HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

Birger Horstmann

Theory-Based Development of Metal-Air Batteries

ulm university universität ulm

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

KIT ulm university universität ulm ZSW DLR


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Eating and Breathing

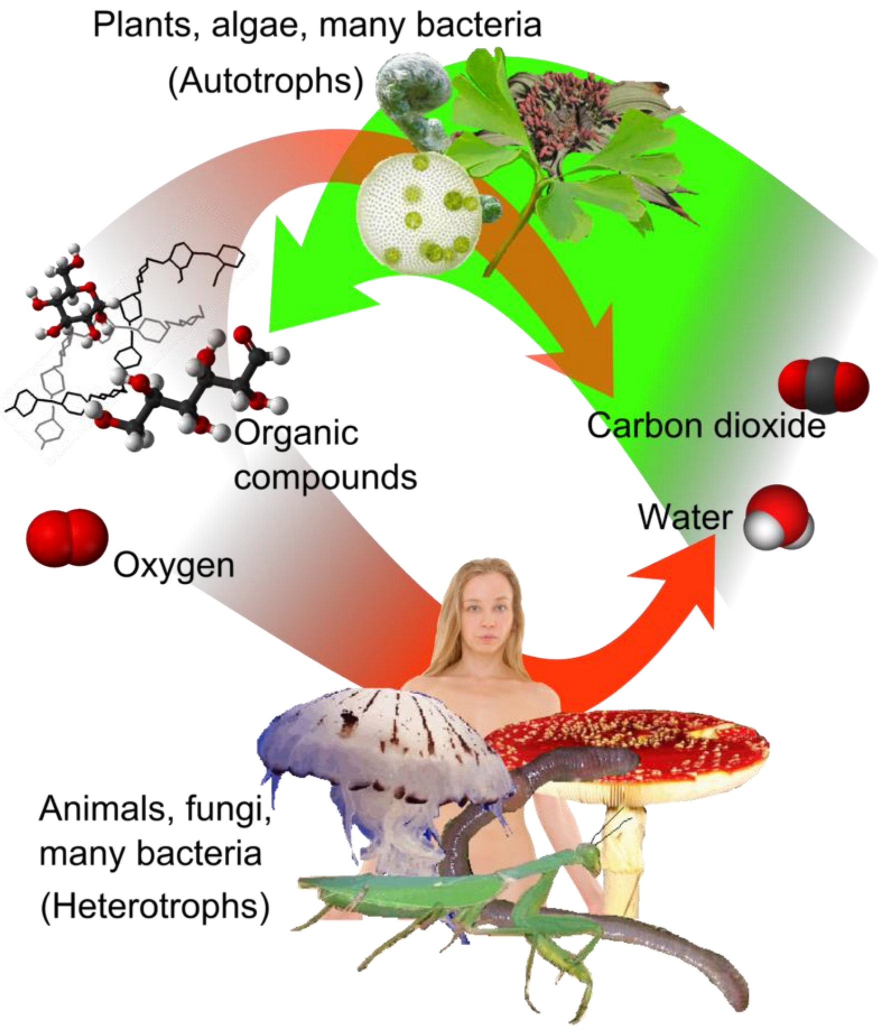
- Animals
  - Breathing and eating
  - Aerobic cellular respiration

$$C_6H_{12}O_6 + 6\ O_2 \rightharpoonup 6\ CO_2 + 6\ H_2O + \text{energy}$$

- Plants
  - Photosynthesis

$$\text{light} + 6\ CO_2 + 6\ H_2O \rightharpoonup C_6H_{12}O_6 + 6\ O_2$$

- **Two different chemical routes!**



Chemical Energy Storage

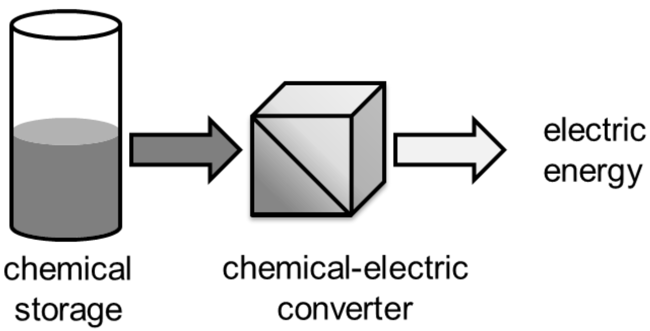
Sugar $(C_6H_{12}O_6)$

Oxygen (O_2)

Fuel Cell and Electrolyzer

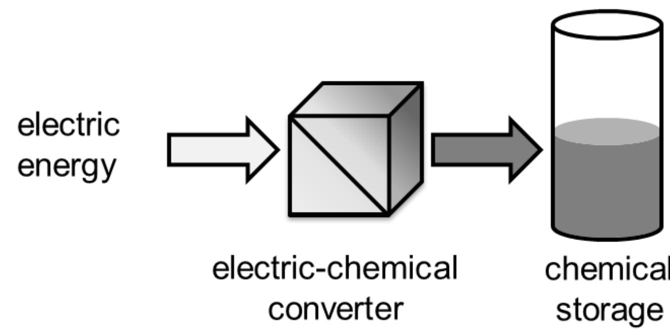
- Fuel Cell

$$\frac{1}{2}H_2 + O_2 \rightharpoonup H_2O + \text{energy}$$



- Electrolyzer

$$H_2O + \text{energy} \rightharpoonup \frac{1}{2}H_2 + O_2$$

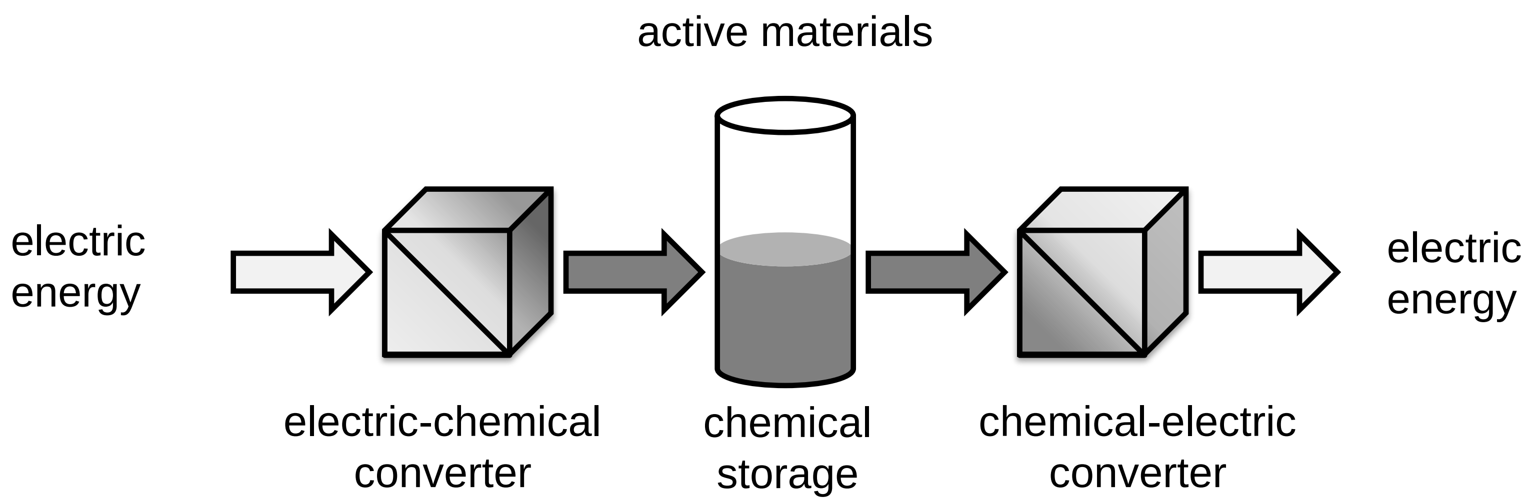


- Chemical energy storage

Hydrogen (H_2)

Oxygen (O_2)

Rechargeable Batteries



- Chemical storage in **active materials inside the battery**
- **Both conversions** in a single device

