Helmholtz Institute Ulm
Electrochemical Energy Storage

Birger Horstmann

Theory-Based Development of Safe High-Energy Batteries

ulm university universität ulm

Deutsches Zentrum für Luft- und Raumfahrt e.V.
German Aerospace Center

Why do we need (metal-air) batteries?

THE ELECTRIC AUTOMOBILE

Air pollution and other drawbacks inherent in the internal-combustion engine make this early kind of car seem increasingly attractive. All

ments for its revival are cogent and becoming stronger year by year. Chief among these is the increasingly dangerous pollution of our air by the millions of gasoline-burning vehicles in-

g our cities and countryside. We ace the inescapable fact that the y of cheap gasoline will not last decades longer at the present rate sumption of fossil fuels. And while

of feasibility.

The design of such a car must be based in the first instance on the realization that the American public is highly resistant to radical change in it mobiles. The electric car will fore have to conform as clo possible (at least at first) to the

50 percent of the vehicle's weight) for the batteries.

The battery problem is the principal obstacle that has discouraged serious

tric automobile teries for pro- range of the travel between -and therefore

only 50 to 100 miles.

The innovation that now makes the electric automobile thinkable is a device called the air battery. Still in an early experimental stage, it employs a

34

G. A. Hoffman, *Scientific American* 215(4), 34-41 (1966).

Lithium Ion Battery Applications

- Standard energy storage device
- Stationary, mobile, and portable applications

5 MWh

27 kWh

10 kWh

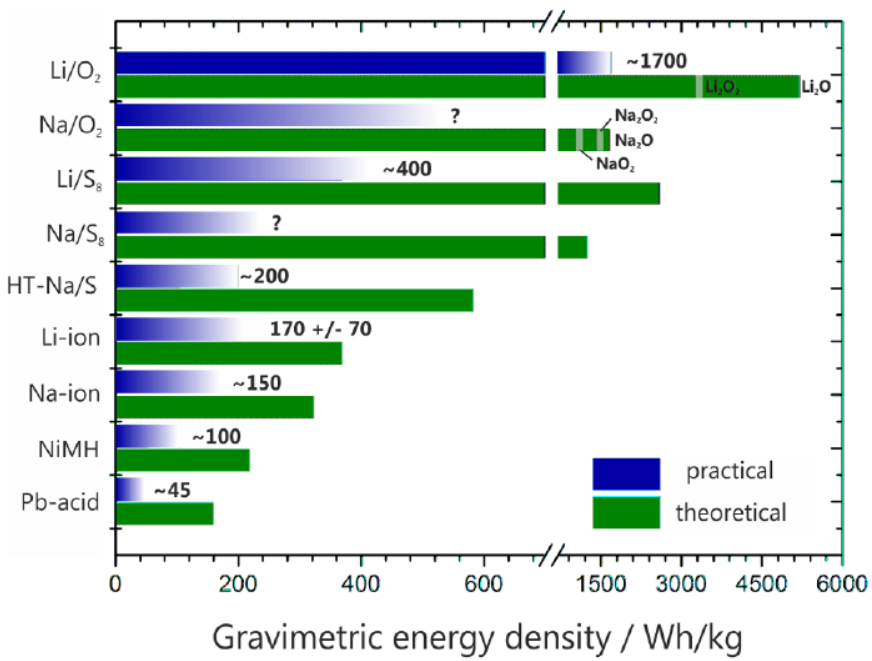
1 Wh

5 Wh

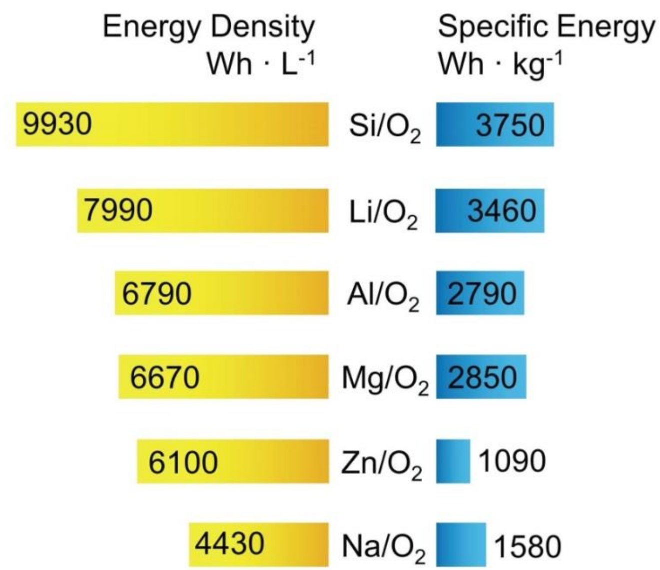
500 Wh

Battery Types and Energy Densities

- **Examples** of rechargeable batteries
  - Lithium ion (standard)
  - Metal air
  - Metal sulfur
  - Metal ion



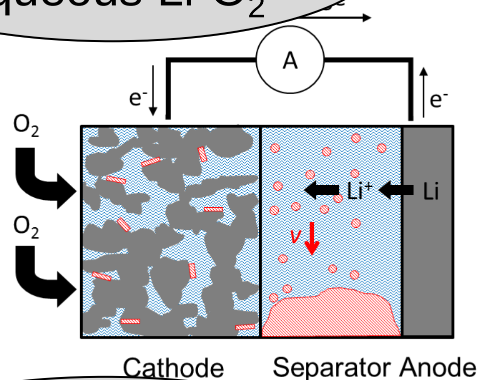
Adelhelm P. et al., *Beilstein Journal of Nanotechnology* 6(1), 1016–1055 (2015).



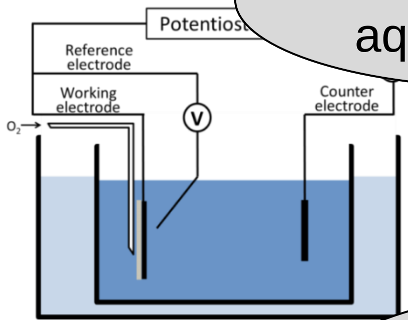
Clark S., Latz A. Horstmann B., *Batteries*, 4(1), 5 (2018).

