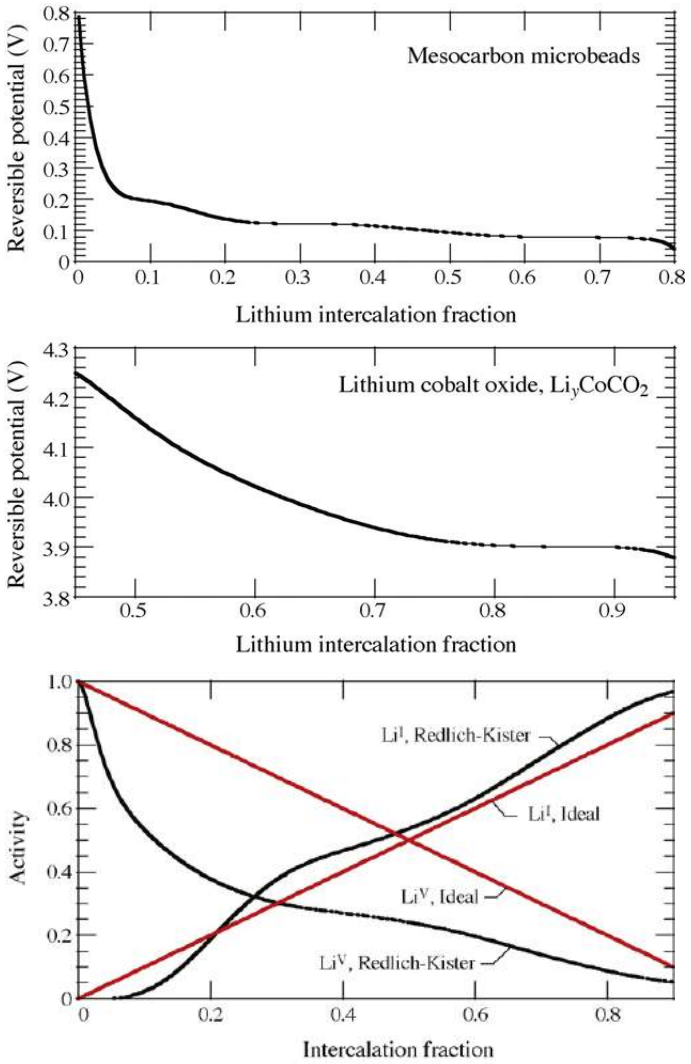
Data adapted from Kumaresan, et al., *J. Electrochem. Soc.* (2008), as reproduced in Mayur, et al., *Echim. Acta* (2019)

Previous approaches put significant effort into EoS development, give accurate cell voltages

Guo, et al., J. Electrochem. Soc. (2011)



Colclasure and Kee, Echim. Acta (2010)



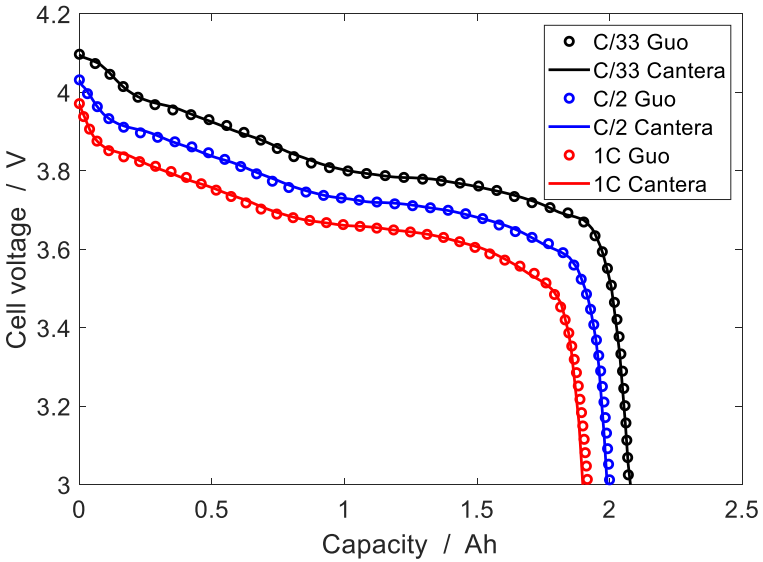
Temperature dependence:

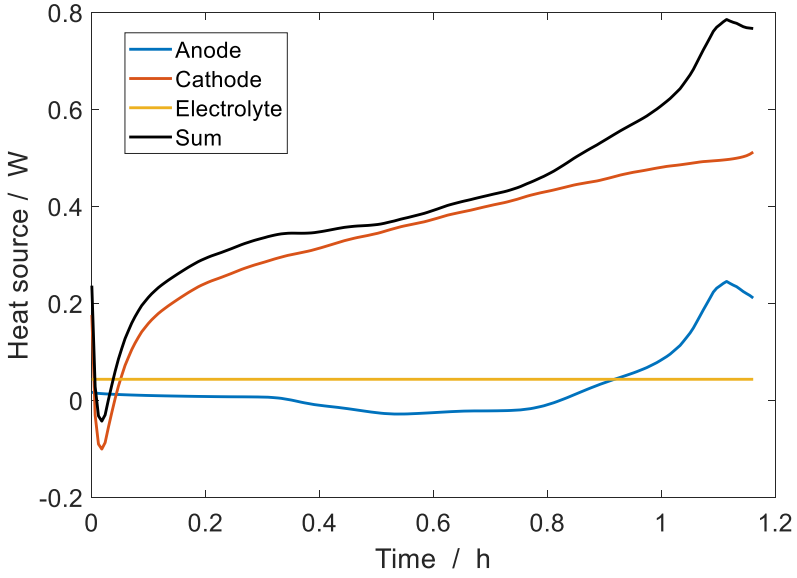
$$\frac{\partial U_n}{\partial T} = \frac{(0.00527 + 3.29927x_n - 91.79326x_n^2 + 1004.91101x_n^3 - 5812.27813x_n^4 + 19{,}329.75490x_n^5 - 37{,}147.89470x_n^6 + 38{,}379.18127x_n^7 - 16{,}515.05308x_n^8)}{(1 - 48.09287x_n + 1017.23480x_n^2 - 10{,}481.80419x_n^3 + 59{,}431.30001x_n^4 - 195{,}881.64880x_n^5 + 374{,}577.31520x_n^6 - 385{,}821.16070x_n^7 + 165{,}705.85970x_n^8)}$$

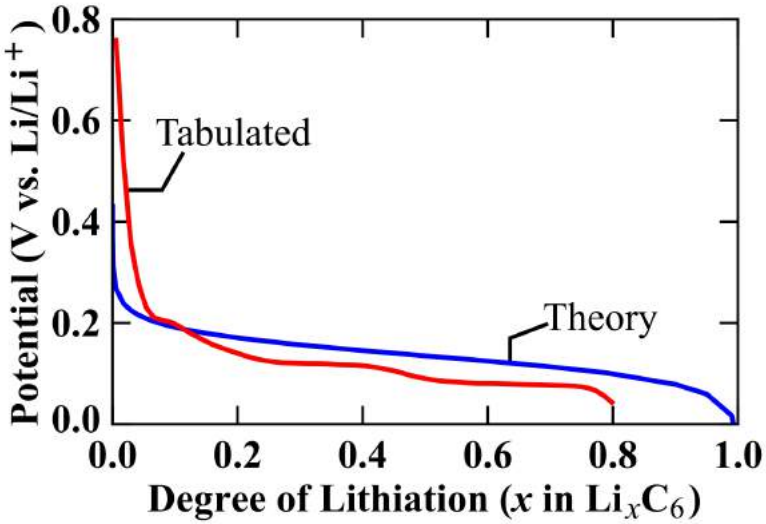
Tabulated species thermodynamics: accurate properties and easily extensible

Bessler Group (Hoschule Offenburg): Tabulated thermodynamics

- **Half-cell data are easily convertible to species enthalpy and entropy values**
- **Cantera software interpolates as a function of intercalation fraction, *x***
- **Mayur, et al., Echim Acta (2019), mathematical framework for extension.**







Jupyter Notebook Demonstration

http://localhost:8888/notebooks/electrochemistry/lithium_ion_battery.ipynb

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Li-S batteries: high energy density, limited by solution-phase electrochemical degradation

Korff, D.M., DeCaluwe, S.C. (CSM); Colclasure, A.M., Smith, K.A. (NREL)

Li-Sulfur batteries:

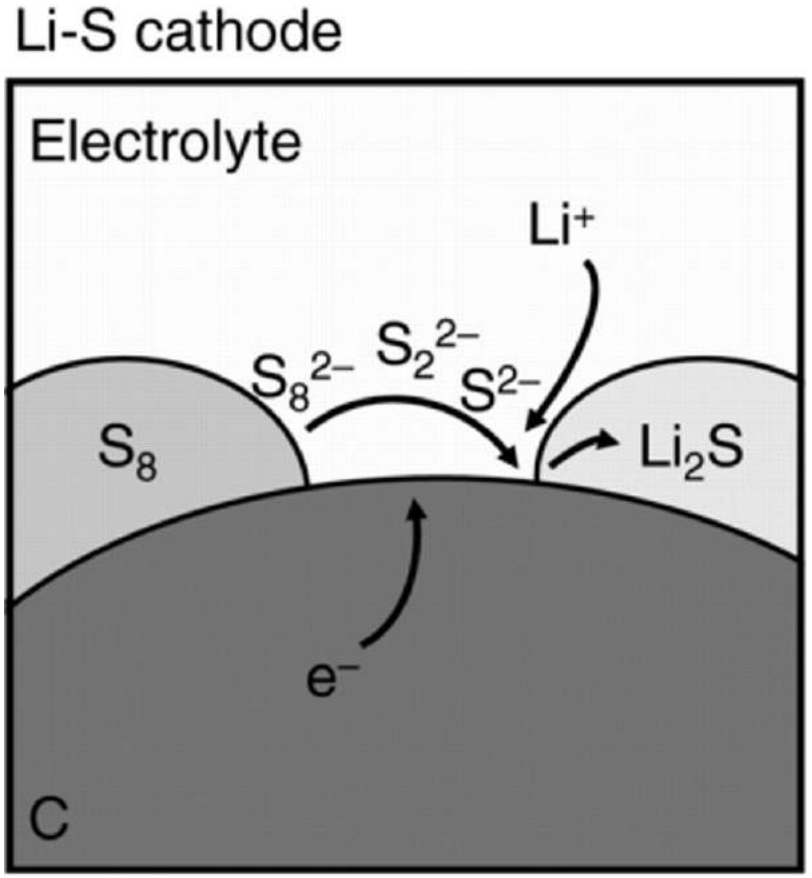
- High theoretical capacity (~1675 mAh/g)
- Lighter-weight, Earth-abundant materials

Limitations:

- Intermediate polysulfide shuttling
- Poorly-conducting end-states (S_8, Li_2S)
- Intermediates have limited solubility.
- Challenging to balance energy and power densities (electrolyte:sulfur ratio)

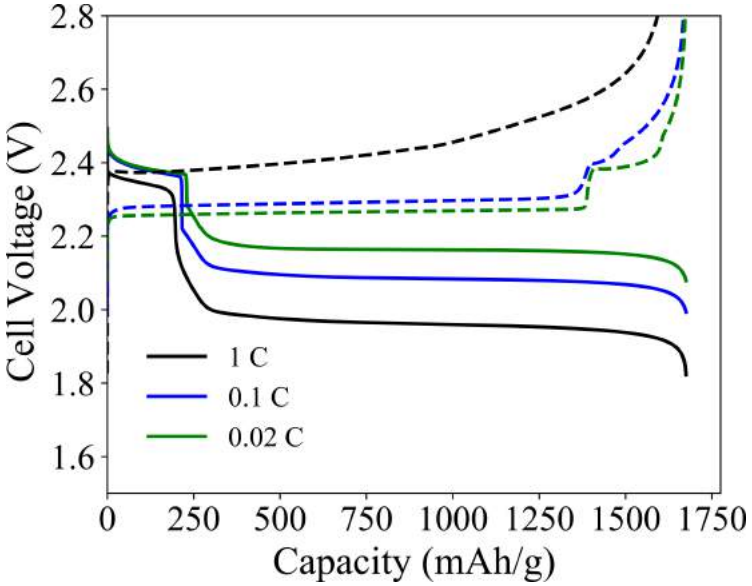
Chemical complexity: Li-S chemistry can involve up to (*Assary, et al., JPCC, 2014*)

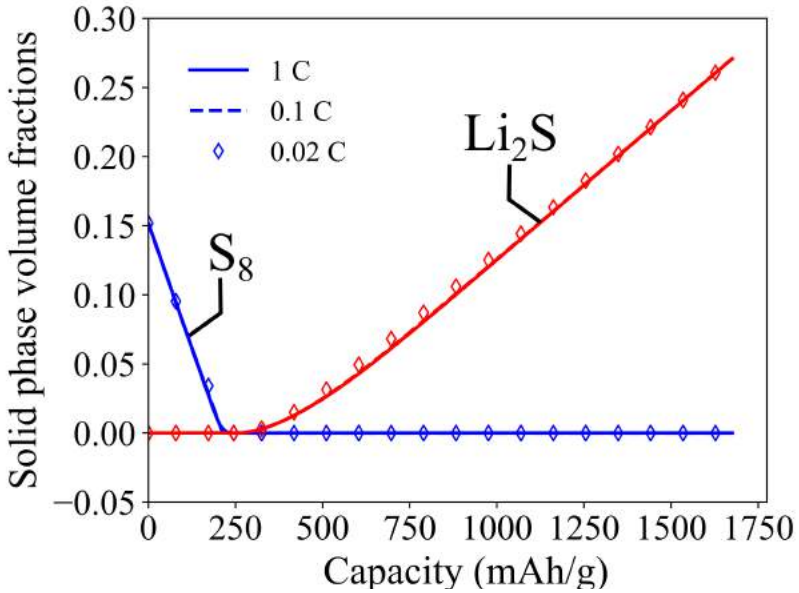
- 21 different species
- 26 association/dissociation reactions
- 50 different disproportionation reactions

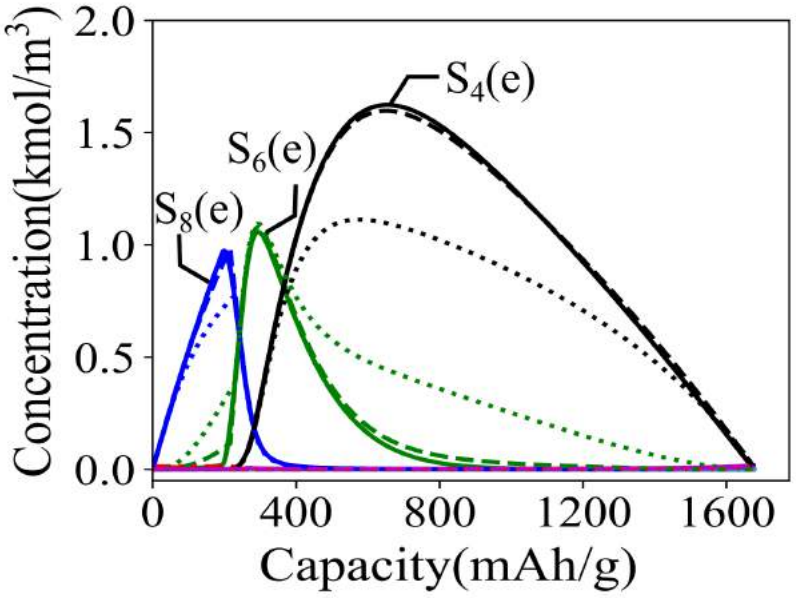


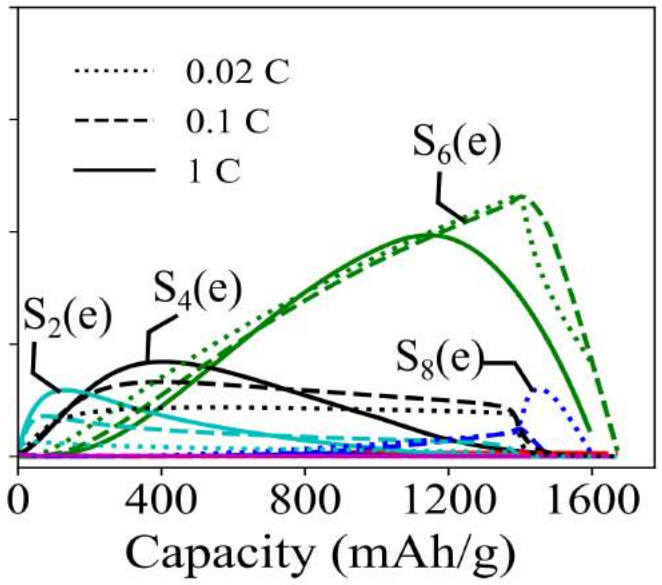
Neidhardt et al, JECS, 2012

Li-S batteries: high energy density, limited by solution-phase electrochemical degradation









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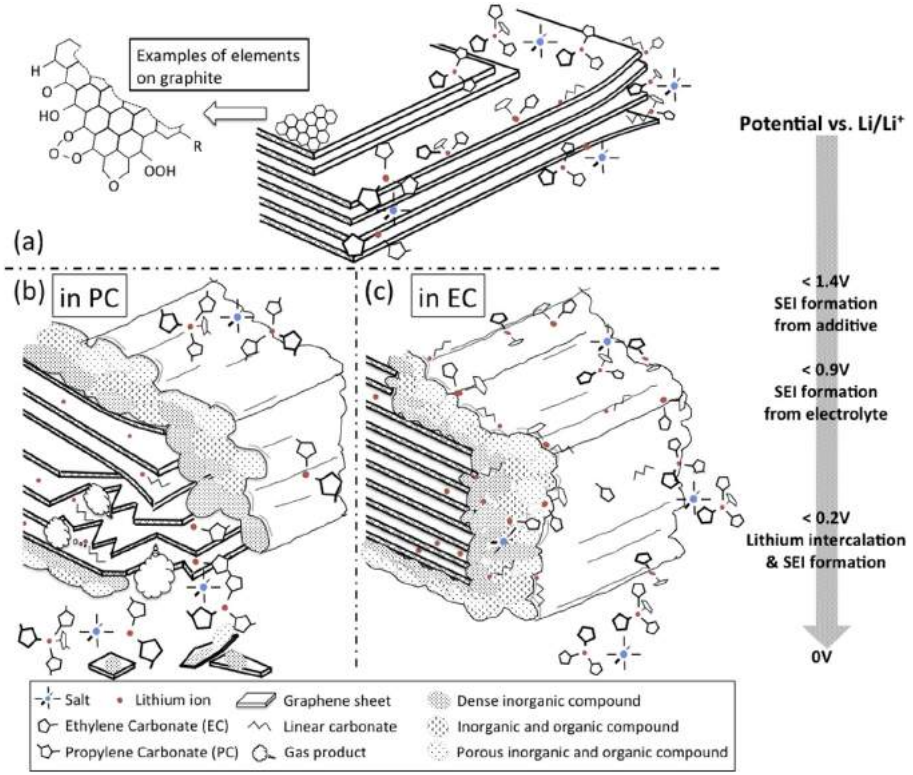
State of SEI understanding: Many reactions are identified, few are quantified (1/3).