Lithium Ion Battery Applications

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

5 MWh

27 kWh

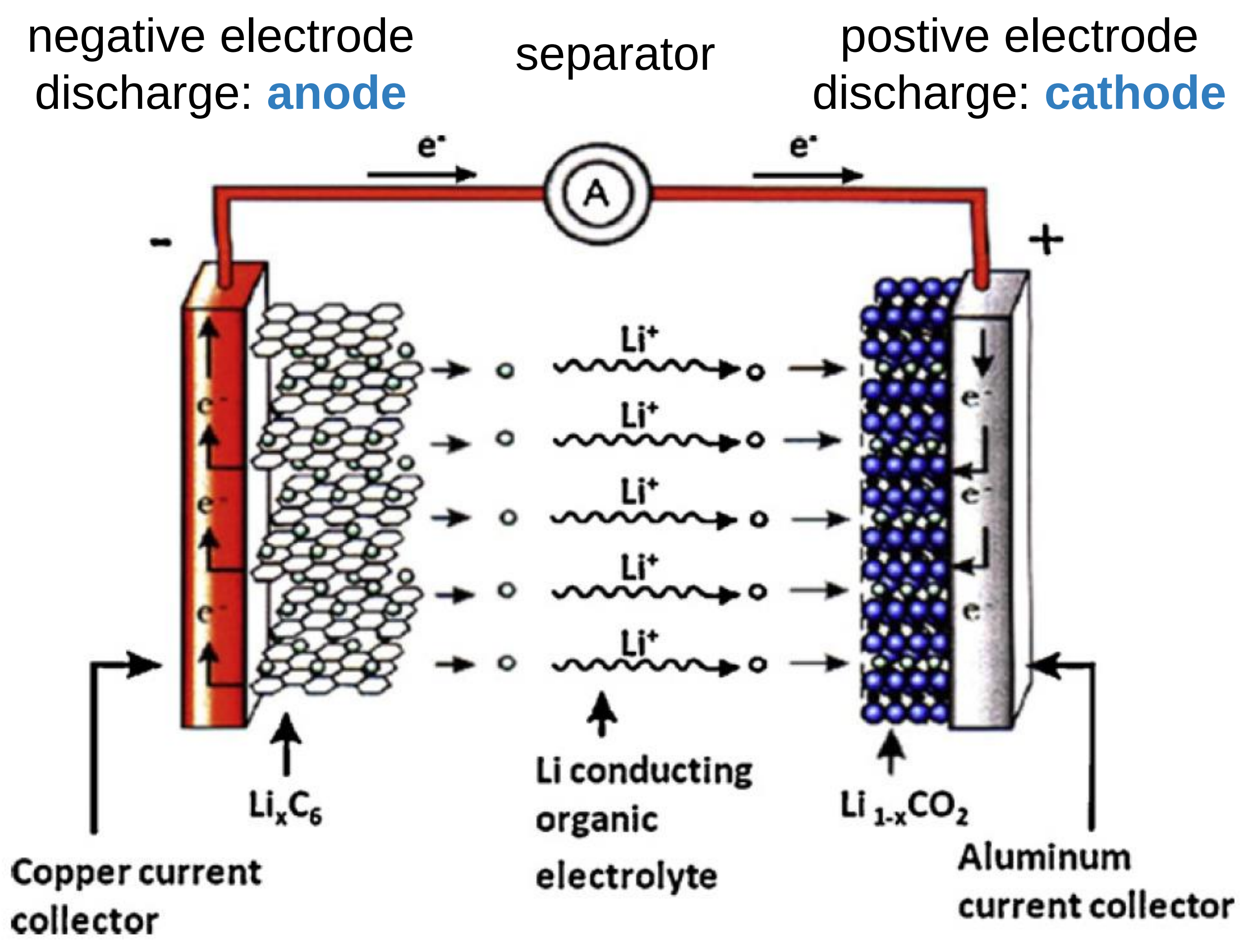
10 kWh

1 Wh

5 Wh

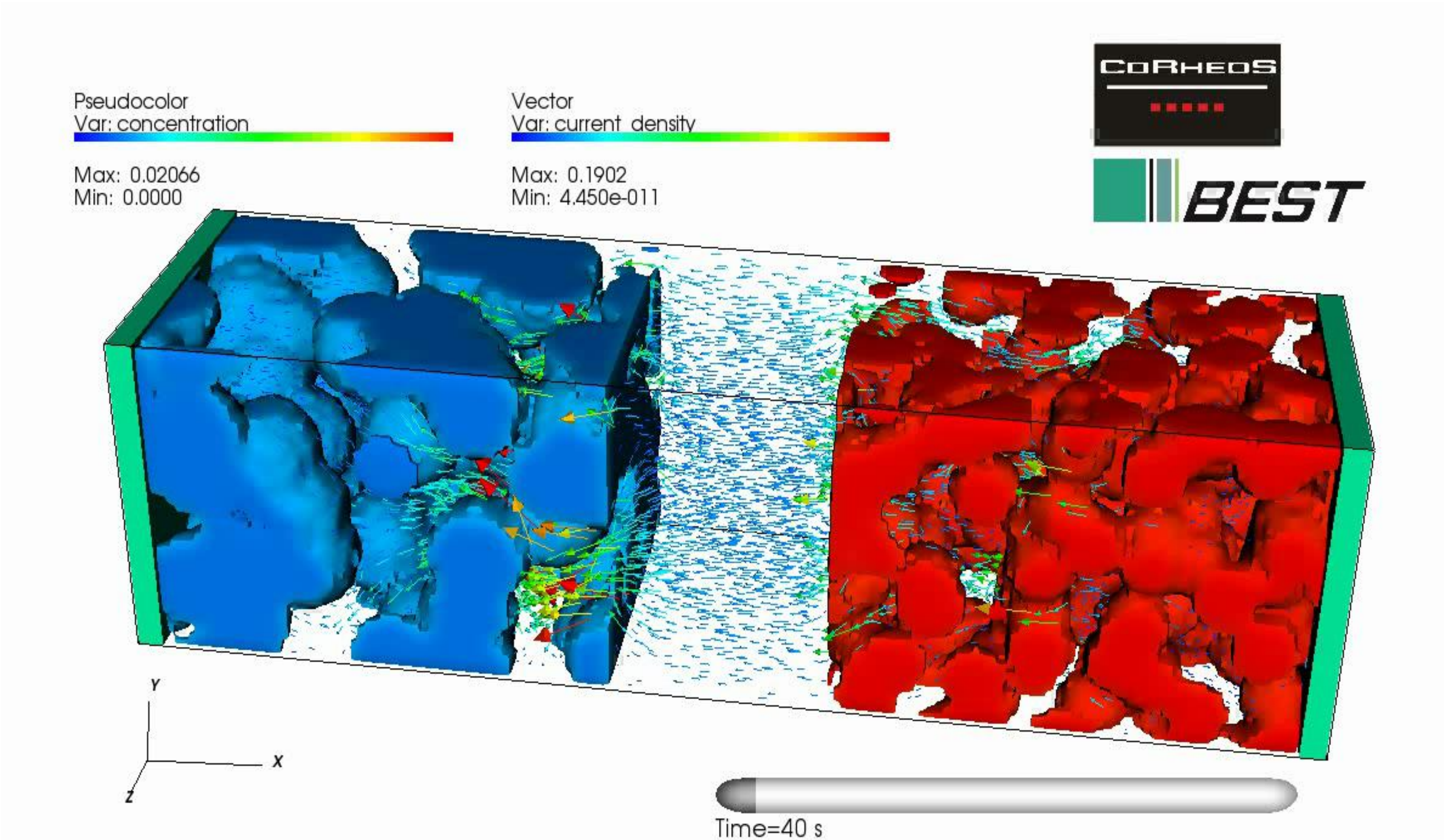
500 Wh

Lithium Ion Batteries: Electrochemical Cell



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

Microstructure of Lithium-Ion Battery



Scale-bridging simulation methodology

Theory II
A. Groß

density functional theory (DFT)