Macroscopic Models

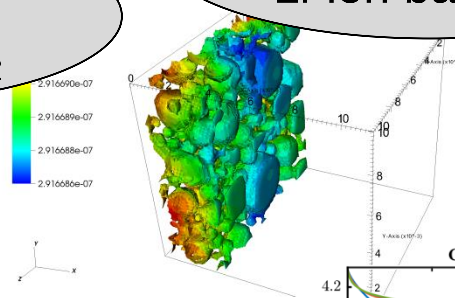
precipitation aqueous Li-O_2

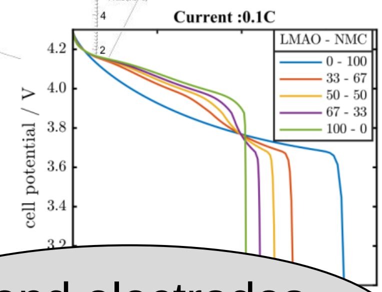


validation GDE aqueous Li-O_2

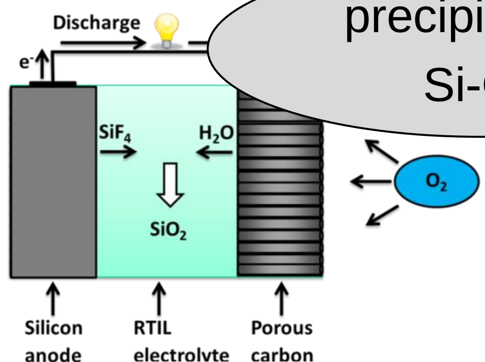


inhomogeneous SEI Li-ion batteries



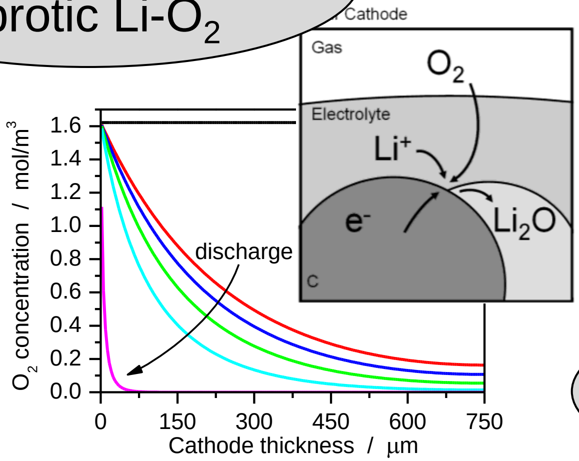


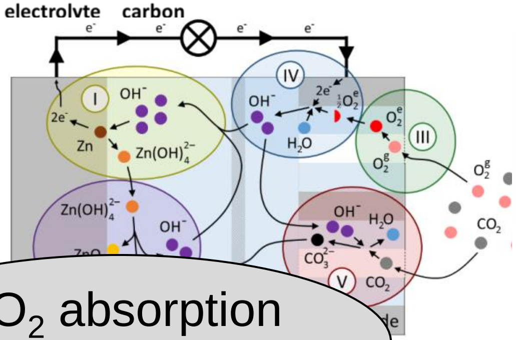
precipitation Si-O_2

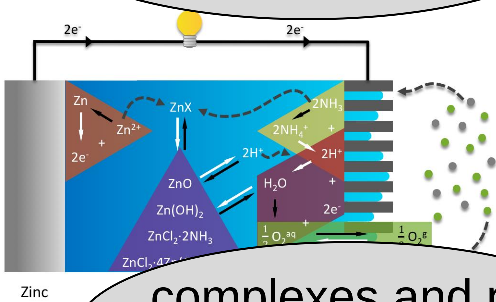


blend electrodes Li-ion batteries

pore-clogging aprotic Li-O_2





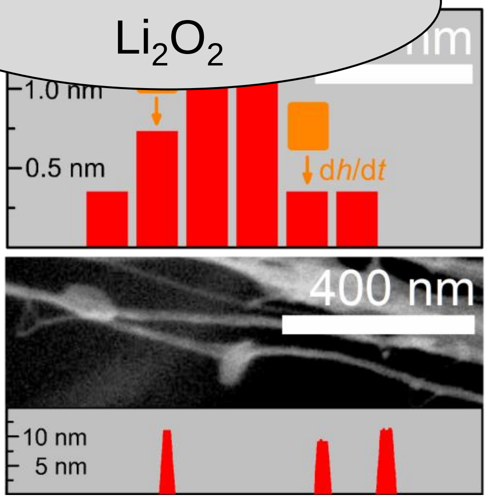


complexes and pH neutral Zn-O_2

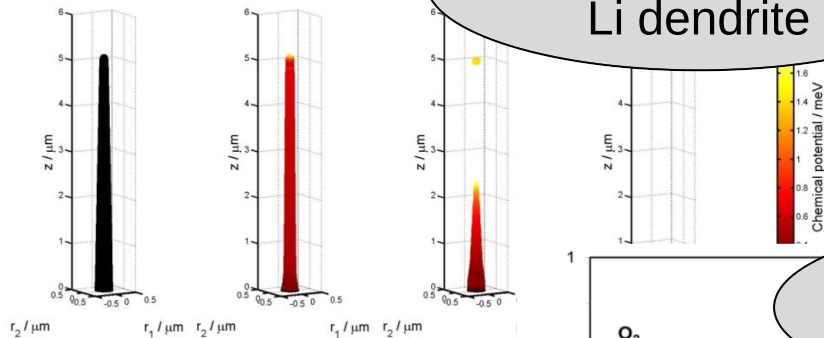
CO_2 absorption alkaline Zn-O_2

Mesoscopic Models

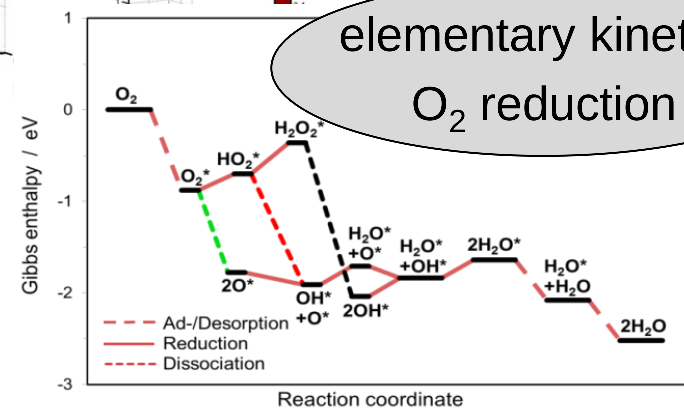
surface growth
Li_2O_2

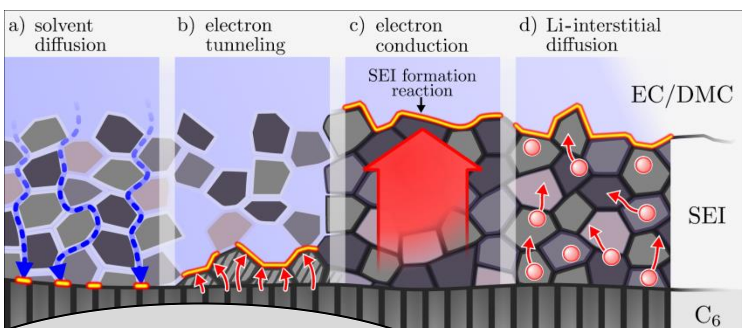


dissolution
Li dendrite

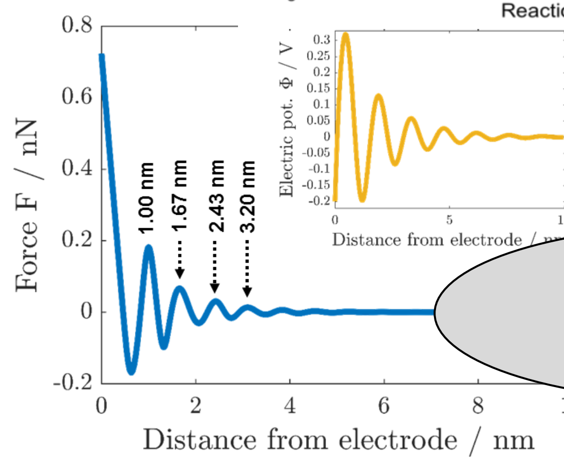


elementary kinetics
O_2 reduction





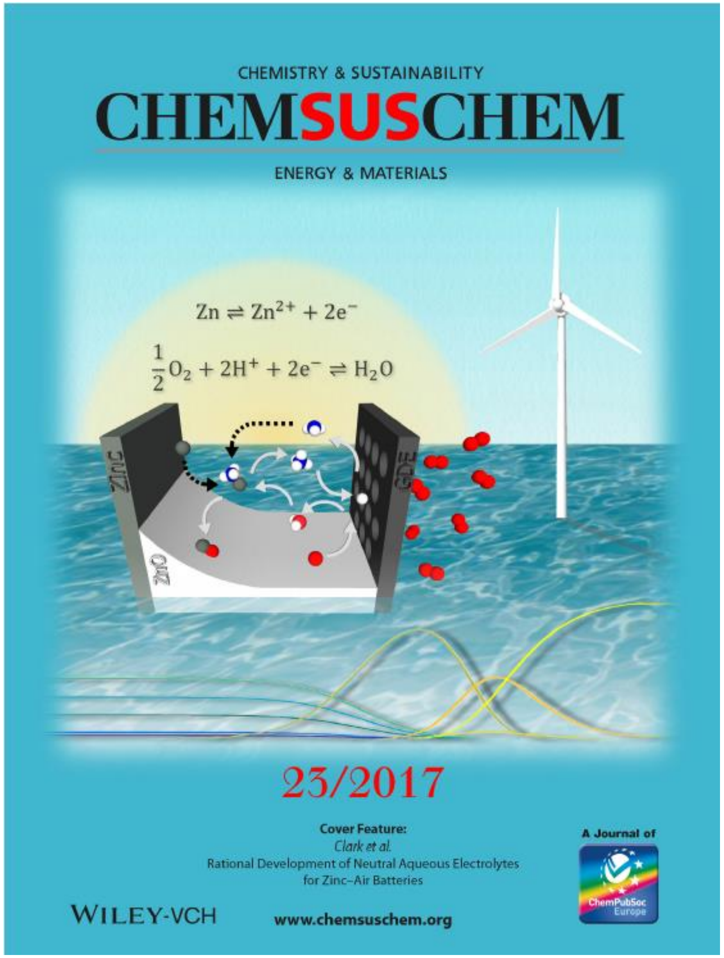
growth
SEI



double layer
ionic liquids

Content

1. Introduction
2. **Aqueous Zinc-Air Batteries**
   - Alkaline Electrolyte
   - Near-Neutral Electrolyte
3. Lithium-Ion Batteries
   - Growth of Solid Electrolyte Interphase
4. Conclusion



Overview

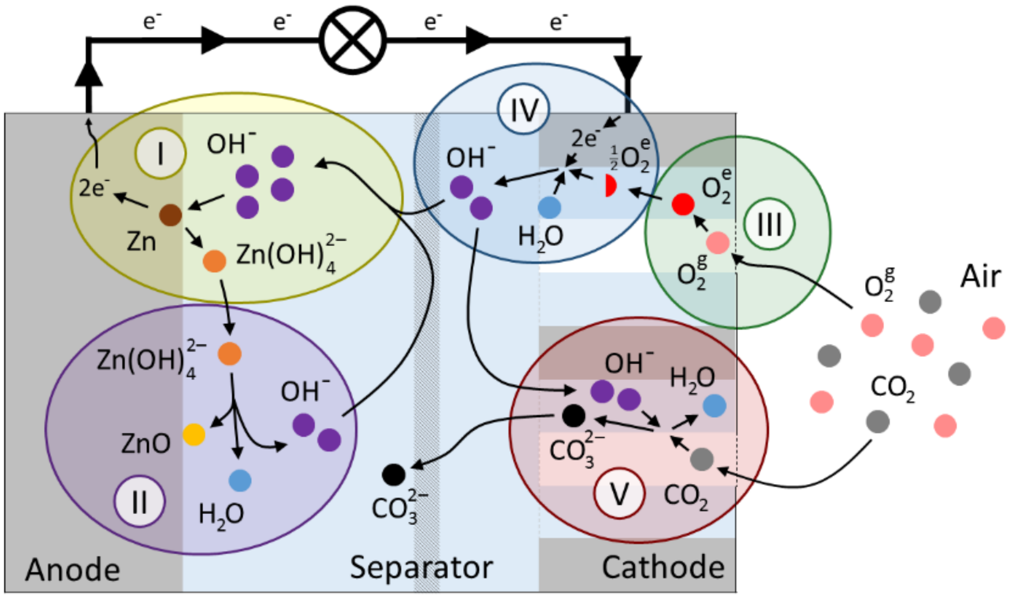
- Primary zinc-air battery **commercial**
  - High specific energy (1086 Wh·kg^{-1})
  - Low cost
  - High operational safety
- **Development of zinc-air batteries**
  - Goal: electrochemical rechargeability
  - Application: stationary energy storage
- Electrolytes:
  - Aqueous alkaline
  - Aqueous neutral
  - Ionic liquids

VARTA

Alkaline Electrolyte: Overview

KOH

- $Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$
- $Zn(OH)_4^{2-} \rightleftharpoons ZnO + 2OH^- + H_2O$
- $O_2^g \rightleftharpoons O_2^e$
- $\frac{1}{2}O_2^e + H_2O + 2e^- \rightleftharpoons 2OH^-$
- $CO_2^e + 2OH^- \rightleftharpoons CO_3^{2-} + H_2O$



Advantages

- High ionic conductivity
- Stable discharge voltage
- Reliable at low currents

Challenges

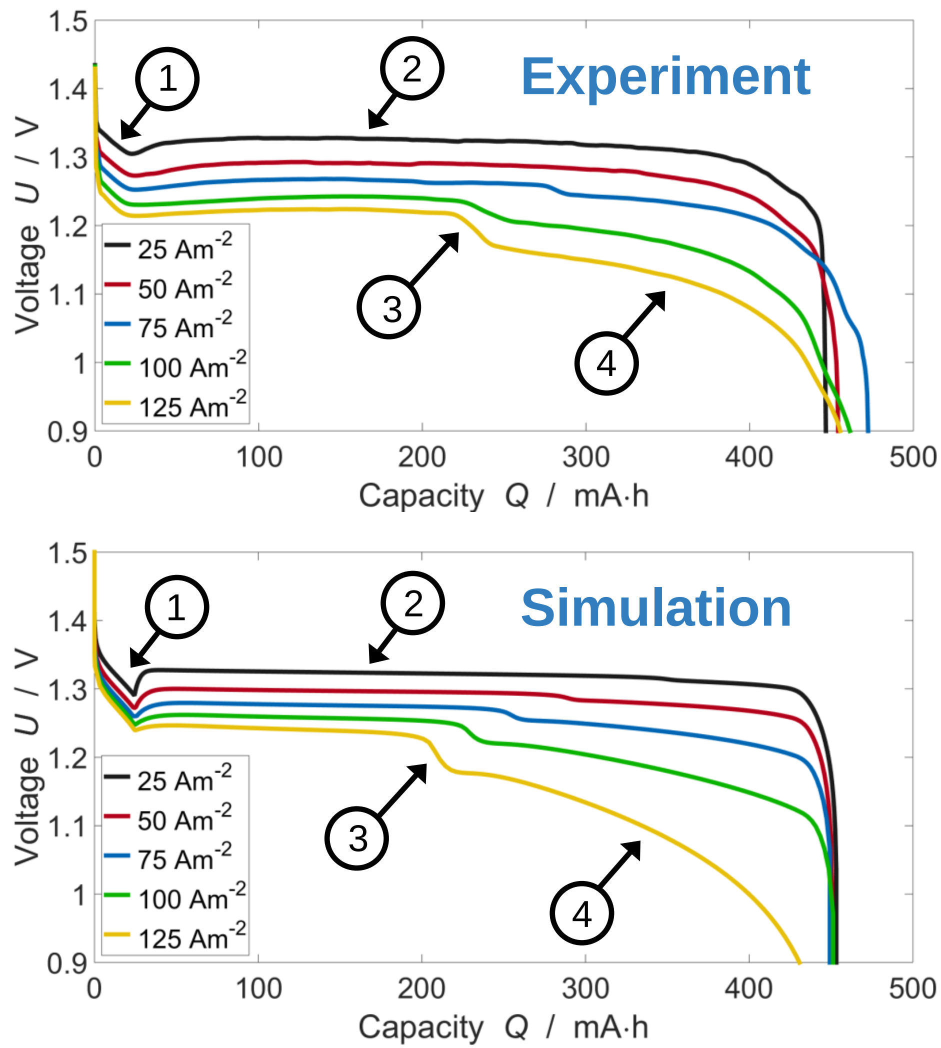
- Carbonation of electrolyte
- Dendritic/mossy Zn deposition
- Zn passivation