DeCaluwe, S.C., Korff, D.M. (CSM); Bessler, W.G., Carelli, S (Hoschule Offenburg); Colclasure, A.M. (NREL)



An, et al., Carbon, 2016

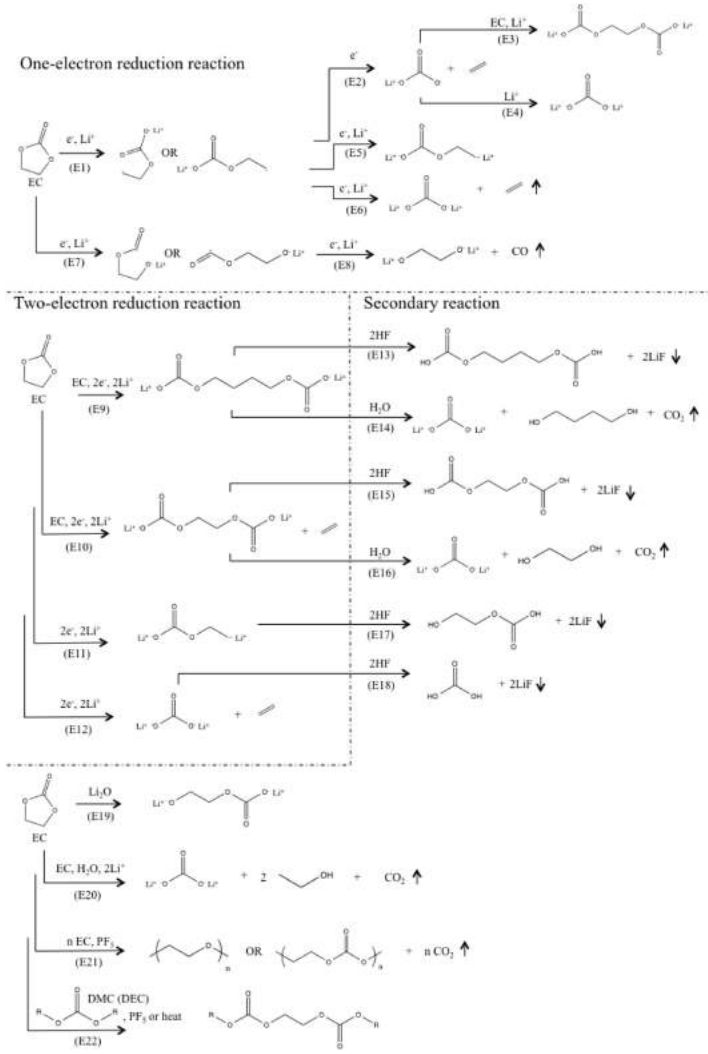
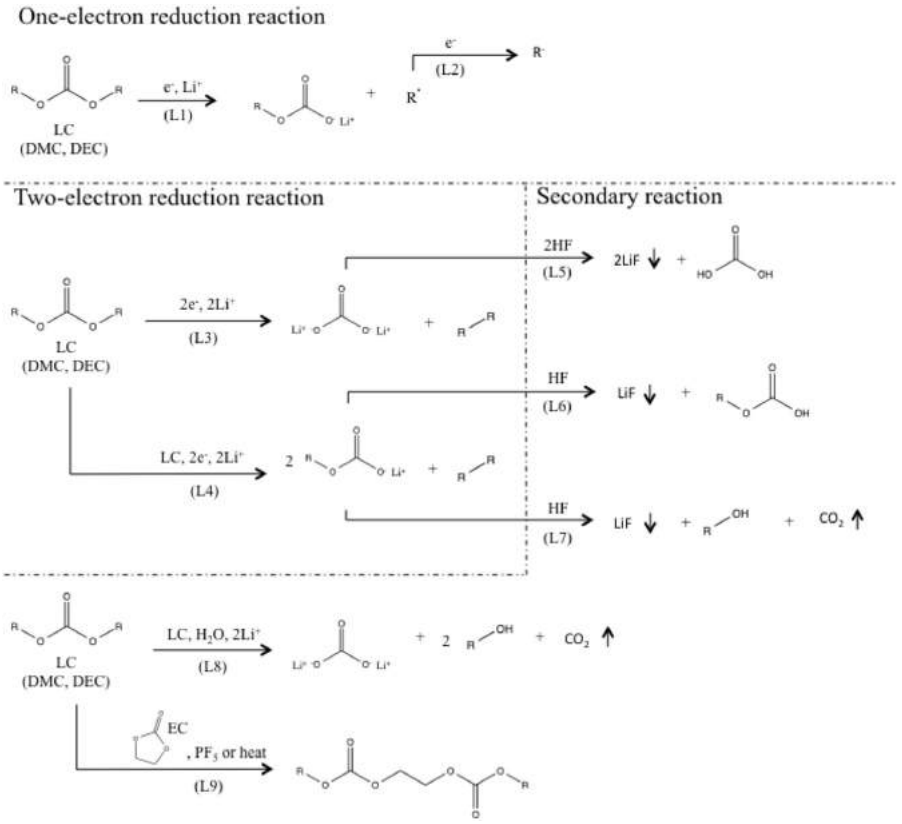
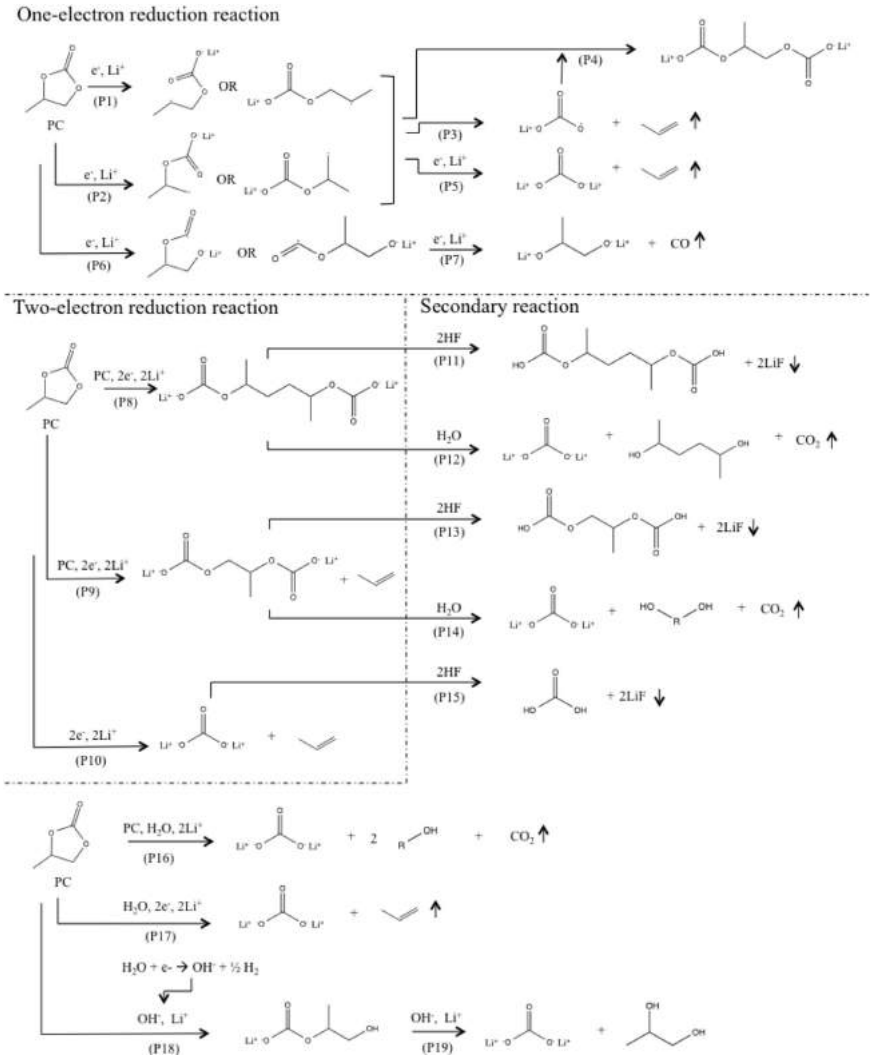


Fig. 8. Ethylene carbonate (EC) reduction process (reference groups in parentheses; details are shown in Table 2).