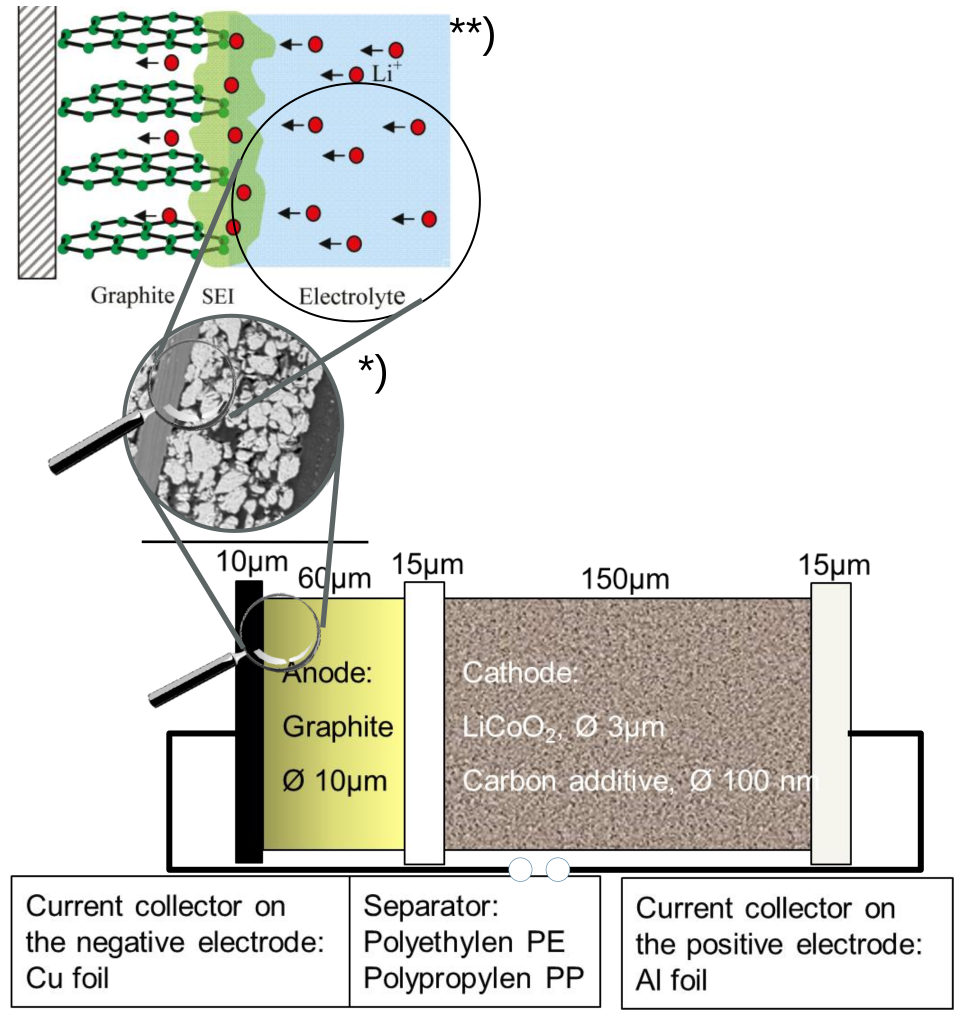
Theory I
T. Jacob

molecular dynamics, monte carlo

Theory III
A. Latz

continuum mechanics

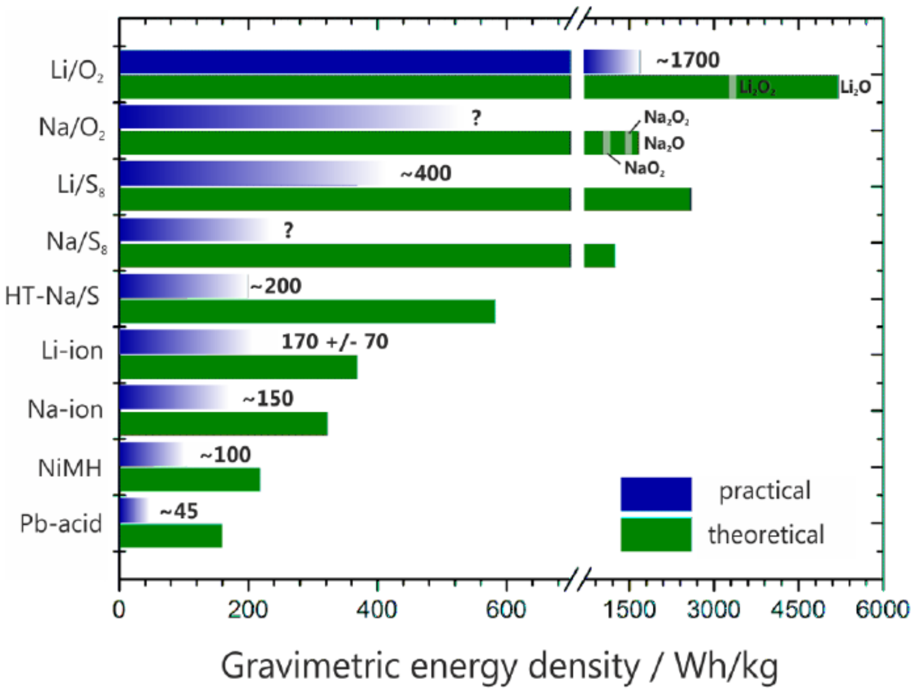
equivalent networks

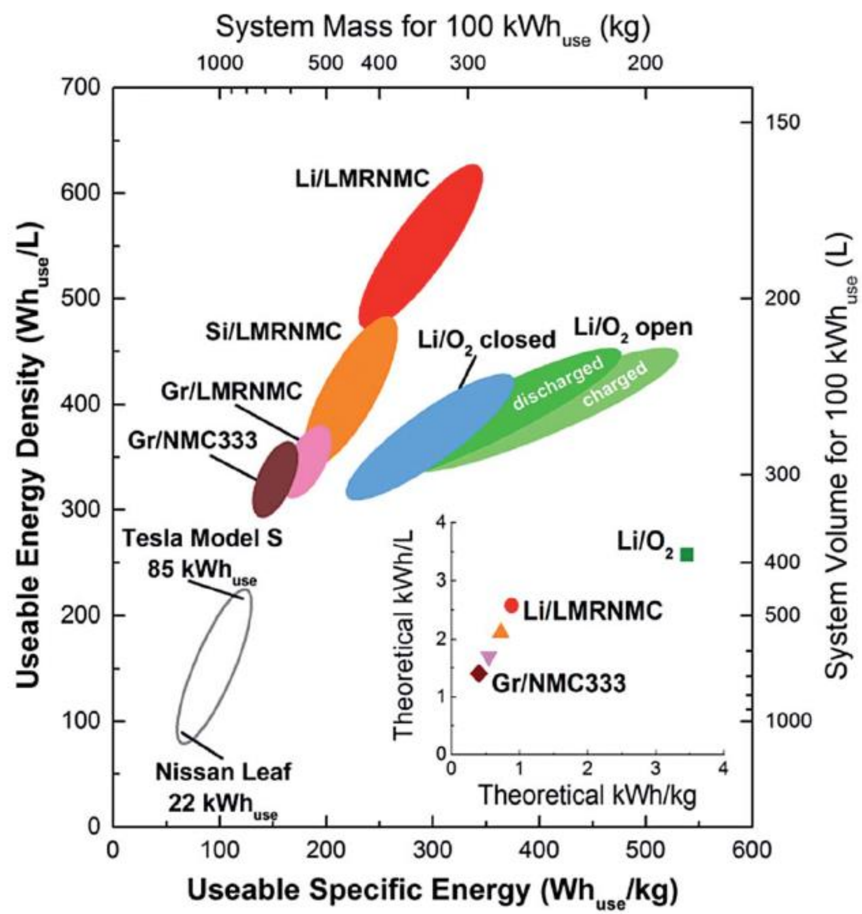


*Harris et al., Chem. Phys. Lett. 485, 265 (2010).
** Goodenough and Kim, Chem. Materials (2010)

Examples: Battery Energy

- Energy density central for driving range and cost
- **Examples** of rechargeable batteries
  - Lithium ion (standard)
  - Metal air
  - Metal sulfur
  - Metal ion





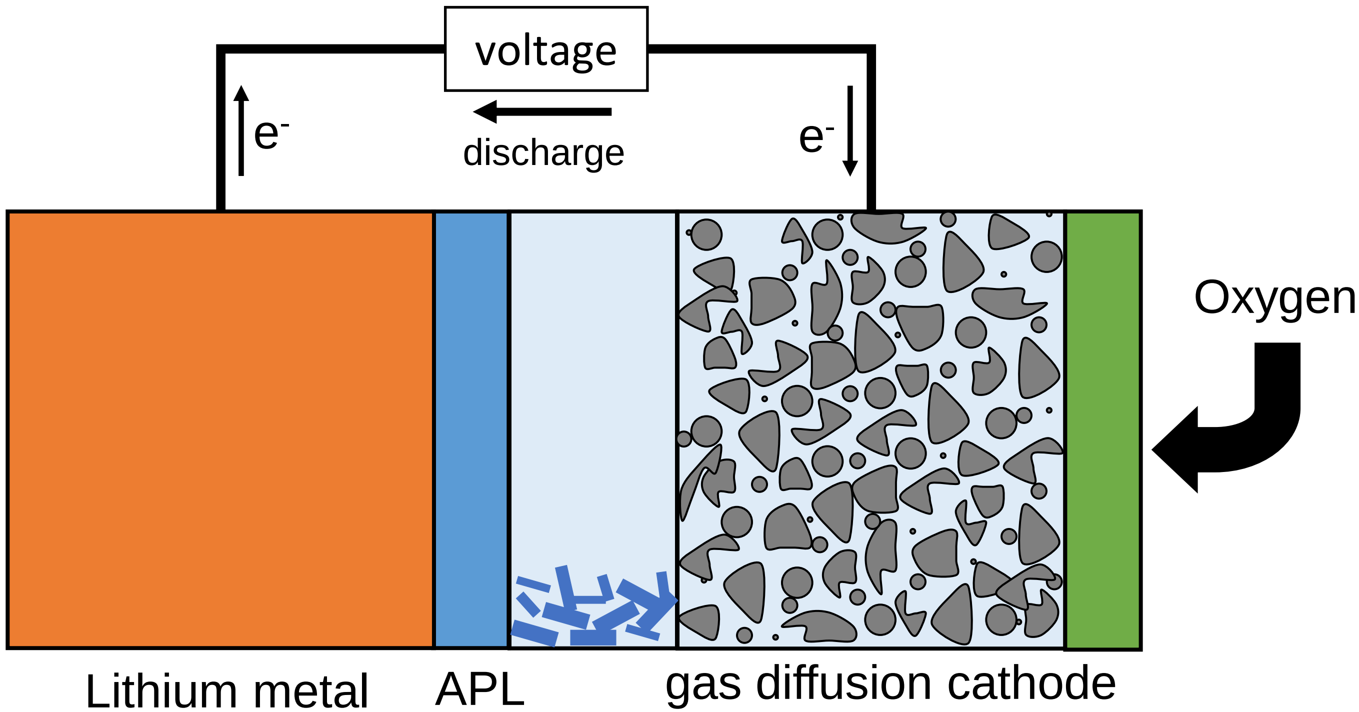
Gallagher, K.G. et al., *E*
Science, 7(5), 1555 (2014).
Adelhelm, P. et al., *Beilstein Journal of Nanotechnology*, 6(1)1016–1055 (2015).