J. Stamm, A. Varzi, A. Latz, B. Horstmann, *Journal of Power Sources*, *360*, 136-149 (2017).

Galvanostatic Discharge

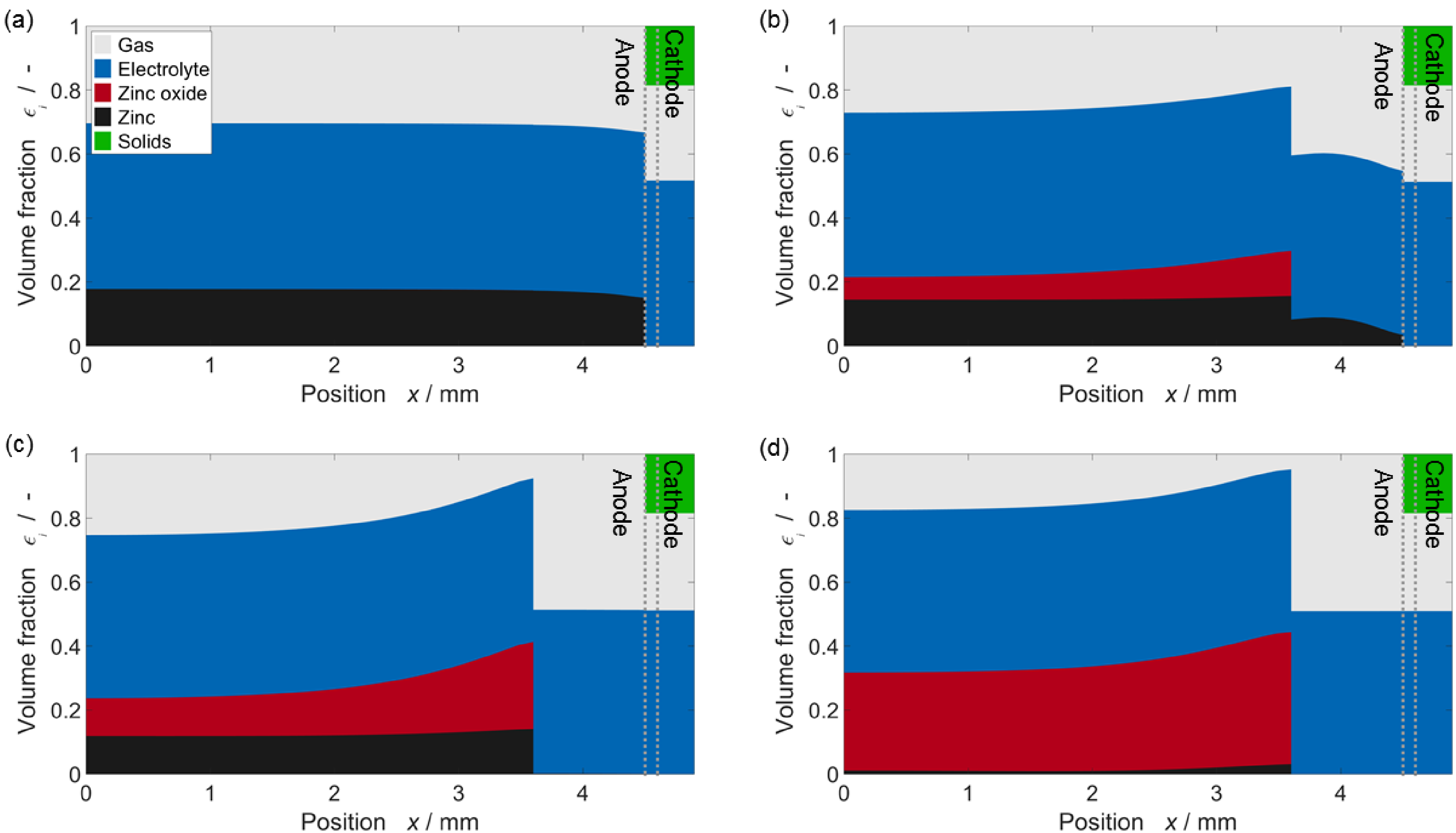
Simulated ZAB discharge
validated by experiment

1. **Nucleation** of ZnO
2. **Conversion** reaction
3. Step due to **inhomogeneous ZnO precipitation**
4. Voltage loss due to **zinc passivation**



J. Stamm, A. Varzi, A. Latz, B. Horstmann,
Journal of Power Sources, *360*, 136-149 (2017).

Alkaline Coin Cell: Volume Fractions



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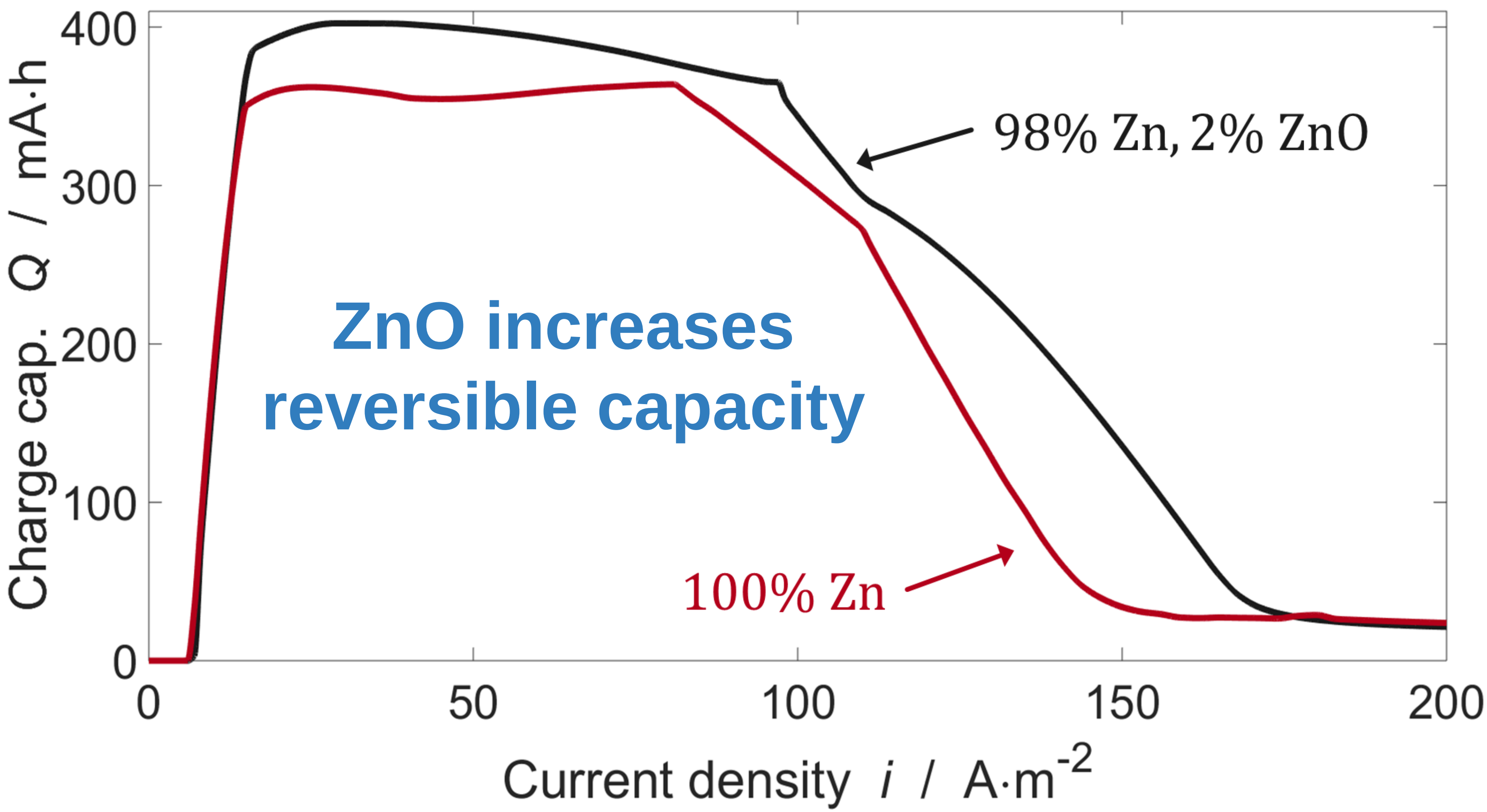
Journal of Power Sources, *360*, 136-149 (2017).

Galvanostatic Discharge



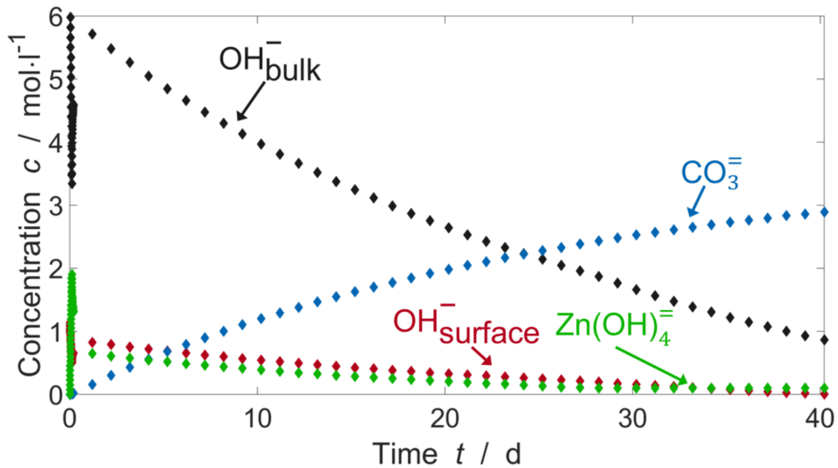
J. Stamm, A. Varzi, A. Latz, B. Horstmann,
Journal of Power Sources, *360*, 136-149 (2017).

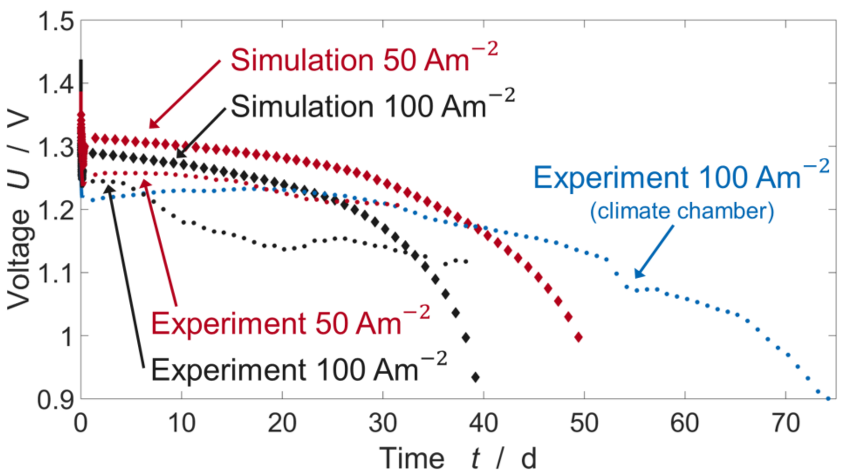
Lifetime Limitation

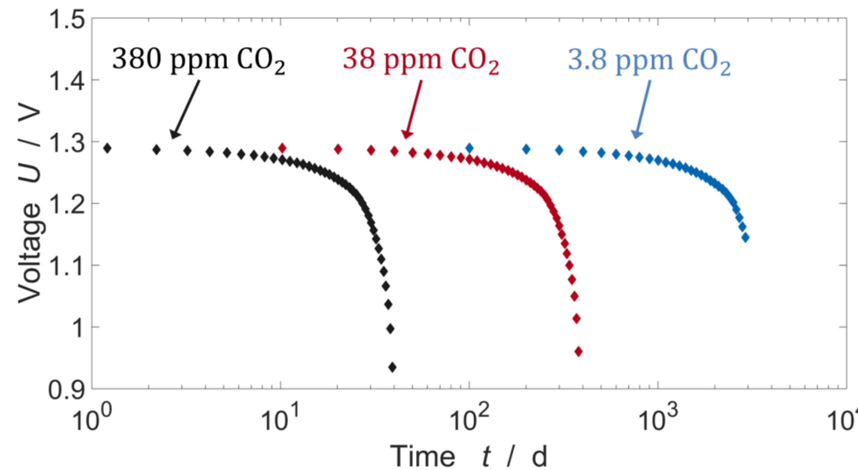
- **Exposure to CO_2 limits alkaline ZAB lifetime**

$$CO_2^{e} + 2OH^- \rightleftharpoons CO_3^{2-} + H_2O$$

- Lowers electrolyte conductivity
- Slows reaction kinetics





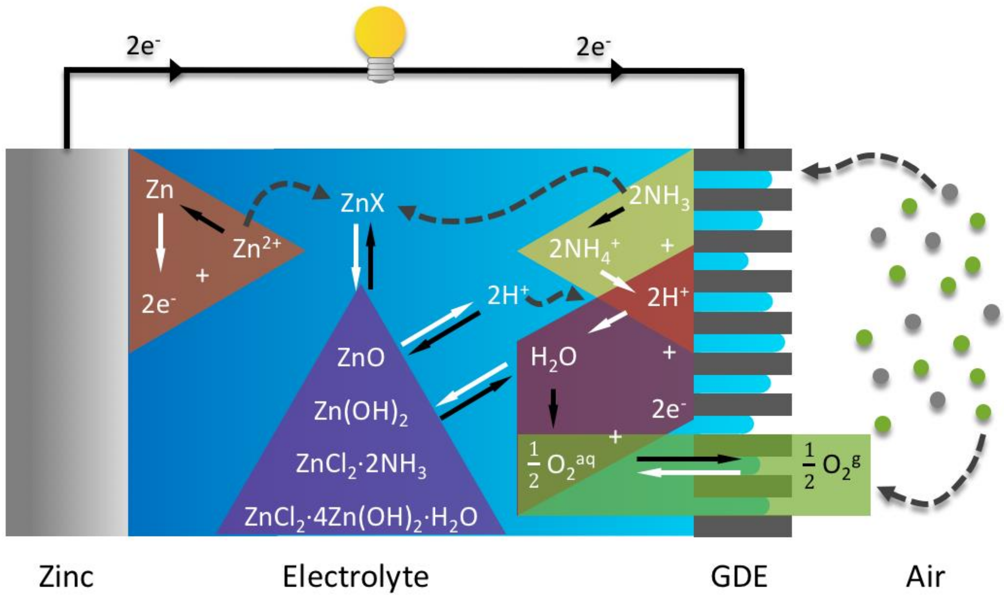


J. Stamm, A. Varzi, A. Latz, B. Horstmann,
Journal of Power Sources, *360*, 136-149 (2017).

Near-Neutral Aqueous Electrolyte: Overview

$ZnCl_2$ – NH_4Cl – NH_4OH

- $Zn \rightleftharpoons Zn^{2+} + 2e^-$
- $Zn^{2+} + xX \rightleftharpoons Zn(X)_x^y$
- $Zn(X)_x^y + H_2O \rightleftharpoons Zn(X)_x\ (s) + yH^+$
- $NH_4^+ \rightleftharpoons NH_3 + H^+$
- $O_2^g \rightleftharpoons O_2^e$
- $\frac{1}{2}O_2^e + 2H^+ + 2e^- \rightleftharpoons H_2O$