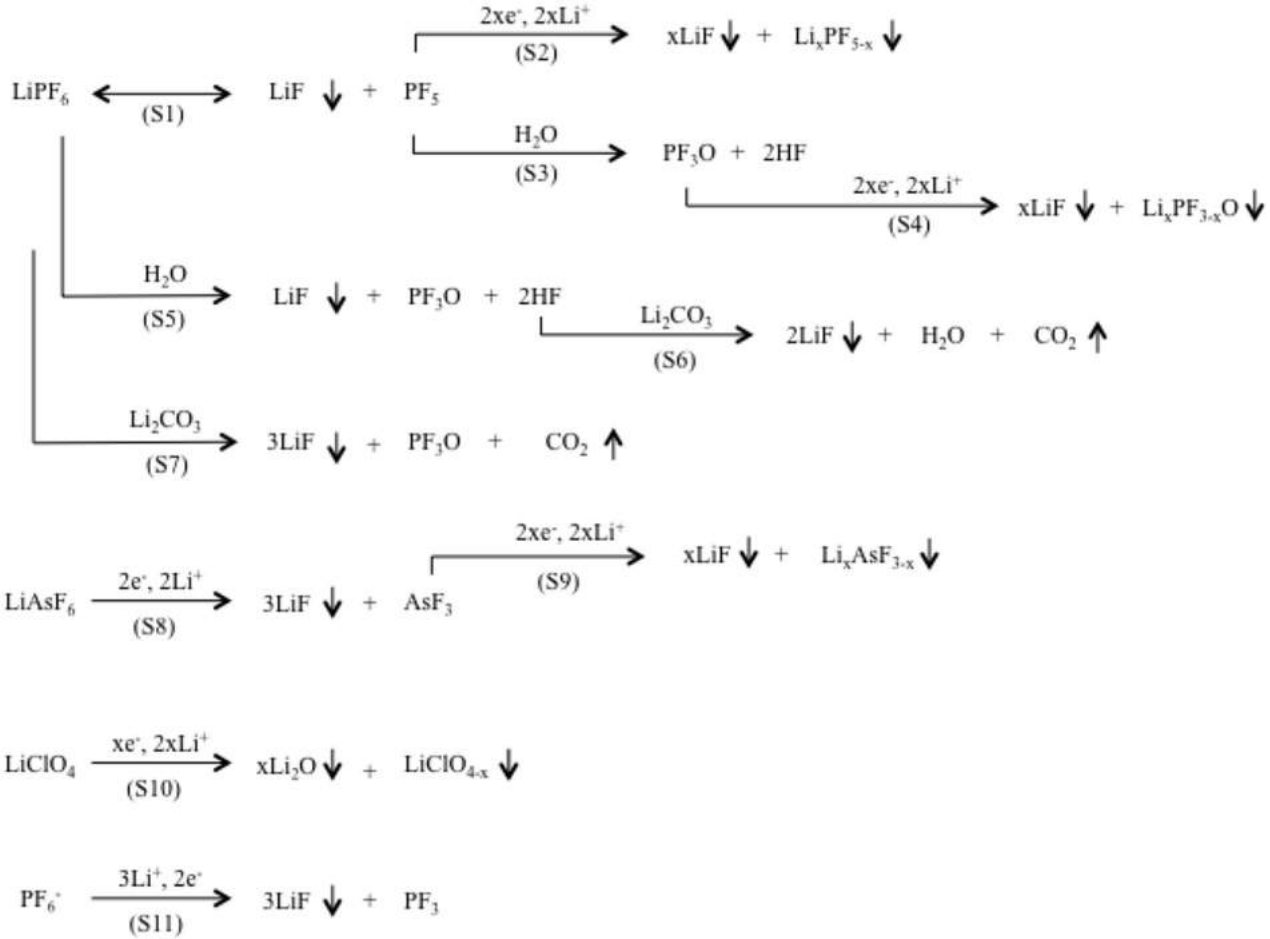
State of SEI understanding: Many reactions are identified, few are quantified (2/3).





An, et al., Carbon, 2016

State of SEI understanding: Many reactions are identified, few are quantified (3/3).



An, et al., Carbon, 2016

There are 2 primary needs, for mechanistic understanding of SEI growth and evolution

Need #1: Operando validation data with high spatio-chemical resolution.

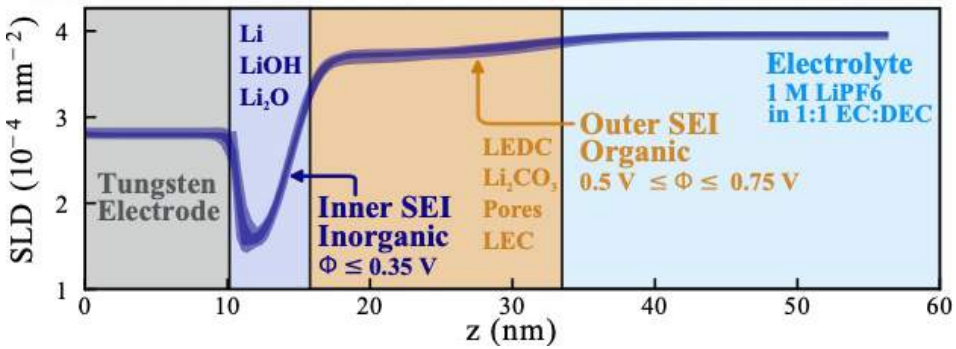
Need #2: Detailed electrochemical modeling tools, with flexible and robust mechanism implementation

Recent advances in *operando* characterization of SEI gives spatio-chemical sensitivity

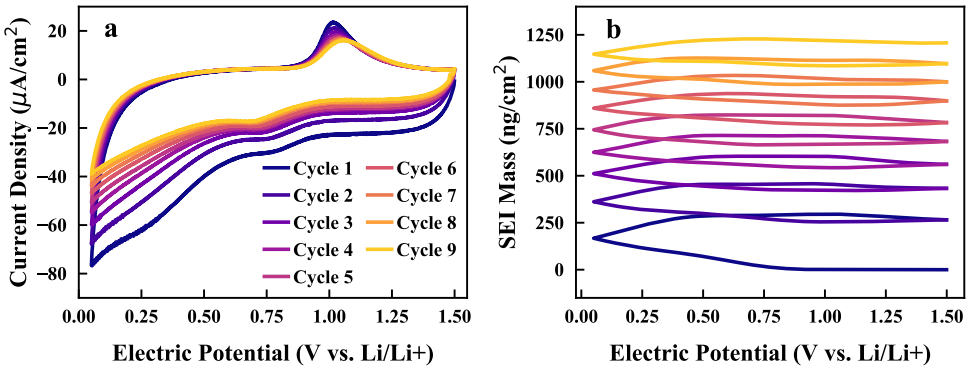
Non-intercalating electrodes (Cu, W)

Lee, C.H., et al., J. Power Sources, 2019
See also, Dura (NIST)

Depth Profiling: Neutron Reflectometry



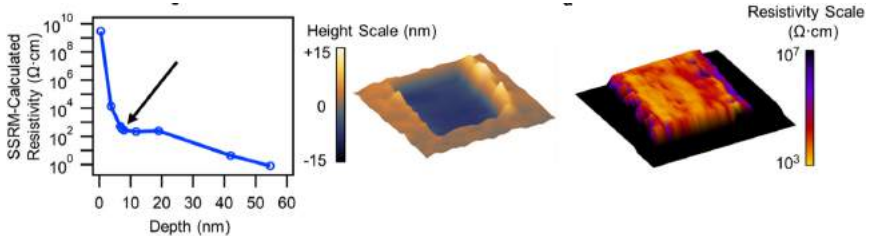
QCM-D + electrochemistry: mass uptake, visco-elastic properties

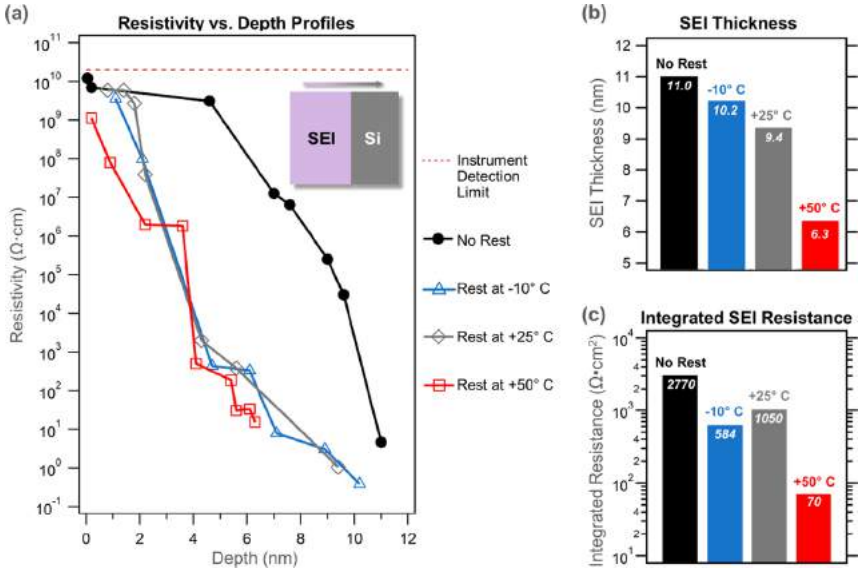


Functional anodes (Si, Graphite)