Metal Air Batteries

$$\text{metal} + O_2 \rightleftharpoons \text{metal(hydr)oxide} + \text{energy}$$

- Prospects
  - Large **energy density**: high voltage, external oxygen
  - Cheap, **abundant materials**
- IBM Battery 500 promises (2009)
  - 800 km driving range
  - 10 fold increase in energy density
- Challenges
  - **Shape change** of metals (e.g. dendrites)
  - **Pollution** from ambient air
  - Electrolyte/electrode **degeneration** (oxygen + high voltage)
- Research:
  - **Metals**: lithium, zinc, sodium, …
  - **Electrolytes**: aqueous (pH), organic, ionic liquids, solid state
  - **Electrodes**: shape change, degeneration, storage of discharge product

Aqueous Lithium-Air Batteries



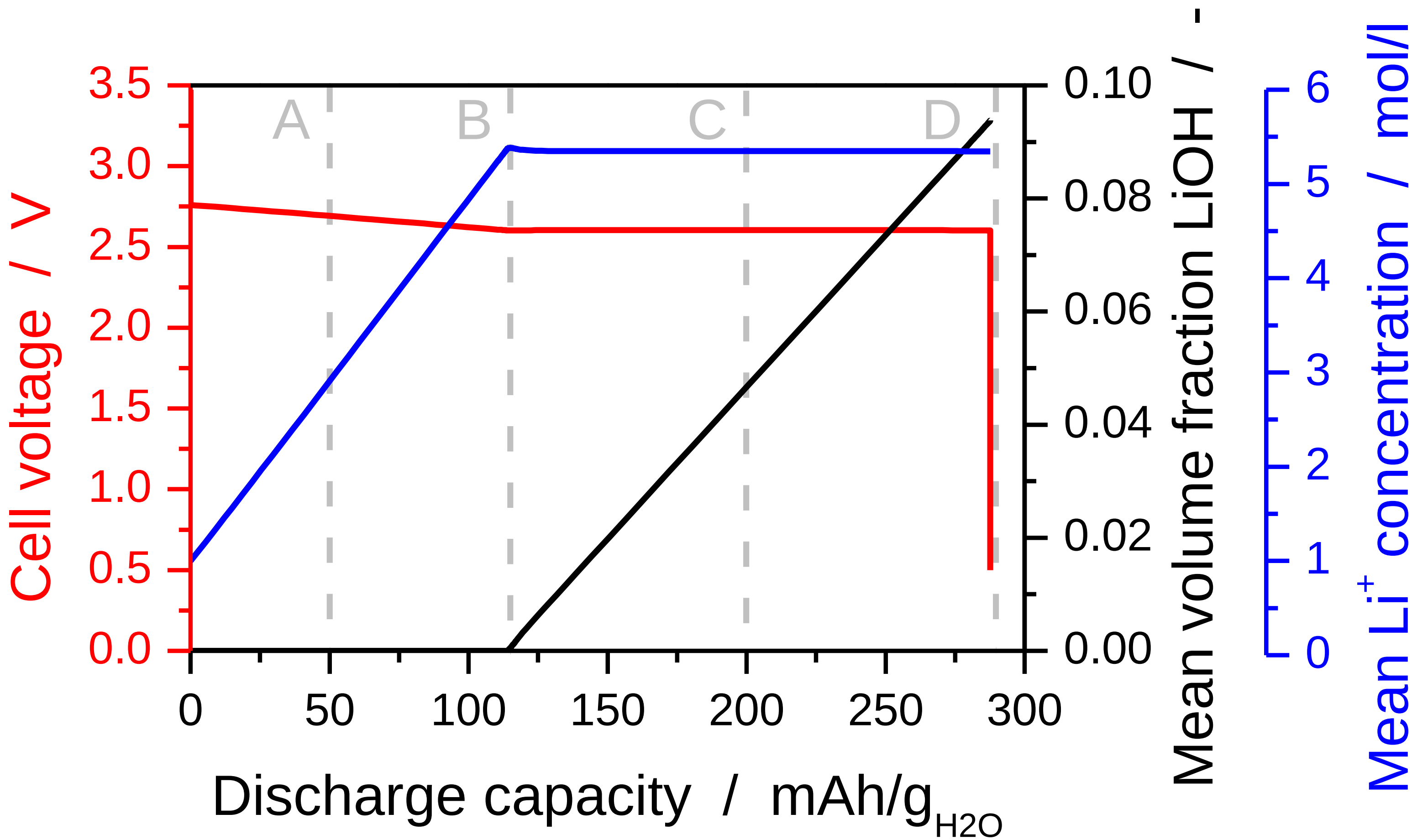
$$Li \rightleftharpoons Li^{+} + e^{-}$$

$$O_2 + 2\,H_2O + 4\,e^{-} \rightleftharpoons 4\,OH^{-}$$

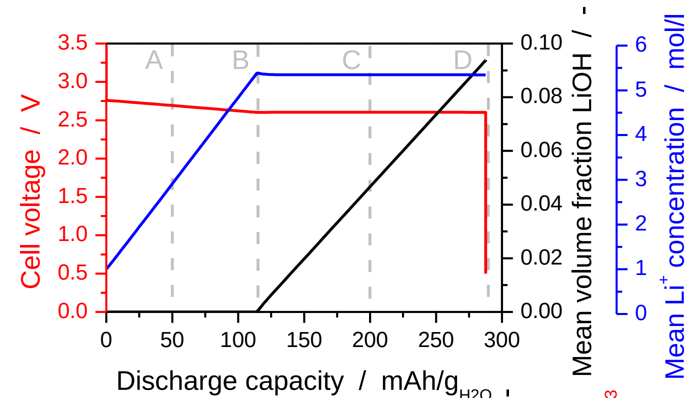
$$Li^{+} + OH^{-} + H_2O \rightleftharpoons LiOH.H_2O$$

discharge product (anode / separator)