Advantages

- No carbonation of the electrolyte
- More homogeneous zinc deposition
- Improved cycling stability

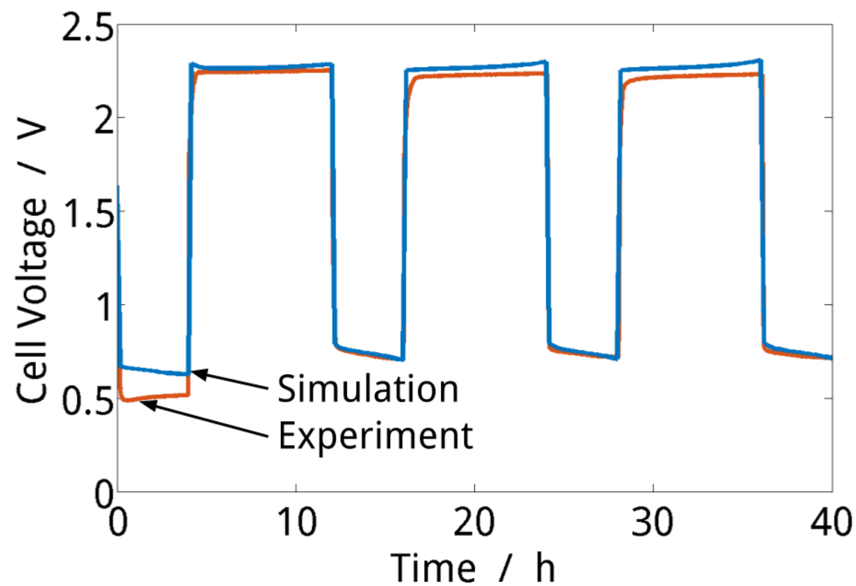
Challenges

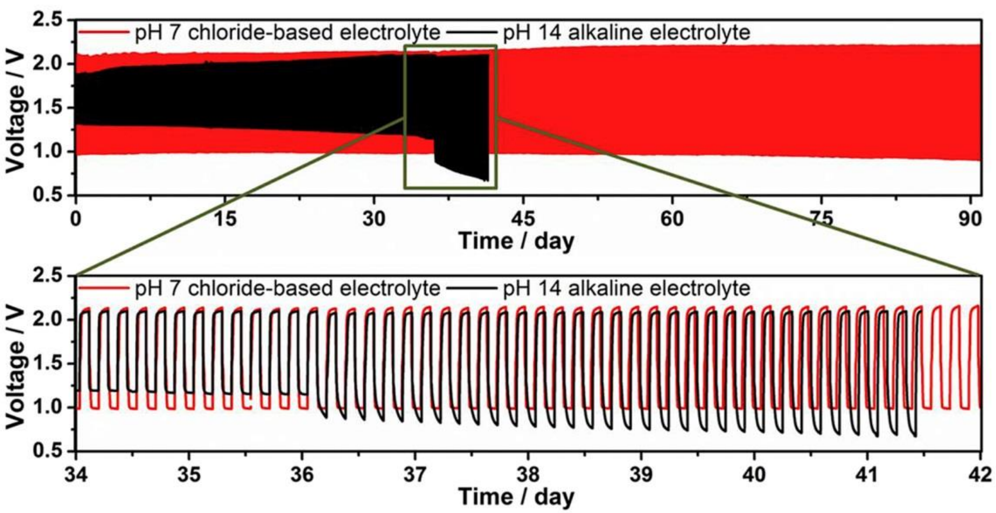
- pH stability
- Solid discharge product
- Stable air electrode

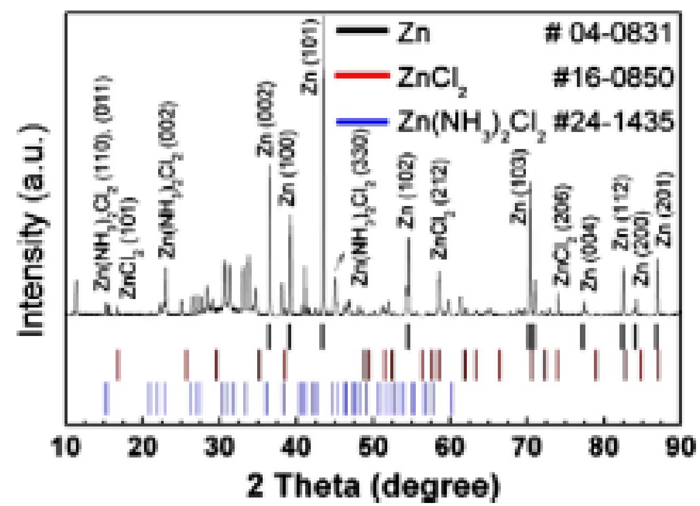
S. Clark, A. Latz, B. Horstmann,
Rational Development of Neutral Aqueous Electrolytes for Zinc-Air Batteries.
ChemSusChem 10, 4735–4747 (2017).

Experimental Validation

- A*STAR-IMRE, Singapore (Prof. Yun Zong)
- Experiments proof cycling stability



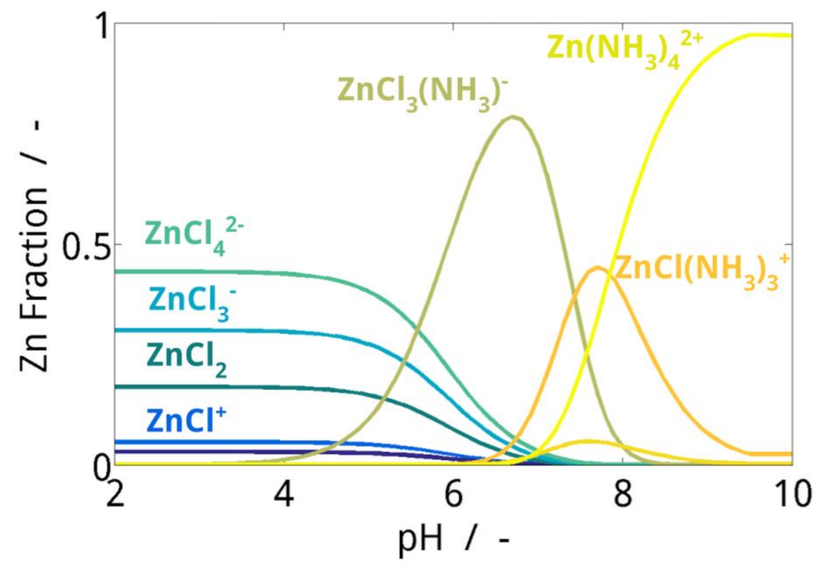




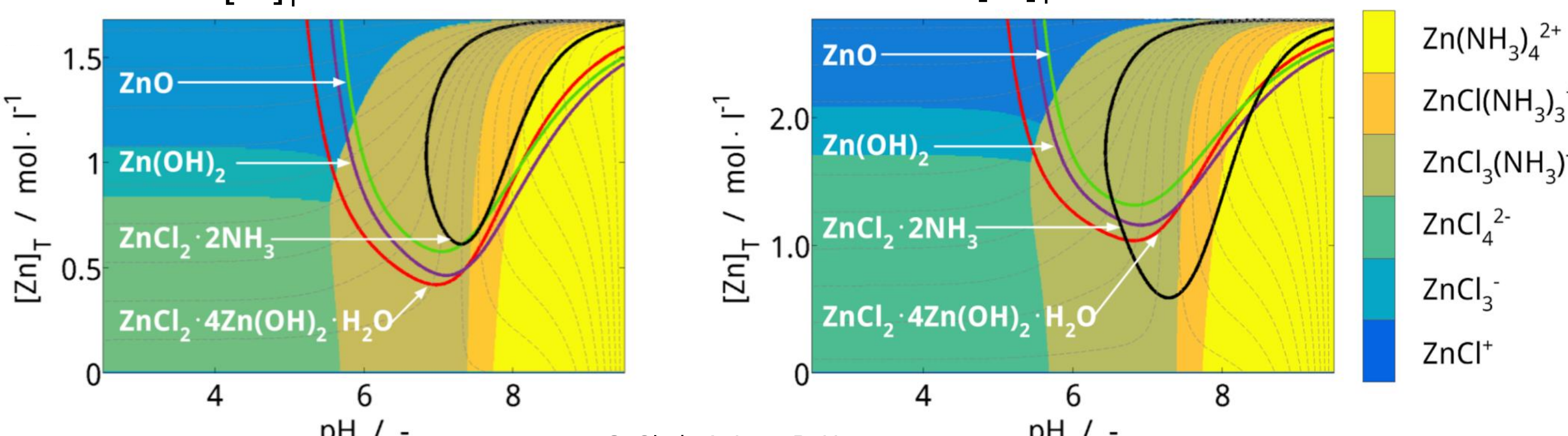
Goh, et al., *J. Electrochem. Soc*. **161** (14) A2080-2086, (2014).
Sumboja et al., *Power Sources* **332,** 330–336 (2016).
S. Clark, A. Latz, B. Horstmann, *ChemSusChem* 10, 4735–4747 (2017).

Thermodynamics of Neutral Electrolyte

- **Quasiparticle model** for zinc complexes
- Various zinc precipitates



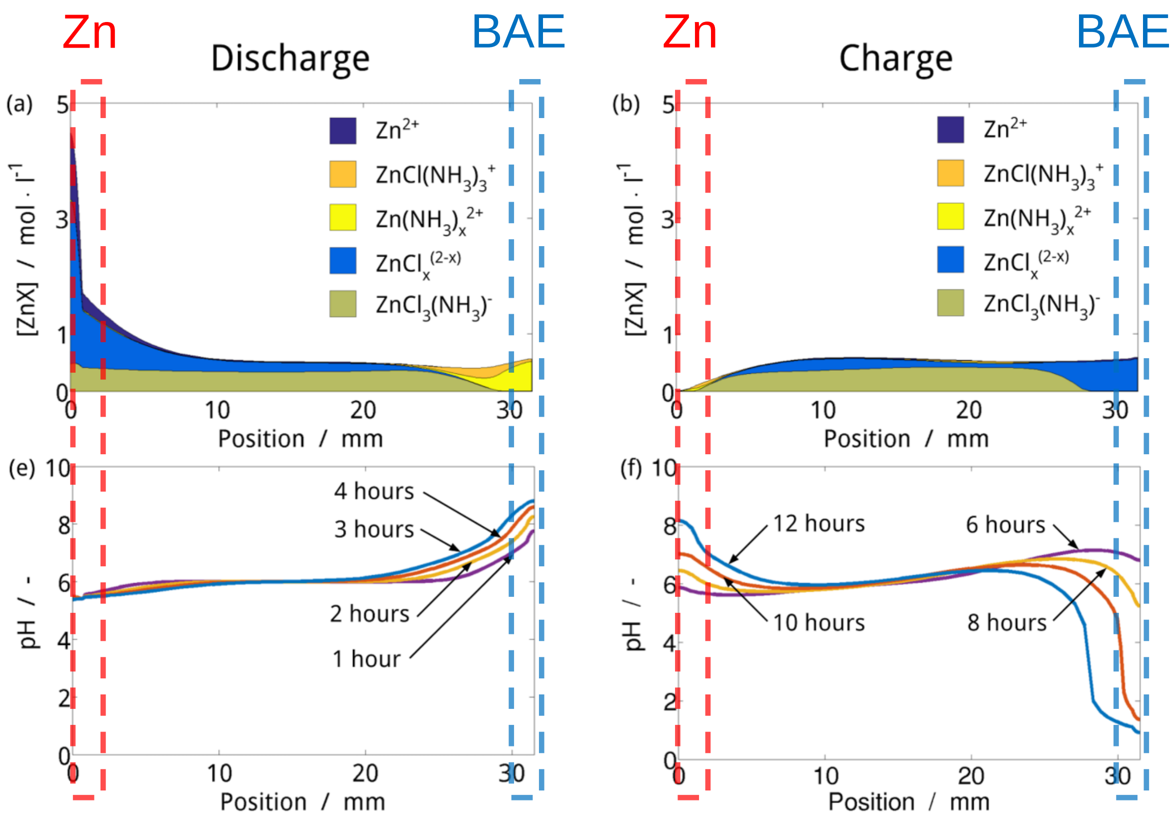
$[Cl]_T = 3.36M$ $[Cl]_T = 5.54M$



S. Clark, A. Latz, B. Horstmann,
Rational Development of Neutral Aqueous Electrolytes for Zinc-Air Batteries.
ChemSusChem 10, 4735–4747 (2017).