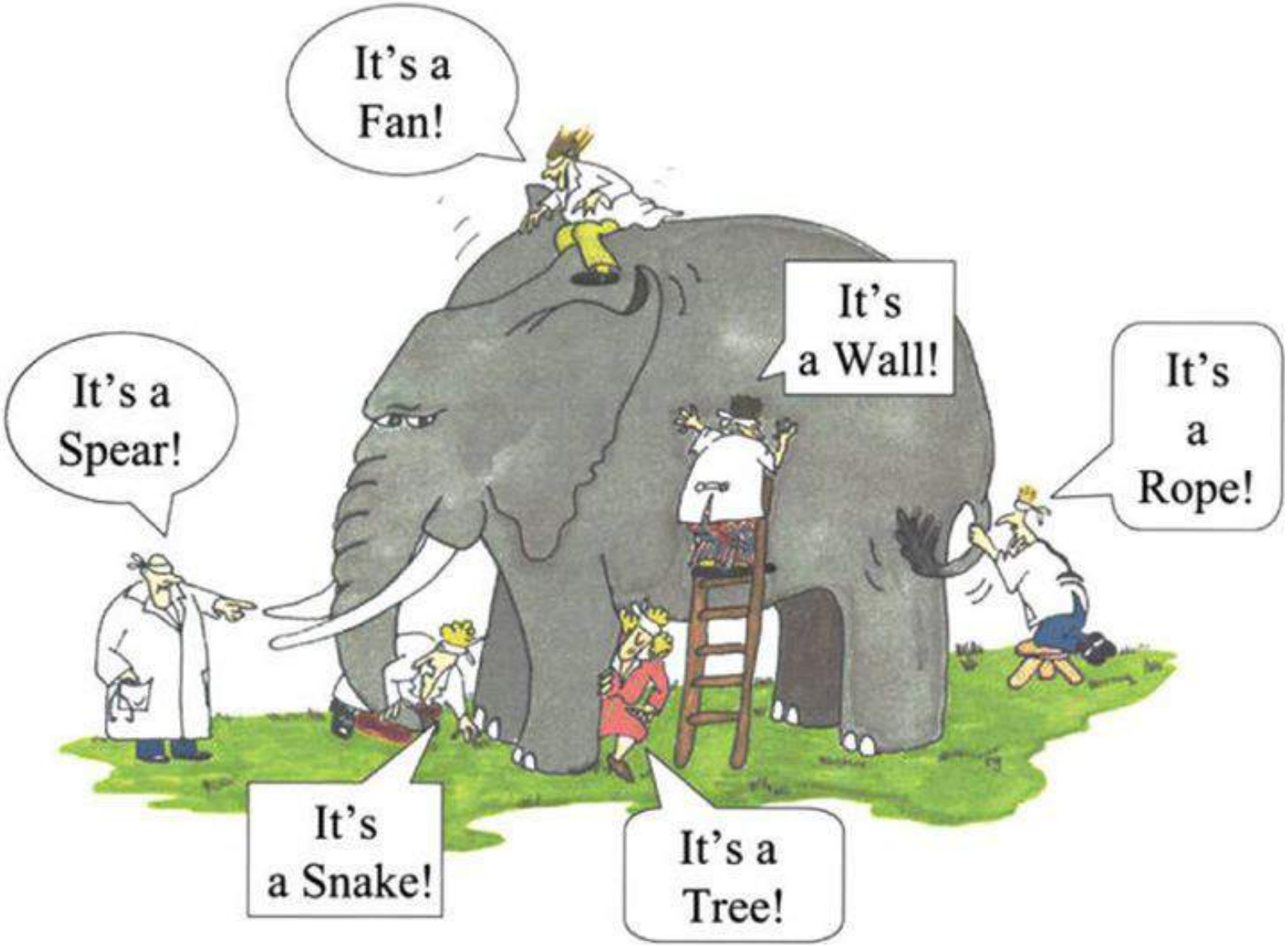
Stetson, et al., Nano Energy (2019)
Stetson, et al., ACS Energy Lett (2019)

3-D Resistivity depth profiling via AFM-based techniques





However, humility on the part of the modeler is strongly encouraged…



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Two-step pathway toward understanding SEI growth and evolution

Growth of SEI modeled via elementary electrochemistry:

$$\dot{q}_i = k_{\text{fwd}} \prod_j a_j^{\nu_{j,i,\text{fwd}}} - k_{\text{rev}} \prod_j a_j^{\nu_{j,i,\text{rev}}}$$

where:

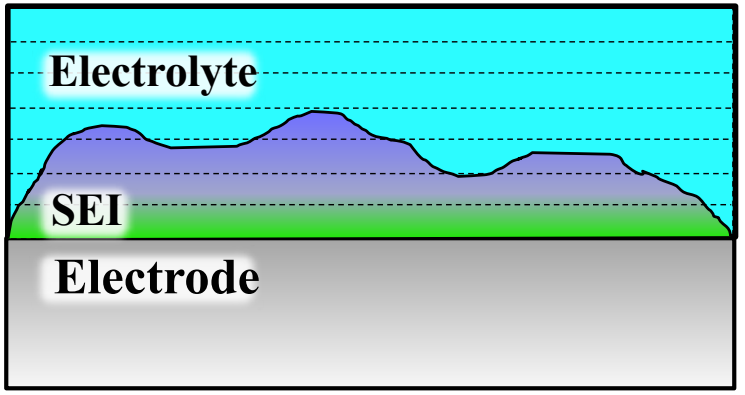
$$k_{\text{fwd}} = k_{\text{fwd}}^{\circ} \exp\left(\frac{nF\beta\Delta\phi}{RT}\right)$$

$$k_{\text{rev}} = k_{\text{rev}}^{\circ} \exp\left(\frac{nF(1-\beta)\Delta\phi}{RT}\right)$$

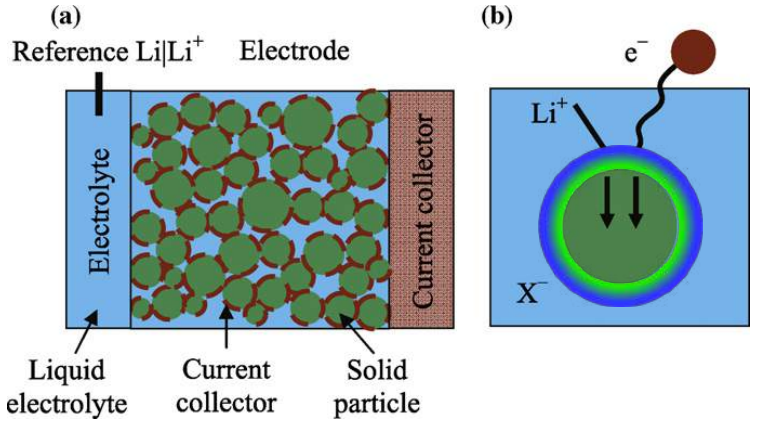
Initial simulation: planar, non-intercalating "model" electrode

Depth profiling: divide electrolyte at electrode surface into volumes.

Step 1: Model electrode



Step 2: Newman-type P2D model



W. Lai, F. Ciucci, Electrochimica Acta, 2011

Model implementation compromise between spatial resolution, continuum scale.

Assumptions:

- Charge neutrality: double-layer resolved throughout the SEI depth.
- Finite, volume-averaged σ_{elec}.
- No Li intercalation

Limitations:

- Properties in sub-nm pores?
- Simulation stability highly sensitive to parameter values.
- Spatial discretization at continuum scale: barely sufficient!

Type equation here.

Advantages:

- Mechanistic flexibility!
- Chemical and mechanistic detail.

Cantera Function Calls

$$\dot{s}_{k,SEI} = \underbrace{\varepsilon_{SEI} A_{SEI-elyte} \boxed{\sum_{j,SEI-elyte} \nu_{k,j} \dot{q}_j}}_{\text{Heterogeneous}} + \underbrace{\boxed{\sum_{j,SEI} \nu_{k,j} \dot{q}_j}}_{\text{Homogeneous}}$$

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https://github.com/decaluwe/OBMS_materials/blob/master/OBMS_2020_Battery.ipynb

Results demonstrate cantera's ability to explore chemical space, identify mechanisms

Preliminary (i.e. old) model version:

$$2\,EC_{(elyte)} + 2\,Li^{+}_{(elyte)} + 2\,e^{-}_{(an)} \leftrightarrow LEDC_{(SEI)} + Ethylene_{(gas)} \quad (R1)$$

$$EC_{(elyte)} + 2\,Li^{+}_{(elyte)} + 2\,e^{-}_{(an)} \leftrightarrow Li_2CO_{3\,(SEI)} + Ethylene_{(gas)} \quad (R2)$$

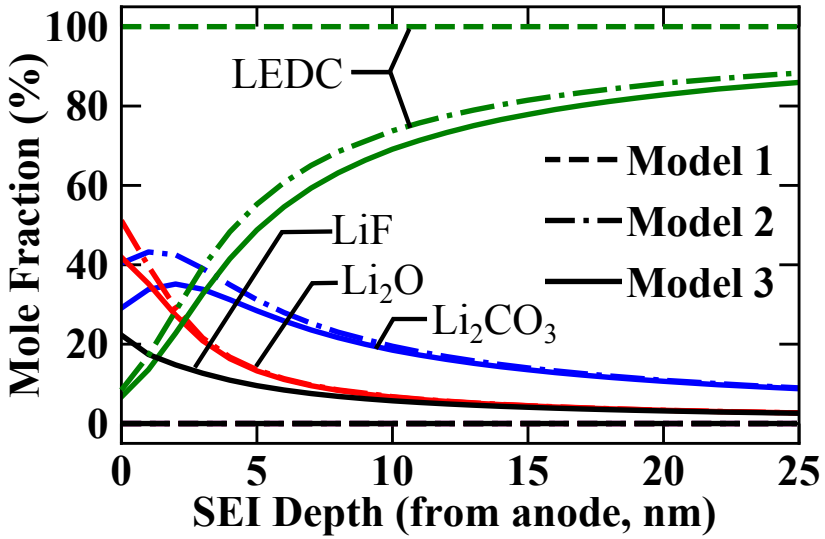
$$Li_2CO_{3\,(SEI)} + 2\,Li^{+}_{(elyte)} + 2\,e^{-}_{(an)} \leftrightarrow 2\,Li_2O_{(SEI)} + CO_{(gas)} \quad (R3)$$