Aqueous Lithium-Air Batteries

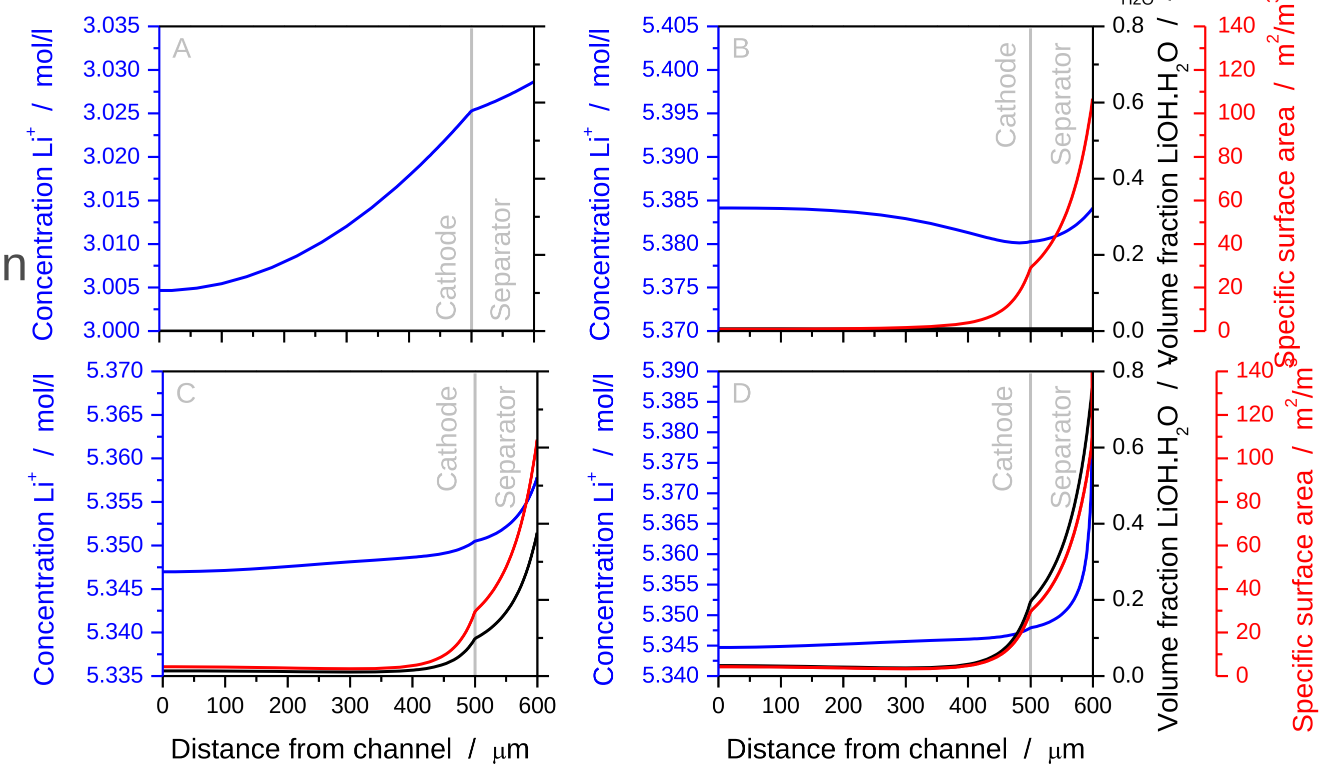


Aqueous Lithium-Air Batteries



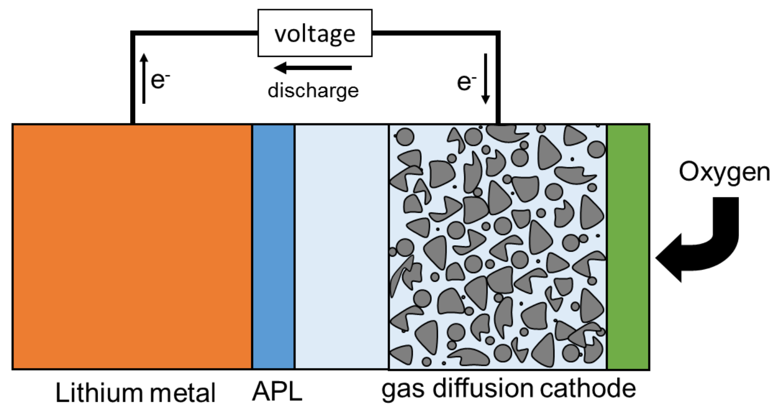
- A. Growing salt concentration
- B. Nucleation
- C. Constant salt concentration
  - Large gradient ($t^+ = 0.16$)
  - Crystallization on anode side
- D. Separator blocked by crystals

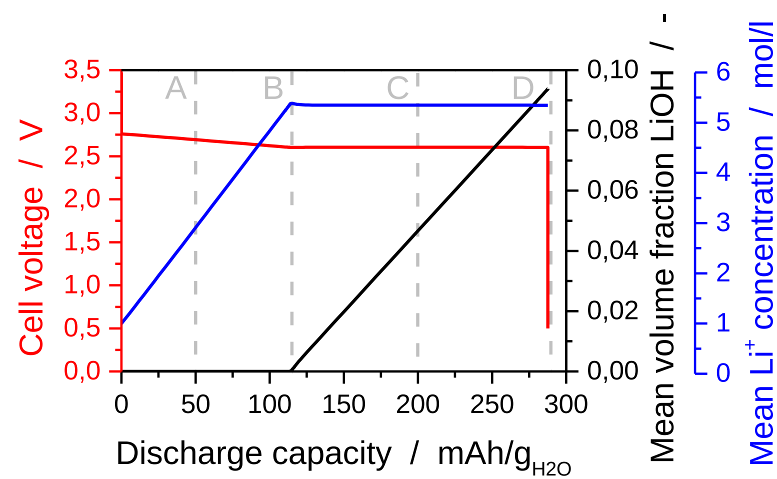
➡ **End of discharge due to LiOH film on separator surface.**



Conclusion: Aqueous Lithium-Air Batteries

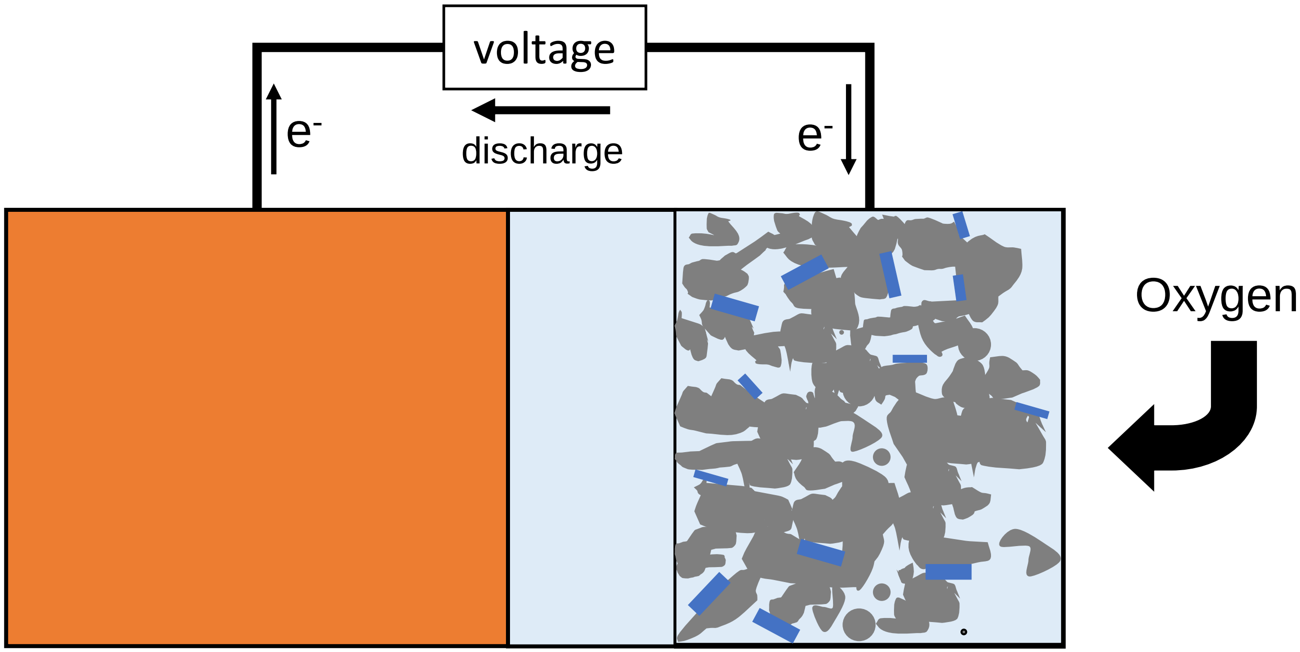
- Aqueous alkaline solution (Li^+, OH^-)
- **1D continuum theory**
- Power limiting:
  - O_2 diffusion and solubility
  ➔ **Gas diffusion electrode**
- Capacity limiting:
  - **Inhomogeneous precipitation**
  ➔ Adjusting cell design
- Efficiency limiting:
  - Multi-step electron transfer
  ➔ Catalyst
- Experimental **validation**
- **Challenge: stable anode protection**





Horstmann, B. et al. *Energy Environ. Sci. 6* (4), 1299 (2013).
Danner, T. et al. *J. Power Sources*, *264*, 320–332 (2014).