Electrolyte Dynamics

- Electrolyte composition strongly coupled with pH, Zn^{2+}



$$NH_4 \leftrightarrows NH_3 + H^+$$

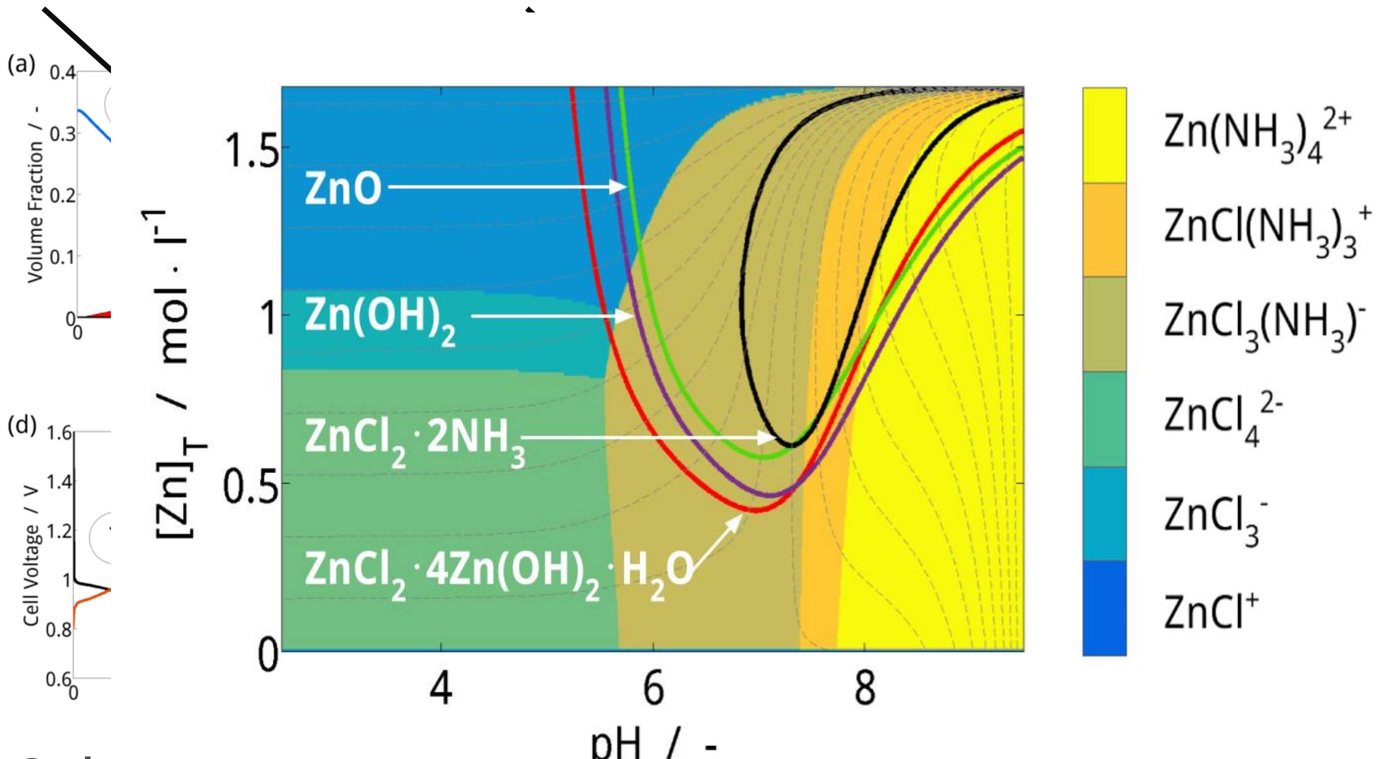
$$Zn^{2+} + nNH_3 \leftrightarrows Zn(NH_3)_n^{2+}$$

- Buffer reactions stabilize pH
- Limited by slow NH_3 transport
- pH in BAE can become acidic during charging

S. Clark, A. Latz, B. Horstmann,
Rational Development of Neutral Aqueous Electrolytes for Zinc-Air Batteries.
ChemSusChem 10, 4735–4747 (2017).

Optimization of Electrolyte Composition

- Electrolyte composition strongly affects cell performance.
- pH 6 - 7, high chloride content = precipitation of unwanted solids



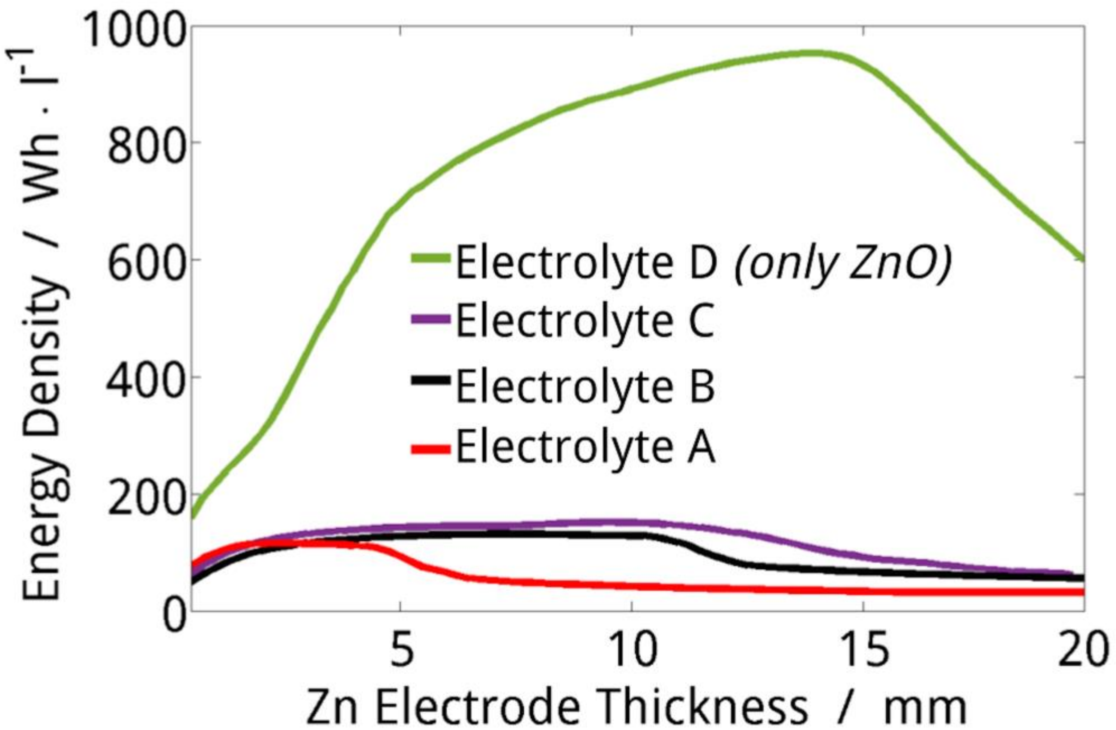
- pH 8, lower chloride content = stable operation

S. Clark, A. Latz, B. Horstmann,
Rational Development of Neutral Aqueous Electrolytes for Zinc-Air Batteries.
ChemSusChem 10, 4735–4747 (2017).

HIU Helmholtz Institute Ulm Electrochemical Energy Storage

Discharge Product and Energy Density

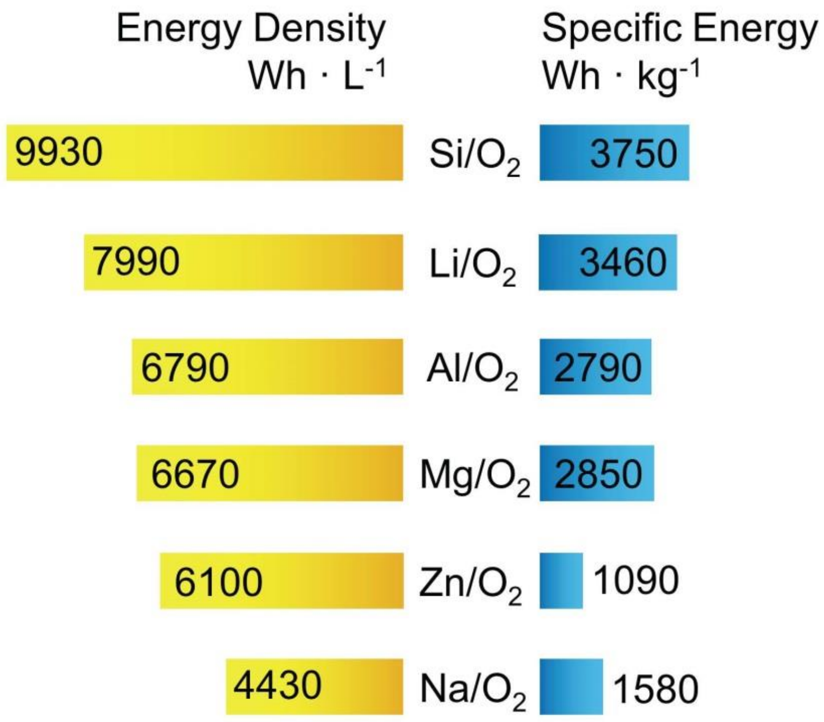
- Unwanted discharge product consumes electrolyte and passivates Zn electrode.



S. Clark, A. Latz, B. Horstmann,
Rational Development of Neutral Aqueous Electrolytes for Zinc-Air Batteries.
ChemSusChem 10, 4735–4747 (2017).