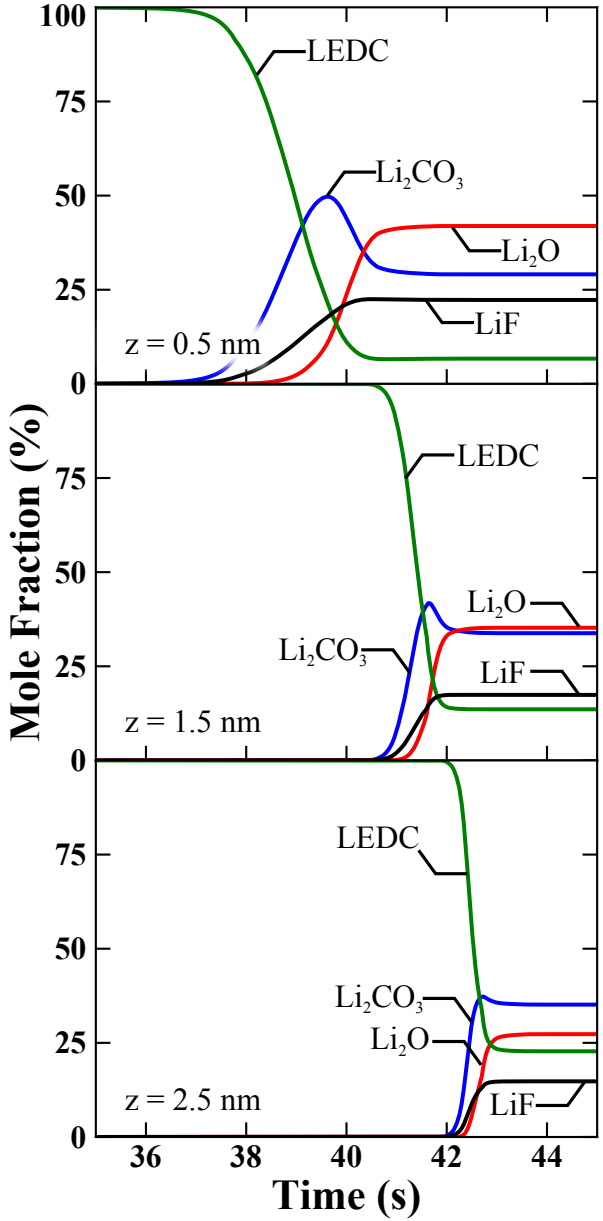
$$LEDC_{(SEI)} + H_2O_{(elyte)} \leftrightarrow Li_2CO_{3\,(SEI)} + CO_{2\,(gas)} + EG_{(elyte)} \quad (R4)$$

$$LEDC_{(SEI)} + 2\,HF_{(elyte)} \leftrightarrow 2\,LiF_{(SEI)} + EDC_{(elyte)} \quad (R5)$$

$$Li_2CO_{3\,(SEI)} + 2\,HF_{(elyte)} \leftrightarrow 2\,LiF_{(SEI)} + Carbonate_{(elyte)} \quad (R6)$$

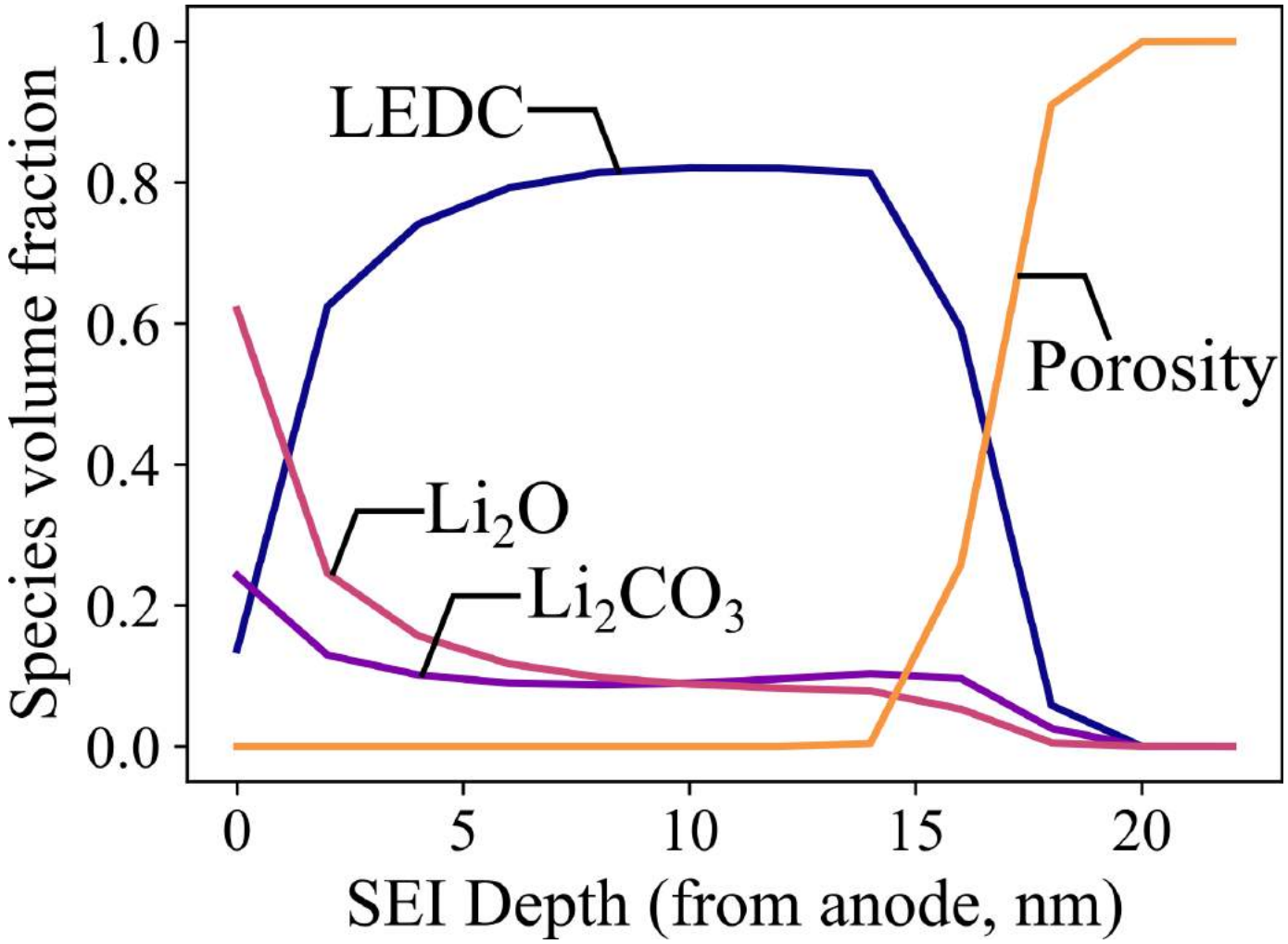
M1
M2
M3





Reduced-order model approaches easily developed, help inform multi-scale approaches

In progress (i.e. less old) model version:



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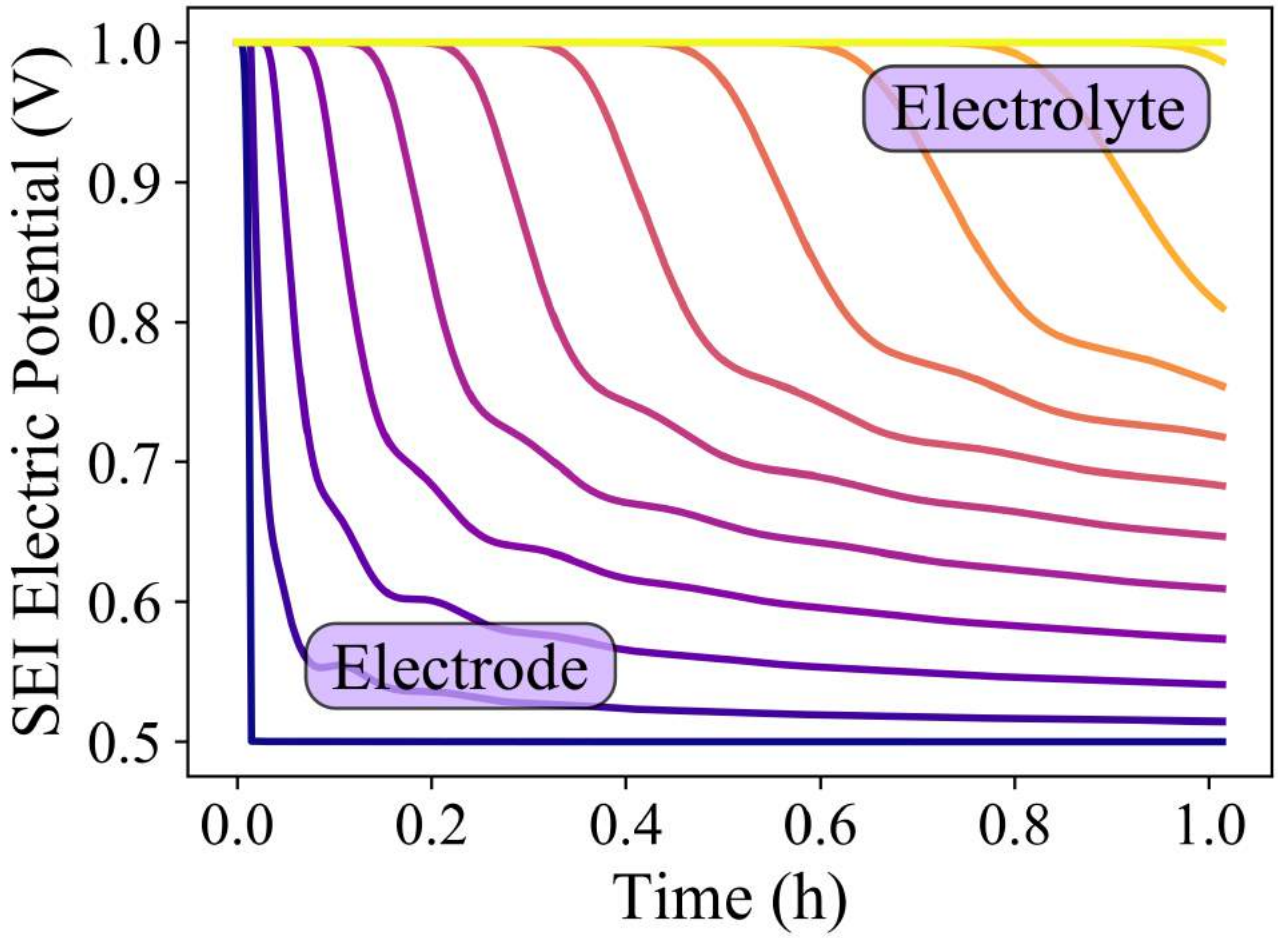