Aprotic Lithium-Air Batteries



Lithium metal

$$\mathrm{Li} \rightleftharpoons \mathrm{Li}^+ + \mathrm{e}^-$$

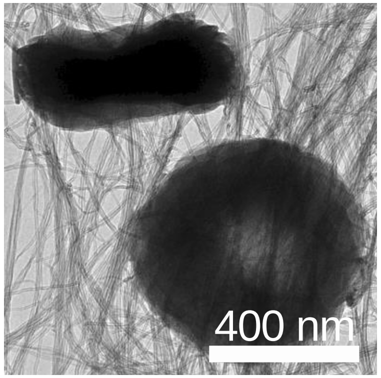
flooded cathode

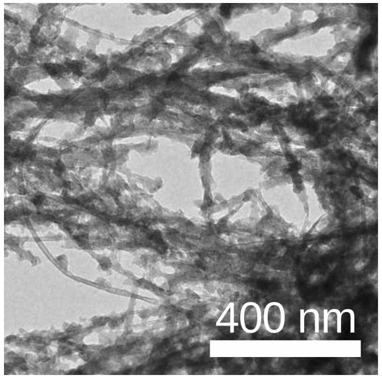
$$2\,\mathrm{Li}^+ + \mathrm{O}_2 + 2\,\mathrm{e}^- \rightleftharpoons \mathrm{Li}_2\mathrm{O}_2$$

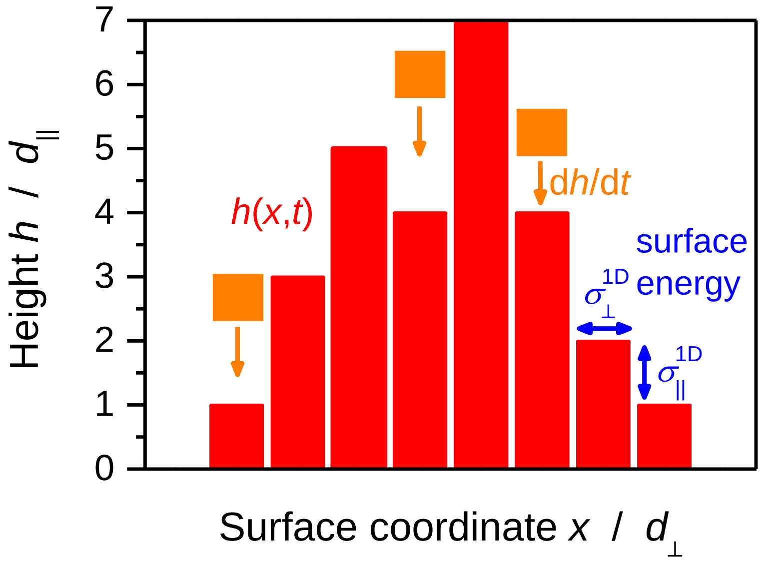
discharge product (cathode)

Discharge Reaction Product

- Electrolyte: search for (meta-)stable electrolyte
- **Transition in Li_2O_2 growth morphology**
  - Particle nucleation at **low rates**
  - Film growth at **high rates**
- (1+1)D reaction limited **surface growth model**
  - Columns of Li_2O_2 molecules $h(x, t)$



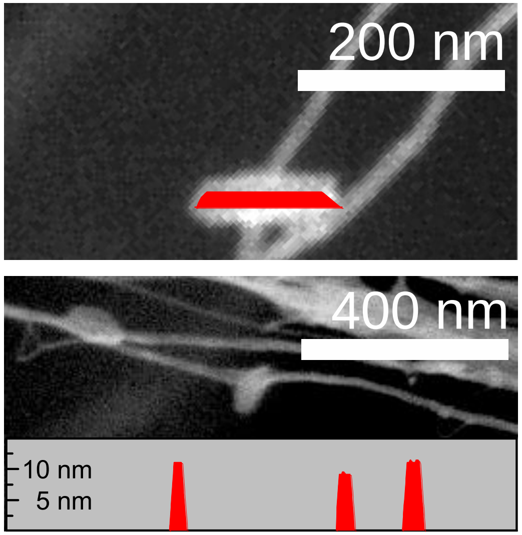


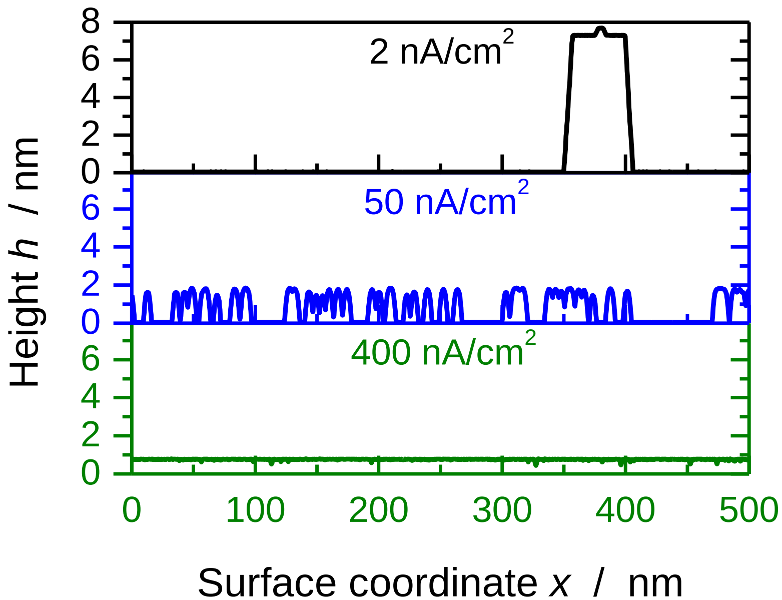


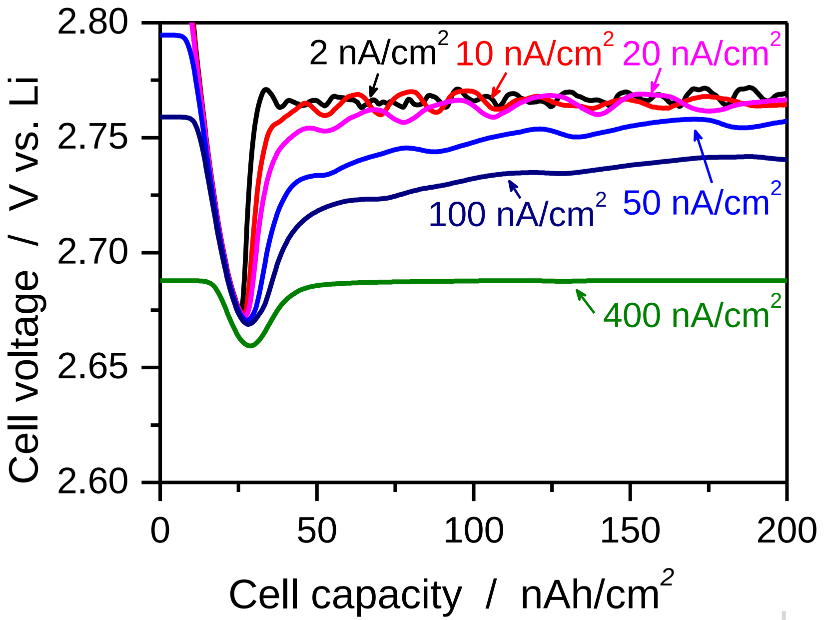
B. Horstmann, B. Gallant, R. Mitchell, W. G. Bessler, Y. Shao-Horn, and M. Z. Bazant, *J. Phys. Chem. Lett.* **4**, 4217–4222 (2013).
R. R. Mitchell, B. M. Gallant, C. V. Thompson, Y. Shao-Horn, *Energy & Environmental Science* **4**, 2952 (2011).
B. M. Gallant, D. G. Kwabi, R. R. Mitchell, J. Zhou, C. V Thompson, Y. Shao-Horn, *Energy & Environmental Science* **6**, 2518 (2013).
R. R. Mitchell, B. M. Gallant, Y. Shao-Horn, and C. V Thompson, *The Journal of Physical Chemistry Letters* **4**, 1060 (2013).
B. D. Adams, C. Radtke, R. Black, M. L. Trudeau, K. Zaghib, and L. F. Nazar, *Energy & Environmental Science* **6**, 1772 (2013).