Conclusion

- Metal air batteries:
  - **High risk / high gain**
- Applications:
  - Stationary, mobile, portable
- Various metal ions
  - **Lithium** air batteries: lightweight
  - **Zinc** air batteries: commercial
- Various electrolytes
  - New **aqueous** electrolytes
  - Ionic liquids



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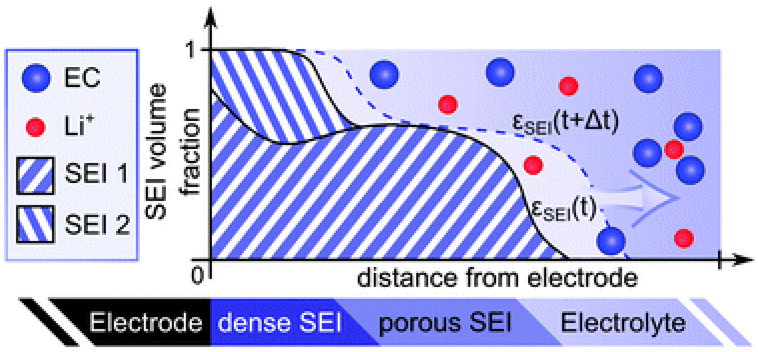
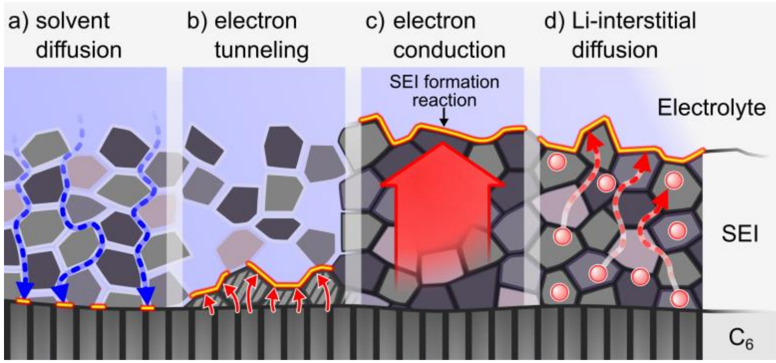
   - Near-Neutral Electrolyte

3. **Lithium-Ion Batteries**
   - Growth of Solid Electrolyte Interphase

4. Conlusion





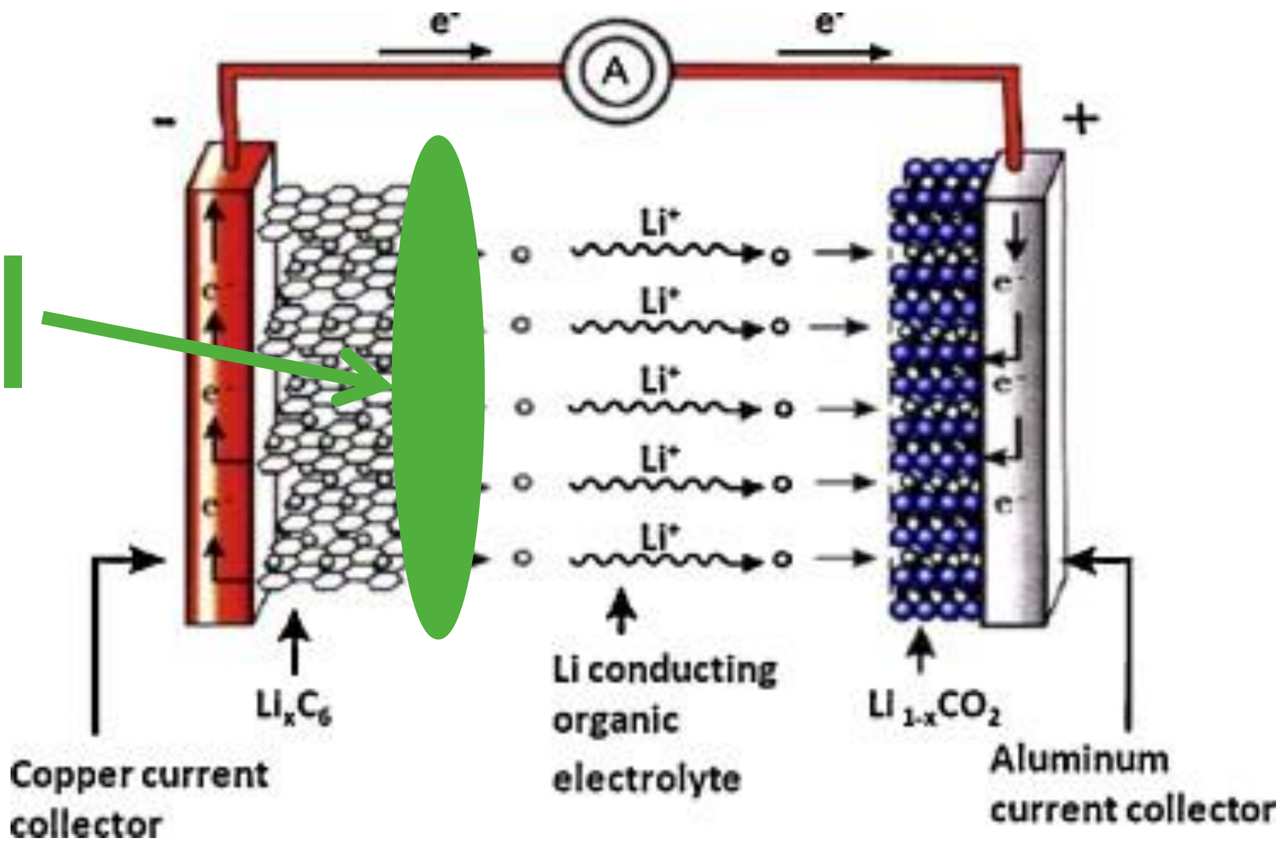
Lithium-Ion Batteries: Electrochemical Cell

negative electrode
discharge: **anode**

separator

postive electrode
discharge: **cathode**

SEI



Scrosati, B. & Garche, J., *Journal of Power Sources*, 195(9), 2419. (2010).

Solid Electrolyte Interphase (SEI)

SEI is complicated

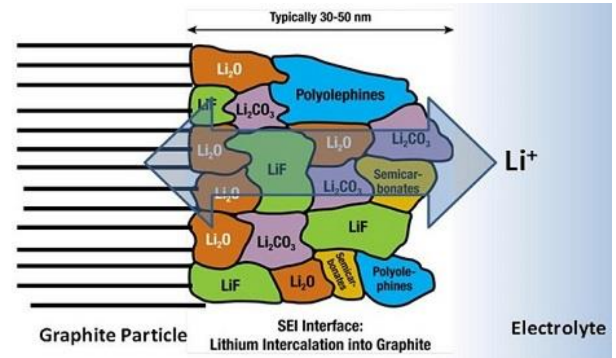
- **Inorganic** and **organic** components
- **Structure**

YES, but universal properties

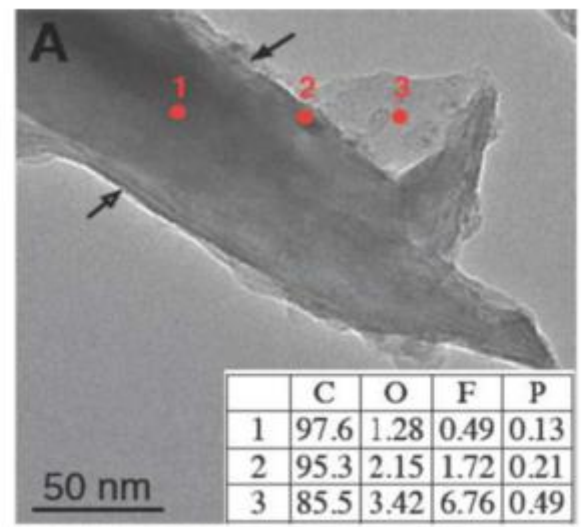
- **Long-term growth** law $L(t) \propto \sqrt{t}$
- SEI works in various systems

Our goal

- Develop **simple mechanistic model**
- **Predict new observable** properties from fundamental assumptions



Source:
https://www.liverpool.ac.uk/chemistry/research/hardwick-group/research



	C	O	F	P
1	97.6	1.28	0.49	0.13
2	95.3	2.15	1.72	0.21
3	85.5	3.42	6.76	0.49

Nie et. Al, JECS, 162 A7008-A7014 (2015)

Solid Electrolyte Interphase (SEI)

Formation

- **Reduction of electrolyte on graphite**, e.g. Ethylene Carbonate (EC)

$$2EC + 2Li^{+} + 2e^{-} \rightleftharpoons (CH_2OCO_2Li)_2 + R$$

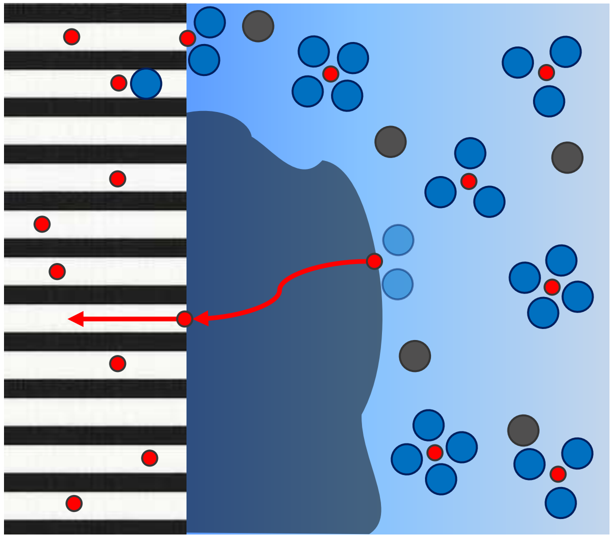
SEI advantages

- Almost **no further electrolyte reduction**
- Protection of graphite from exfoliation
- Increase in mechanical stability of graphite

SEI disadvantages

- Li-ion consumption
- Continuous growth
- Increase in impedance

} **capacity fade** (Li-ion consumption, continuous growth)



Reviews & Papers on SEI composition:

- Agubra, V. a., & Fergus, J. W. *Journal of Power Sources* **268**, 153–162 (2014).
- Verma, P., Maire, P., & Novák, P. *Electrochimica Acta* **55**(22), 6332–6341 (2010).
- Seo, D. M., Chalasani, D., Parimalam, B. S., Kadam, R., Nie, M., & Lucht, B. L. (2014). *ECS Electrochemistry Letters* , **3** (9), A91.

Continuum Models in Literature

Long-term SEI growth

- **Homogeneous** composition
- **Single** transport mechanism
- Fast reaction kinetics
- Single reaction interface

transport-limited growth

$$L(t) \propto \sqrt{t}$$

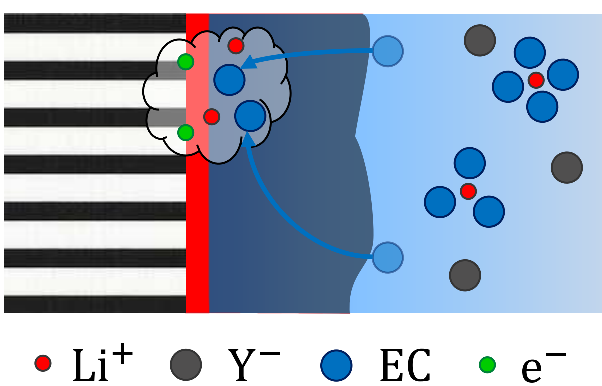
Different rate-limiting transport mechanisms (RLTM) in literature:

Solvent/anion diffusion:
- Pinson, M.B. & Bazant, M.Z. *Journal of the Electrochemical Society* **160**, A243-A250 (2012).
- Ploehn, H.J., Ramadass, P. & White, R.E. *Journal of The Electrochemical Society* **151**, A456 (2004).

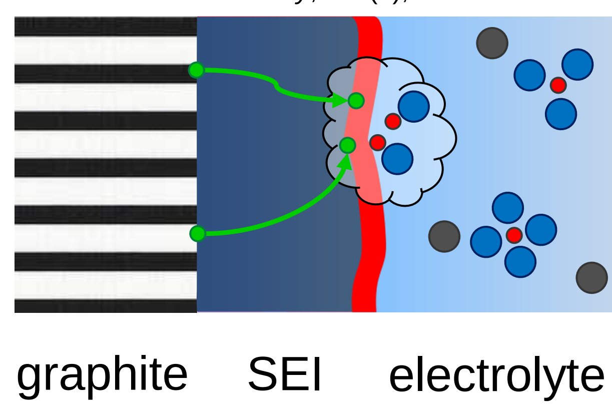
Electron conduction:
- Christensen, J. & Newman, J. *Journal of The Electrochemical Society* **151**, A1977 (2004).

Both:
- Tang, M., Lu, S., & Newman, J. (2012). *Journal of The Electrochemical Society*, **159**(11), A1775

Tunneling:.
– Li et. al (2015). *Journal of the Electrochemical Society*, *162*(6), A858–A869.



vs.