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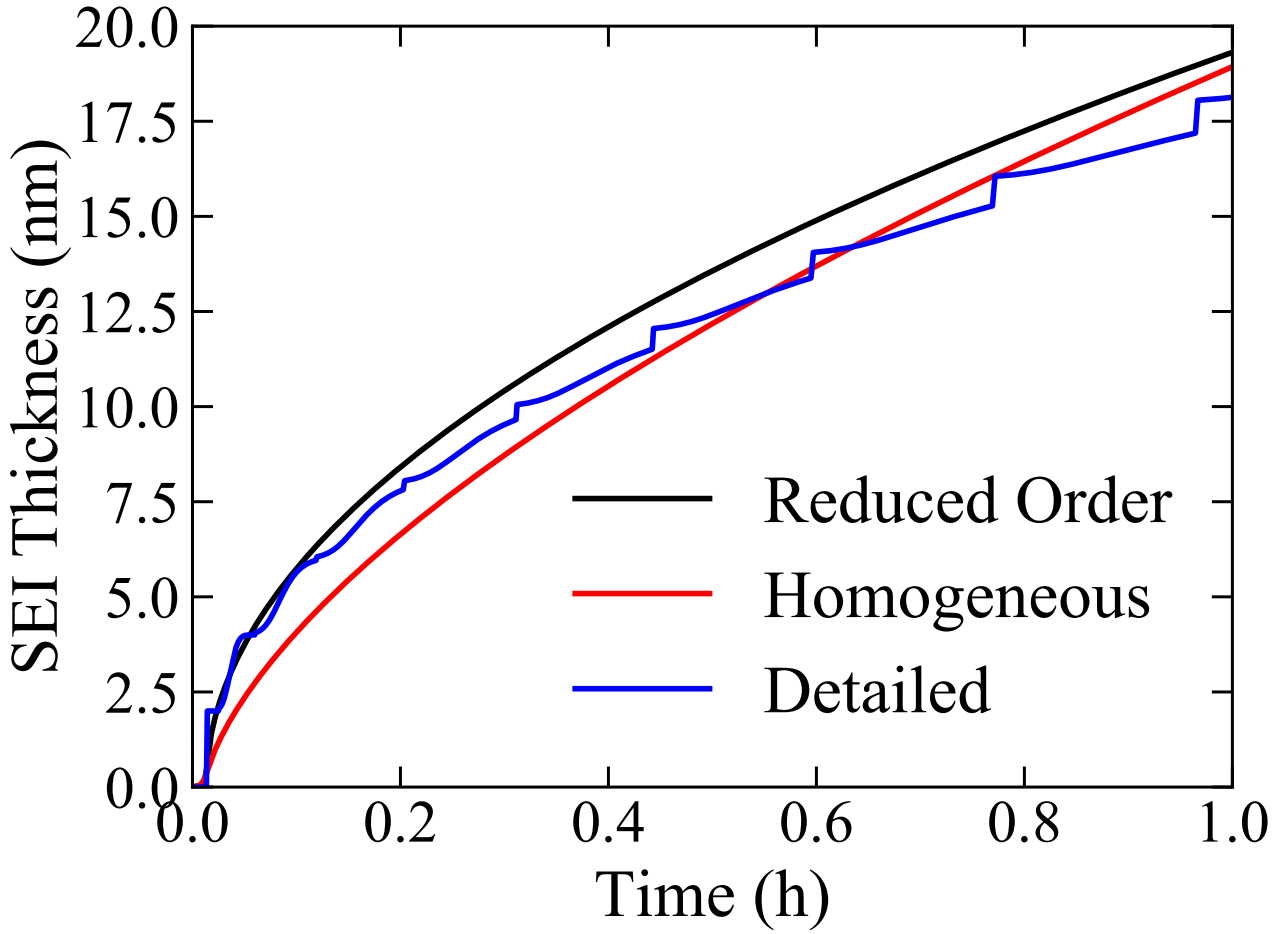
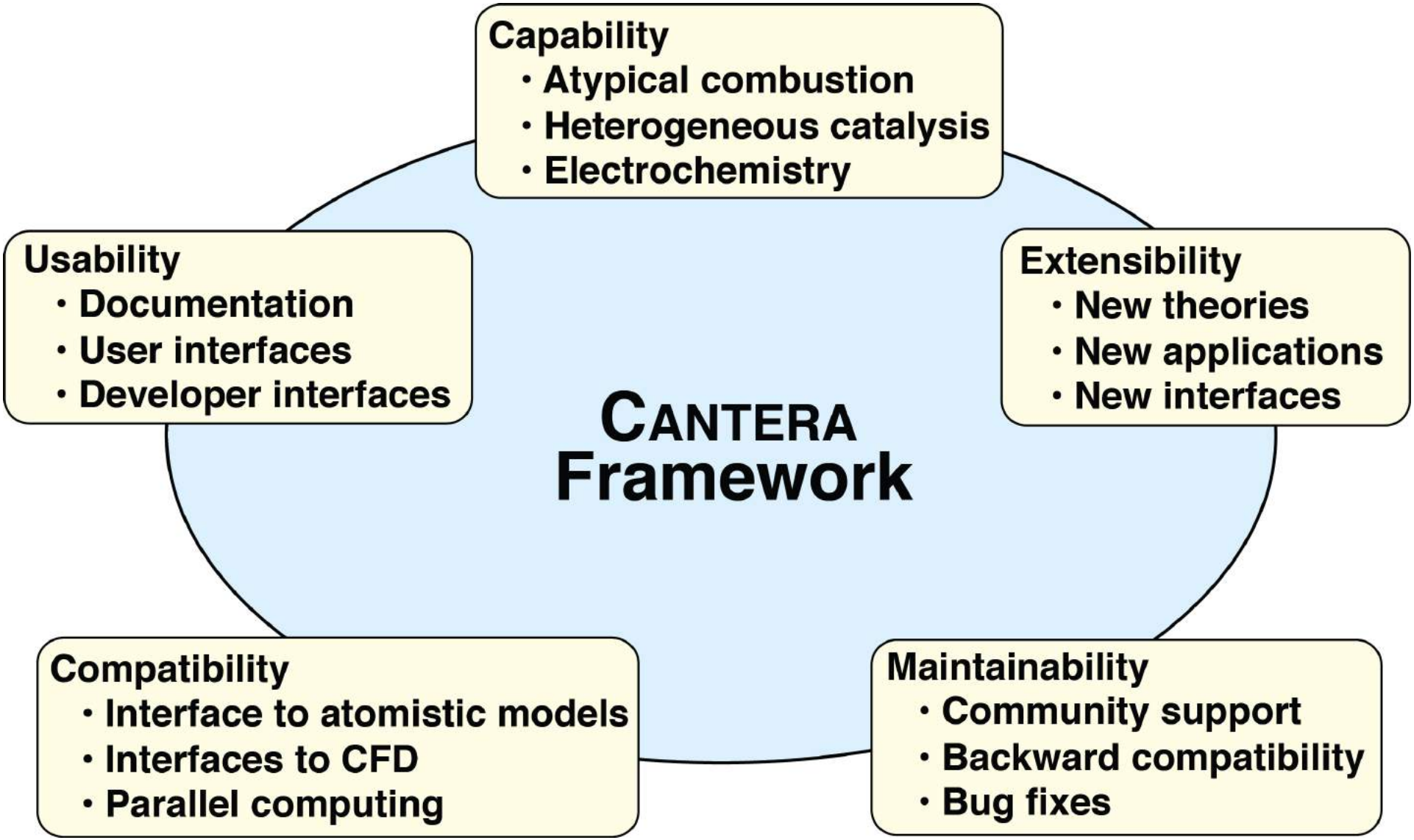