Simulation of Reaction Product

- Parameters
  - DFT: Surface energies σ
  - Tafel analysis
- **Transition at exchange current I_c**
  - Discrete particles: Wulff shape
  - Particle coating
  - Film



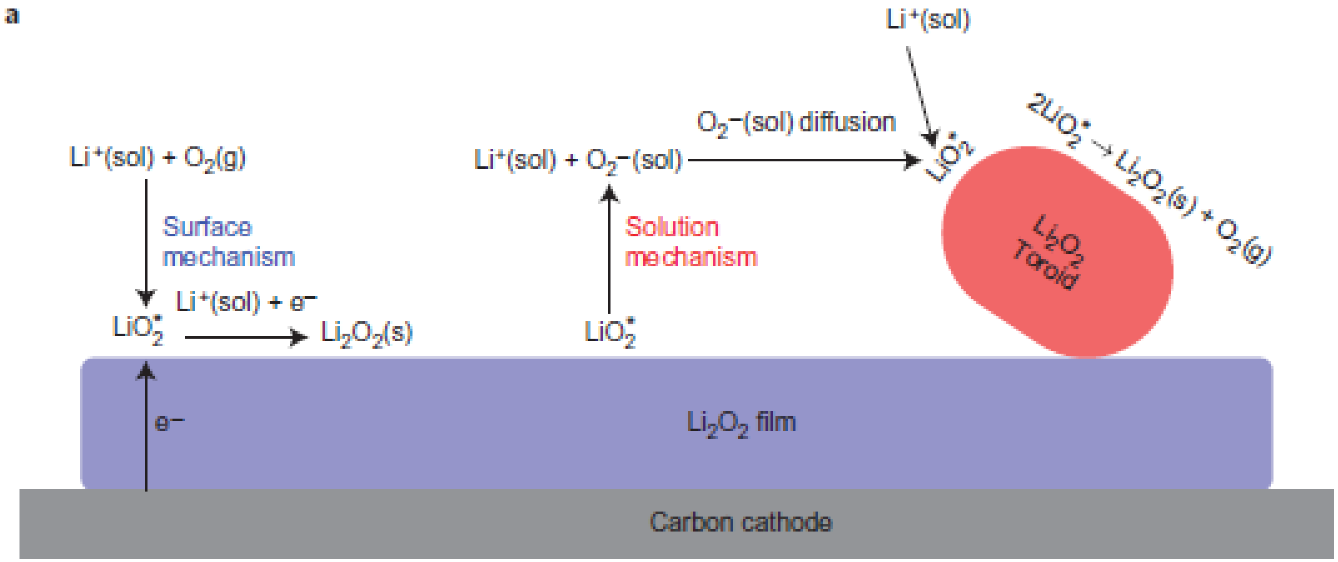




B. Horstmann, B. Gallant, R. Mitchell, W. G. Bessler, Y. Shao-Horn, and M. Z. Bazant, *J. Phys. Chem. Lett.* **4**, 4217–4222 (2013).

Growth Mechanism of Reaction Product

- Growth of toroids requires solvating additives, e.g. water
    - **Solution mechanism**



- Research on additives / electrolytes:
    - Stable at anode and cathode
    - Novel reaction intermediates
    - Novel reaction products

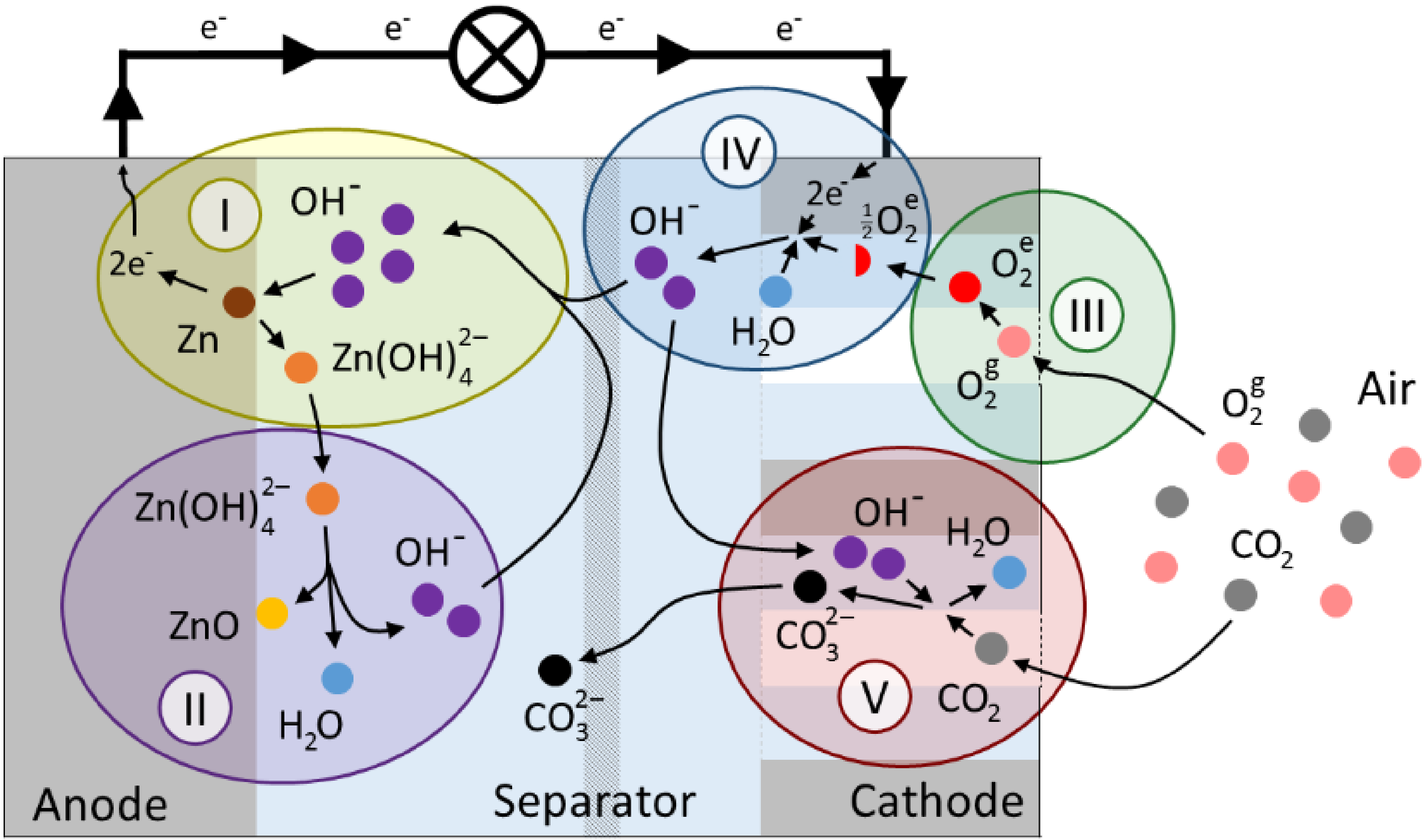
Aetukuri, N.B. et al., *Nature Chemistry*, 7, 50–56 (2015).

Aqueous Alkaline Zinc-Air Batteries

- Primary zinc-air battery **commercially available**
  - High specific energy (1086 Wh·kg^{-1}), low cost, high operational safety
  - Hearing aid battery, e.g., VARTA PowerOne PR44
- **Development of rechargeable zinc-air battery**
  - Zinc dendrites, electrolyte carbonation, oxygen redox chemistry, anode passivation
  - Stationary energy storage
- Electrolytes:
  - aqueous alkaline, aqueous neutral, ionic liquids

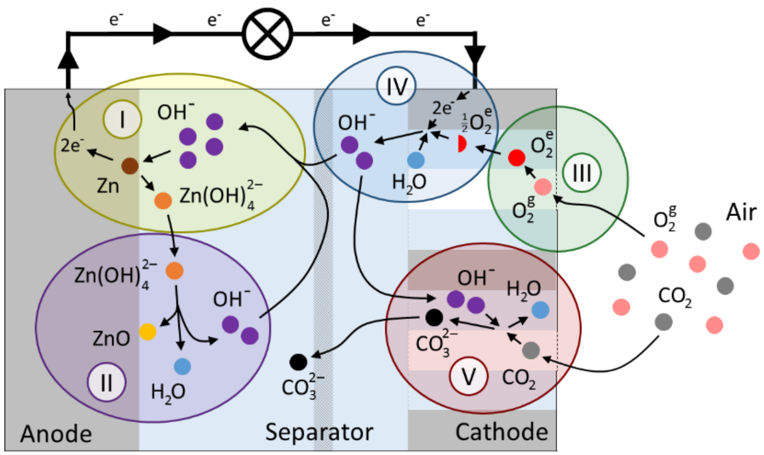
VARTA

Zinc Air Batteries with Alkaline Electrolyte

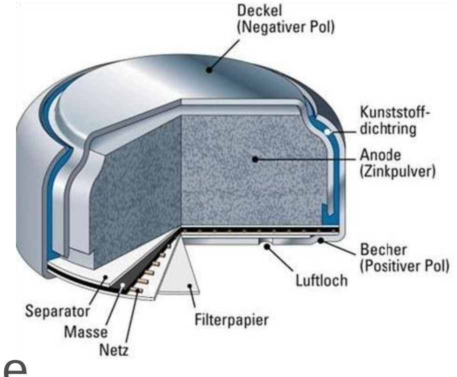


Alkaline Electrolyte

- **Chemical reactions**
  - I. $Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$
  - II. $Zn(OH)_4^{2-} \rightleftharpoons ZnO + 2OH^- + H_2O$
  - *III.* $O_2^g \rightleftharpoons O_2^e$
  - *IV.* $\frac{1}{2} O_2^e + H_2O + 2e^- \rightleftharpoons 2OH^-$
  - V. $CO_2 + 2\,OH^- \rightleftharpoons CO_3^{2-}$