Model Overview - Concept

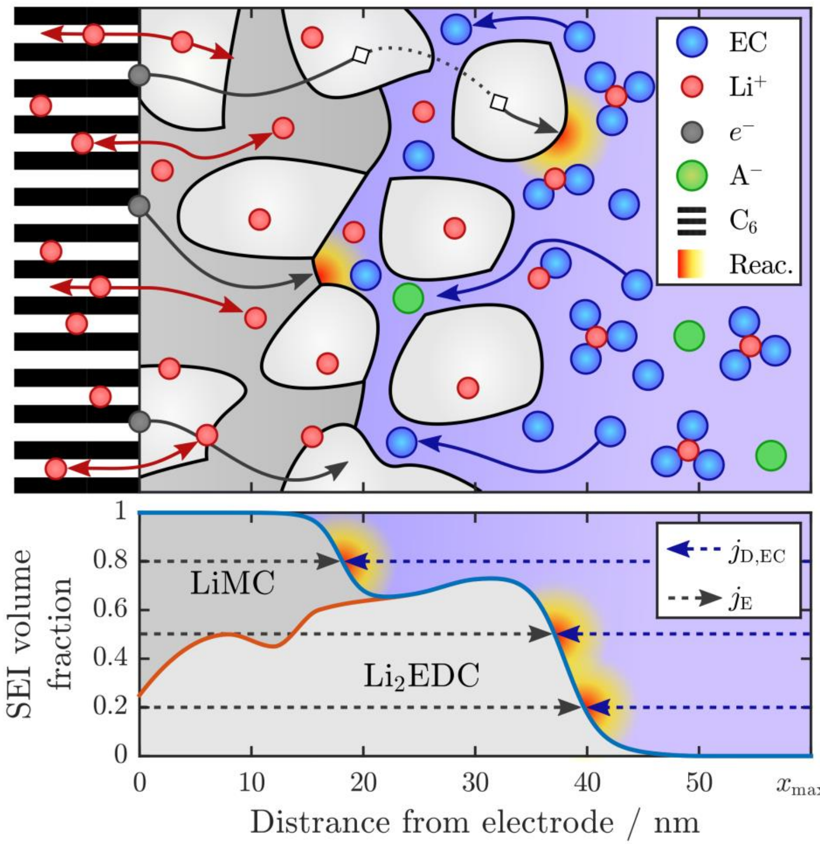
1D model for long-term growth

Transport of **all SEI precursors**
- e^- restricted to SEI
- Solvent restricted to pores

Nano **porous SEI**

Binary solvent mixture
- EC/DMC
- Neglect Li^+ and salt anion

Up to **two SEI compounds**



F. Single, B. Horstmann, A. Latz, *Journal of The Elec. Society*, 164(11), E3132 (2017).
F. Single, B. Horstmann, A. Latz, P*hys. Chem. Chem. Phys*., 18, 178101, (2016).

Model Overview – Transport & Reactions

Electronic current

- Ohm's law $j_E = \sigma \nabla \Phi$

Solvent

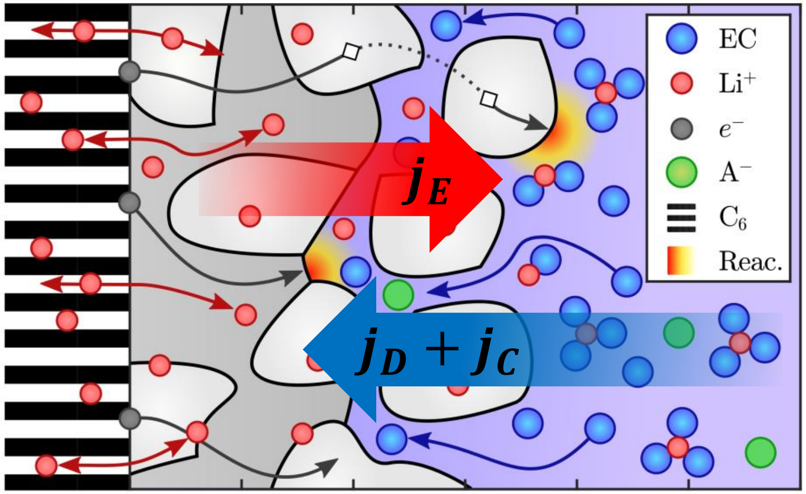
- Fick´s law $j_D = D \nabla c$
- Convection $j_C = c v$

Bruggeman Relation

- $\sigma = (1-\varepsilon)^{1.5} \sigma_{\text{Bulk}}$
- $D = \varepsilon^{\beta} D_{\text{Bulk}}$

B.V. Reaction Rate, $\dot{s} \propto A \sinh(\eta)$

- $\eta = \Phi - \Phi^0_{\text{EC}} + \ln c$
- $A = \frac{6}{a_0} \varepsilon \left(1 - \varepsilon - \frac{a_0^2}{6} \varepsilon''\right)$



Primary Variables

$\varepsilon = \varepsilon_1 + \varepsilon_2$, c, Φ, v

Parameters

β, σ_{Bulk}, D_{Bulk}, a_0, Φ^0_{EC}

F. Single, B. Horstmann, A. Latz, *Journal of The Elec. Society*, 164(11), E3132 (2017).
F. Single, B. Horstmann, A. Latz, *Phys. Chem. Chem. Phys.*, 18, 178101, (2016).

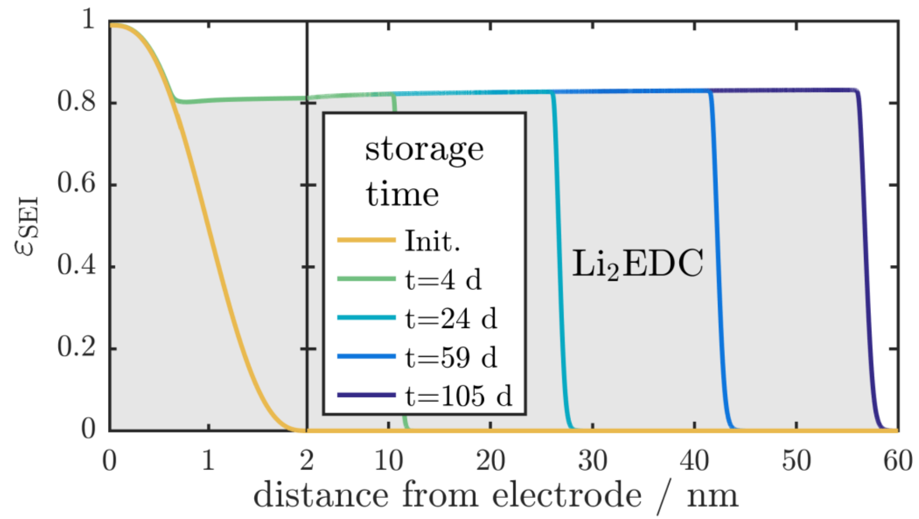
Simulation: Single SEI Compound

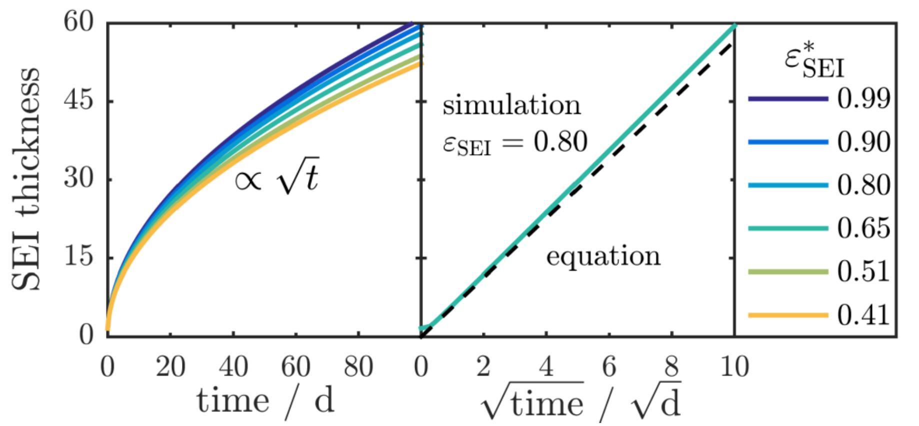
Porous SEI
- **Homogeneous**

SEI growth
- Transport limited
- **$\sqrt{t}$ - growth**
- Governed / limited by **electron conduction**

$$\frac{\boldsymbol{\sigma}^*}{\boldsymbol{D}^*}\frac{2RT}{cF^2} = \frac{1}{2} + \frac{\boldsymbol{\beta}\boldsymbol{\varepsilon}^*_{\mathbf{SEI}}}{\boldsymbol{\varepsilon}^*}$$

$$\boldsymbol{L}(\boldsymbol{t}) = \sqrt{V_1\boldsymbol{\sigma}^*\boldsymbol{\Delta\Phi}/\varepsilon^*_{\mathrm{SEI}}F} \cdot \sqrt{\boldsymbol{t}}$$





F. Single, B. Horstmann, A. Latz, *Journal of The Elec. Society*, 164(11), E3132 (2017).
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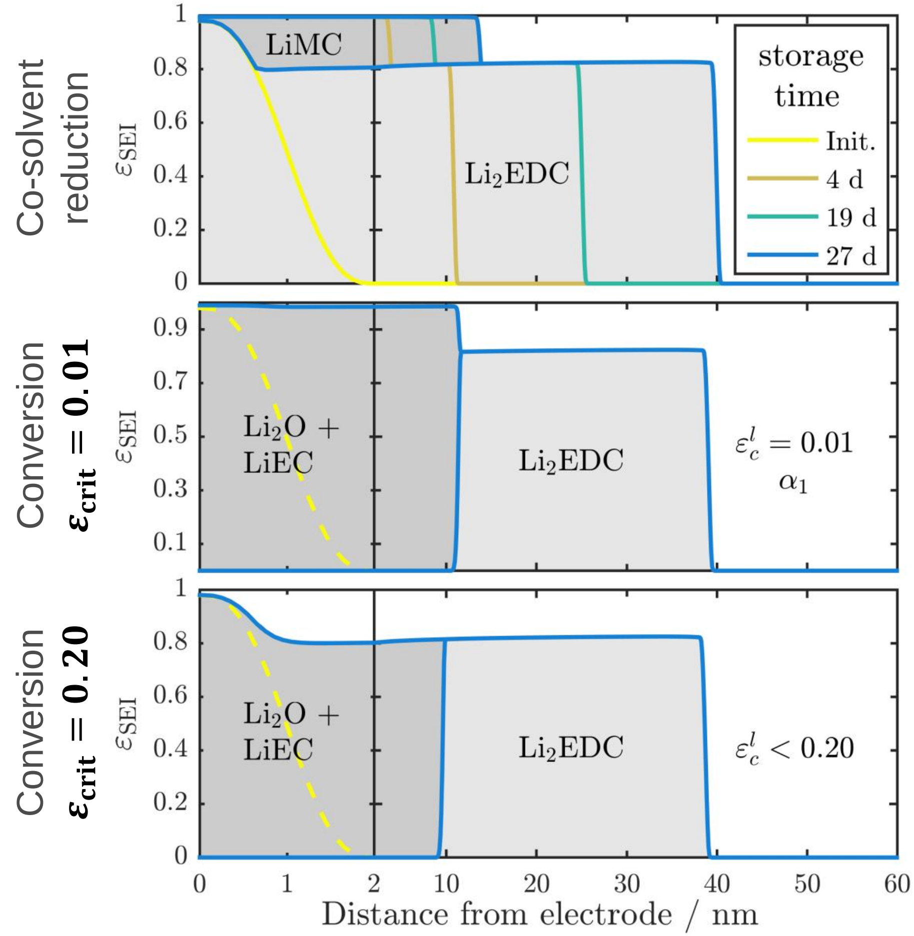
Simulation: Dual-Layer SEI

Second SEI species
- **Co-solvent** reduction
- **Reduction** of Li_2EDC

Different reduction potentials
- $\Phi^0_{EC} = 0.8\ V$
- $\Phi^0_{DMC} = 0.3\ V$