Outline

- The Case for electrochemical complexity
- Cantera: object-oriented, generalized chemical kinetics software
- Case study: Tabulated thermodynamics of lithium intercalation
- Case study: Intermediate polysulfide chemistry in Li-S
- Case study: Chemistry of SEI growth and evolution
- **Next steps: Future development, community input**

Software viability depends on designing and implementing complementary functionalities

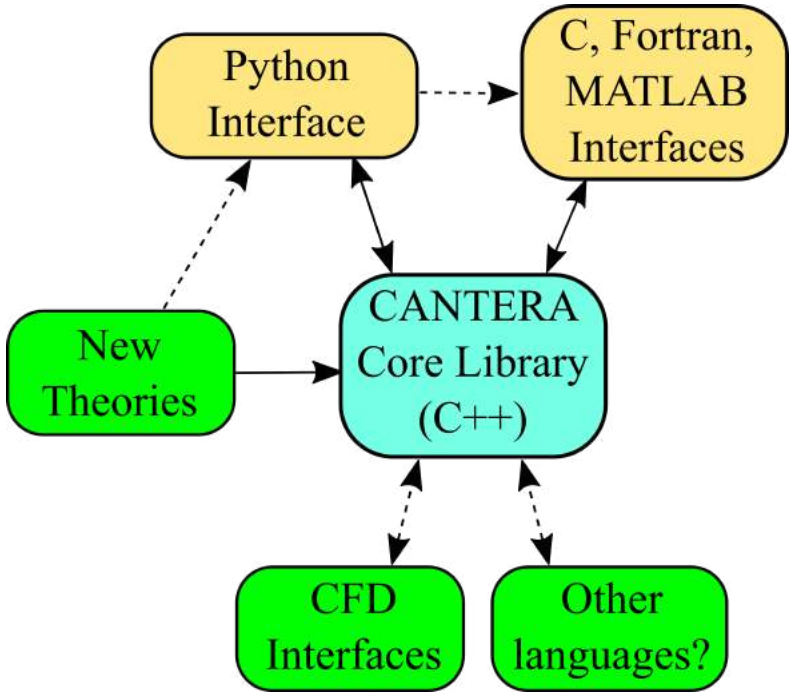


Extensibility and Interoperability help leverage existing and new external software packages

Team: Speth, Niemeyer, West

Milestones:

- **New, flexible input file format based on the YAML standard.**
- **Add interface for serializing Cantera objects to the YAML format.**
- **New "lightweight" interface to the Cantera Python module.**
- **Code-generation approach for C, Fortran, and MATLAB interfaces.**



- **Introduce a Cantera package for Julia.**
- **Document integrating Cantera with CFD software, provide an example using the open-source CFD platform OpenFOAM.**

Scientific Advisory board: provides both high-level and granular input for future direction

Stakeholders from relevant fields provide both high-level and detailed input.

- **L. Árnadóttir (Oregon State U.) - Catalysis**
- **W. Bessler (Offenburg, Germany) – Electrochemistry, combustion.**
- **M. P. Burke (Columbia University) – Combustion, collider effects.**
- **M. Evans (University of York, UK) – atmospheric chemistry modeling.**
- **T. Fuller (Georgia Tech.) – Electrochemistry.**
- **G. Goldin (CD-Adapco/Siemens) – Commercial CFD.**
- **W. Green (MIT) – Combustion, chemical kinetics, molecular simulation**
- **T. Krauss (Argonne Natl. Lab) - Catalysis**
- **R. Lobo (U. Delaware) - Catalysis**
- **P. Pepiot (Cornell U.) – Combustion, novel modeling tools, CFD.**
- **J. Zador (Sandia Natl. Lab) – Catalysis, combustion, atmospheric chem.**

Community development: recruit new users, convert current users into developers

General guidelines for interacting with the community are provided at:

https://cantera.org/community.html

For new users, the website is a valuable resource: https://cantera.org

Questions, input, feedback? In order of preference:

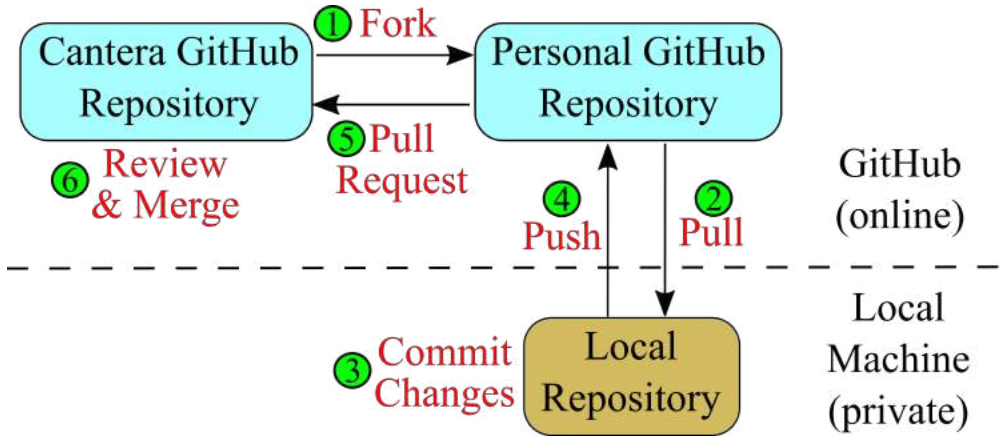
i. **Cantera Users' Group**
ii. **GitHub:** https://github.com/cantera
iii. **Email the steering committee:** steering@cantera.org
iv. **Scientific Advisory Board**

For new developers: start small!

1. **Consult issues page on github:**
   https://github.com/cantera

2. **Develop an approach to address the issue.**

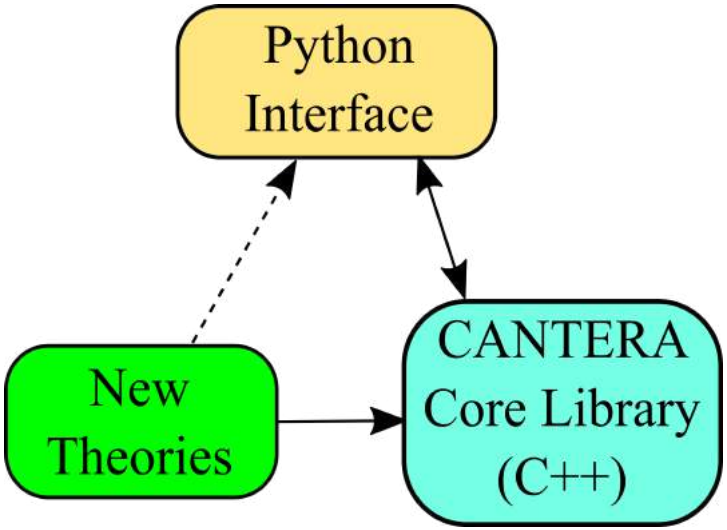
3. **Implement via Git/GitHub**



Developing multi-use, general-purpose code with multiple contributors is not simple

Example: Peng-Robinson EoS:

1. Develop theory
2. Create C++ Class
3. Header files
4. Documentation
5. Test files
6. Code / style review



- For many applications, a light-weight development interface would be more appropriate—decrease the activation barrier.
- Evaluate form and utility within the context of other Cantera functionalities, allow comment and feedback from the community.
- An additional area of need: application-specific toolboxes. E.g. Battery simulation tools separate from the "Core" Cantera library.

Cantera's battery and electrochemistry capabilities are… nascent.

Electrochemical Kinetics:

- ✓ Marcus theory: reversible charge-transfer kinetics
- ✓ Butler-Volmer: reversible, elementary-step; equivalent to Marcus
- ✘ Other Butler-Volmer (global, multi-step, user-specified orders).

Phase Models

- ✓ P-v-T: Constant species molar volume
- ✘ Crystal lattice phases

Species thermo

- ✓ Constant Cp thermodynamic properties
- ✓ Ideal solid solution ($\alpha_k = X_k$) thermodynamic properties
- ✓ Tabulated thermodynamic properties for binary phases
- ✘ Non-ideal, EoS-based species interactions.

Transport

- ✘ Largely based on gas-phase approaches.

Conclusions: NSF funding provides an opportunity to leverage recent developments

1. Recent developments laid groundwork:
   - AFOSR software planning grant
   - Formalization of the leadership structure
   - NumFOCUS fiscal sponsorship

2. NSF funding will help chart a new path for Cantera
   - New software capabilities
   - New user and developer communities
   - Community-led development
   - New interfaces to lower activation barrier for future development.
   - Fiscal sustainability

3. As the software and the community develop and grow, input from and interaction with the electrochemistry community will be invaluable.
   - User group
   - Github issues, pull requests
   - Steering committee
   - Scientific Advisory Board

Acknowledgements

National Science Foundation
- Dr. Stefan Robila (CSSI Program)
- Drs. Raymond Adomaitis, Catherine Walker (Heterogeneous nucleation and growth modelling)

Department of Energy
- Dr. P. Thiyagarajan (Neutron Scattering)
- NREL APUP (Li-S, SEI modeling)

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Air Force Office of Scientific Research
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University of Applied Sciences

NIST

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

OAK RIDGE
National Laboratory

NUMFOCUS
OPEN CODE = BETTER SCIENCE