Dual-layer SEI
- L total SEI thickness
- L_I thickness of the inner layer



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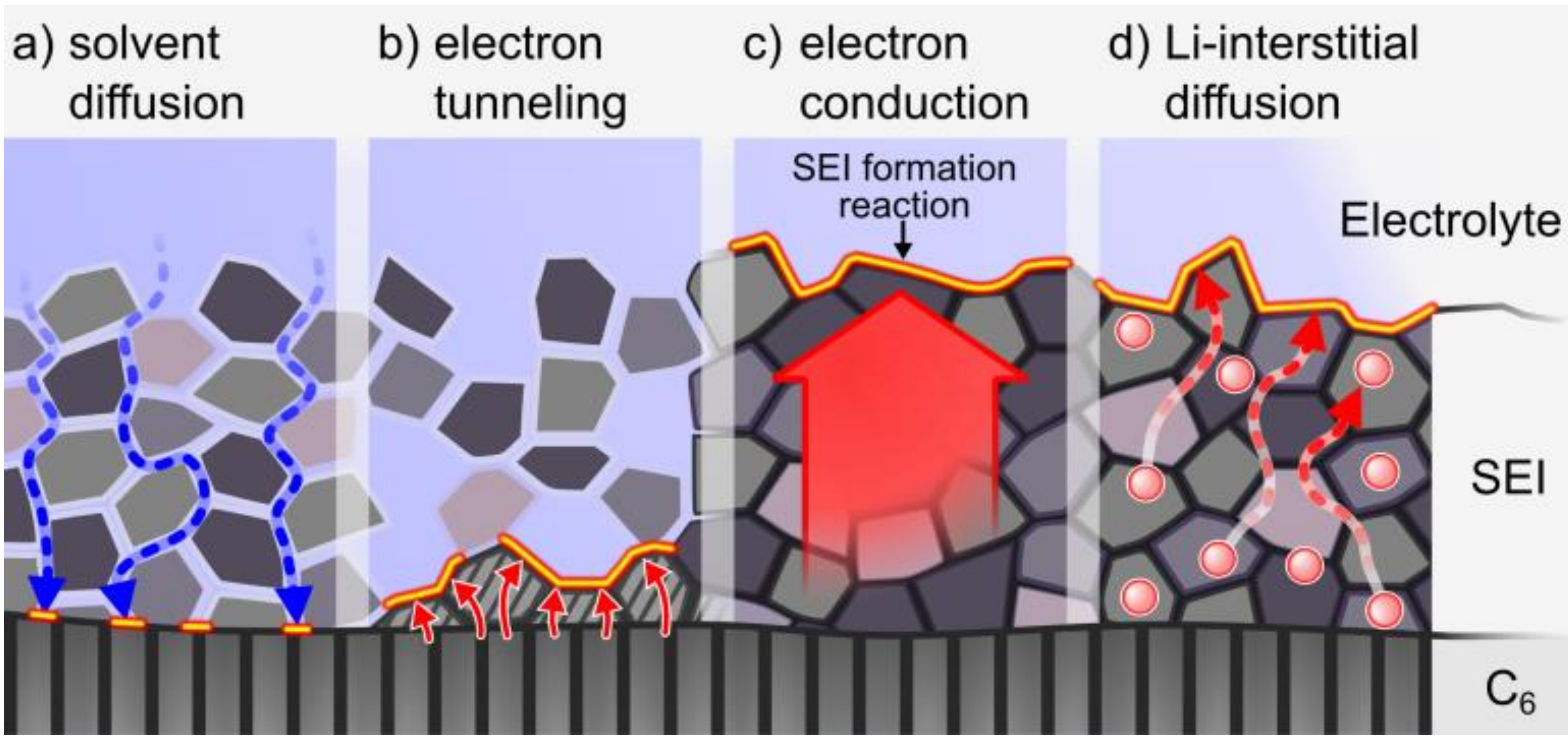
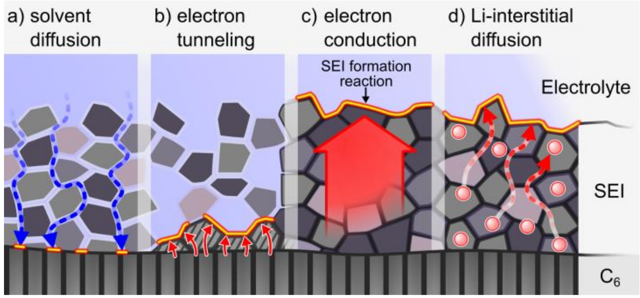
Identifying RLTM



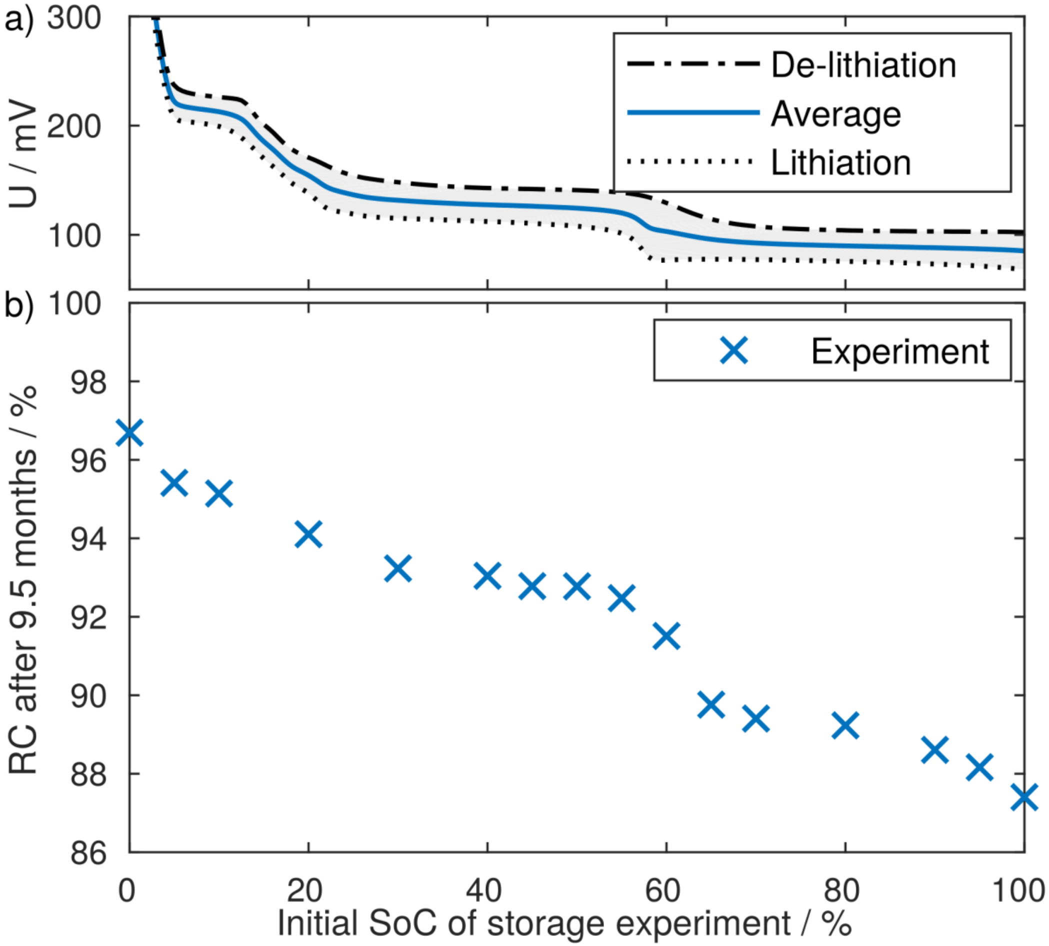
Identifying the RLTM



Compare four different RLT mechanisms

1. Electron conduction
2. Electron tunnelin
3. Li-interstitial diffusion
4. Solvent diffusion

Relative **capacity fade ΔC** after **9.3 months** storage (**open circuit**) vs. the SOC during storage.



Experimental data: Keil, P., et al., (**2016**). *Journal of The Electrochemical Society*, **163**(9), A1872–A1880.

Identifying the RLTM

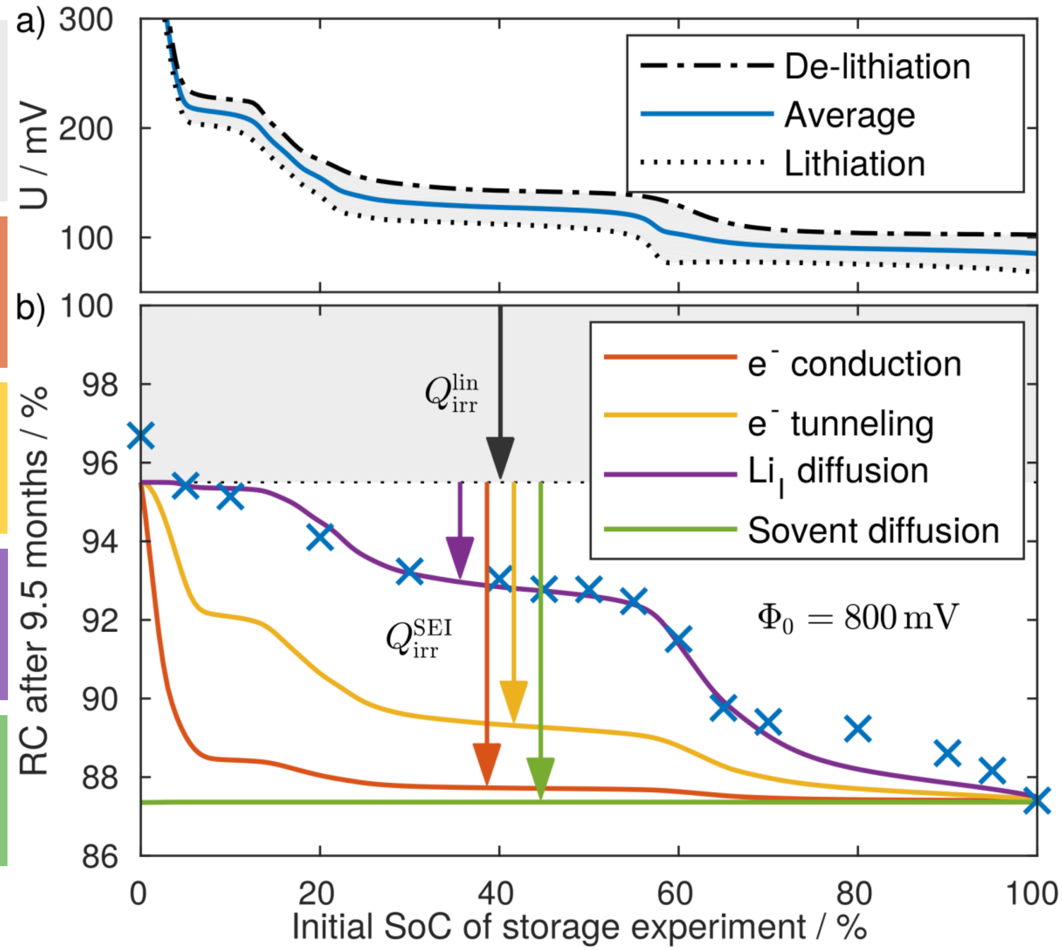
Compare four different RLT mechanisms

$$\Delta C \propto \sqrt{\Phi^{0}_{EC} - OCV(SOC)}$$

$$\Delta C \propto \alpha(SOC)\ln\left(1 + \beta(SOC)\right)$$

$$\Delta C \propto \exp\left(\frac{1}{2}\frac{F}{RT}OCV(SOC)\right)$$

$$\Delta C = const.$$



Experimental data: Keil, P., et al., (**2016**). *Journal of The Electrochemical Society*, **163**(9), A1872–A1880.

Conclusion

Extended SEI modeling approach, predictions:

- **Thickness evolution**
- **Porosity**
- **Dual-layer SEI** (several scenarios)
- **SOC dependence of cap. fade**

Comparison of different RLTMs:

- **SEI thickness fluctuations** (solvent diffusion)
- **SOC dependence** of cap. Fade
- **RLTM: Interstitial Diffusion**
- **Impedance spectroscopy**

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Content

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2. Aqueous Zinc-Air Batteries
   - Alkaline Electrolyte
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   - Growth of Solid Electrolyte Interphase
4. **Conclusion**

Outlook

- Understanding **electrochemical surfaces** (in-situ experiments?)
  - Electrochemical surface layers, e.g., ionic liquids
  - Interfacial stability, e.g., SEI, plating
  - Electrodeposition and –dissolution, e.g., lithium metal

- Designing **next-generation batteries**
  - Metal-air batteries
  - Multi-valent ions
  - Experimental designs …

- Probabilistic/stochastic modeling of **lithium-ion batteries**
  - State estimation
  - Uncertainty propagation
  - Stochastic scale coupling

HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

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- DAAD: PostDoc Scholarship
- Helmholtz Association: HIU, GigaStore

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European Commission

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HELMHOLTZ ASSOCIATION

ulm university universität uulm

DTU Technical University of Denmark

HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

Co-Supervised Students

PhD Students

- Timo Danner
- Fabian Single
- Simon Clark
- Tobias Schmitt
- Max Schammer
- Linda Bolay

Master Students

- Daniel Eberle
- Emre Durmus
- Erkmen Karaca
- Johannes Stamm

ulm university universität uulm

University Stuttgart
Institute for Thermodynamics
and Thermal Engineering

Westfälische
Wilhelms-Universität
Münster