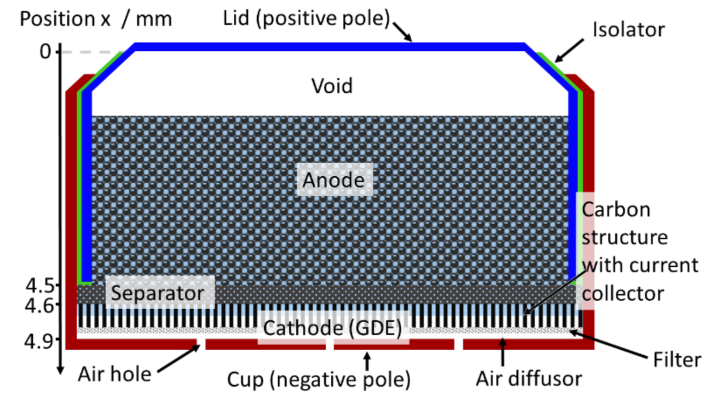
- **Reaction rates**
  - Electrochemical reactions: Butler-Volmer equation
  - ZnO precipitation: diffusion-limited process
  - Oxygen dissolution: Hertz-Knudsen rate
  - Carbon dioxide absorption: quasi-stationary diffusion zone



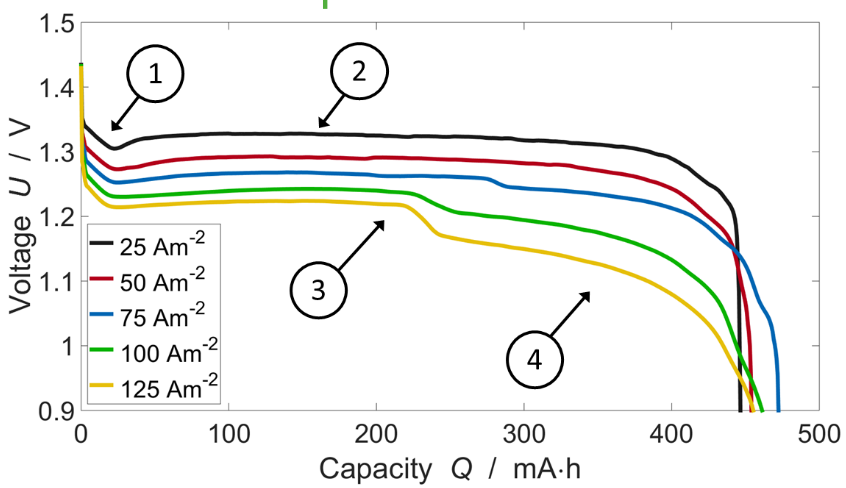
Horstmann, B. et al. *Energy Environ. Sci.* **2013**, *6* (4), 1299.
Danner, T. et al. *J. Power Sources* **2014**, *264*, 320–332.

Zinc Air Coin Cell: Galvanostatic Discharge

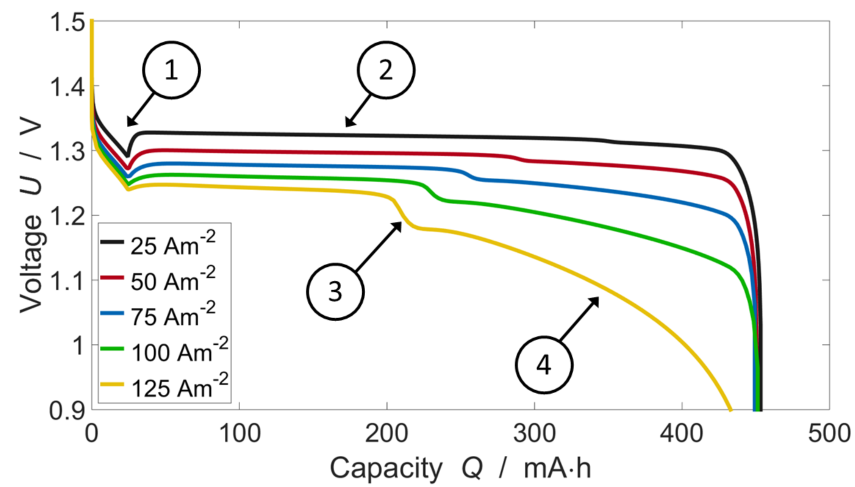
1. Dip: nucleation of ZnO
2. Plateau: conversion reaction
3. Step: inhomogeneous nucleation
4. Drop: OH^- diffusion through ZnO



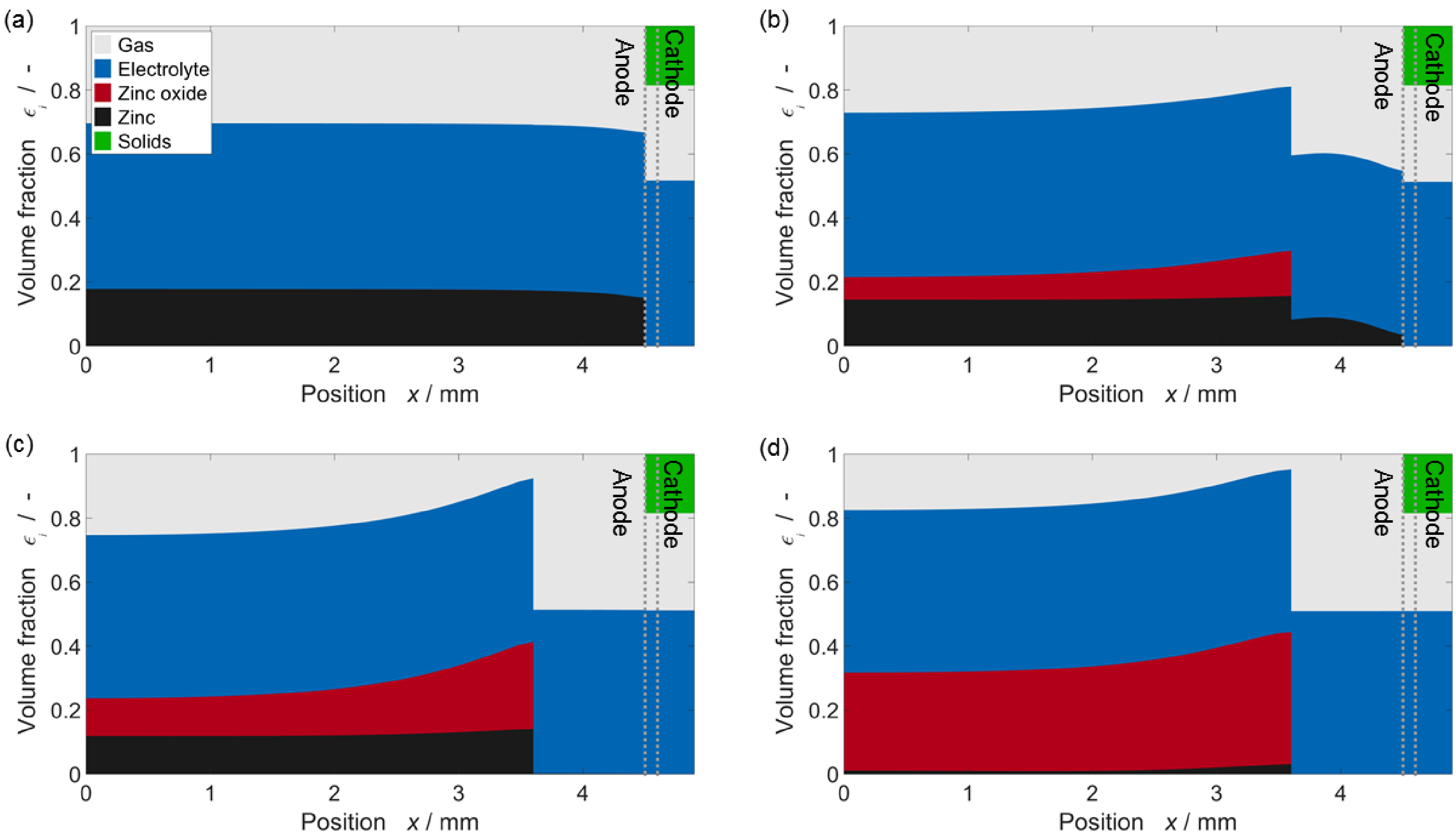
experiment



simulation

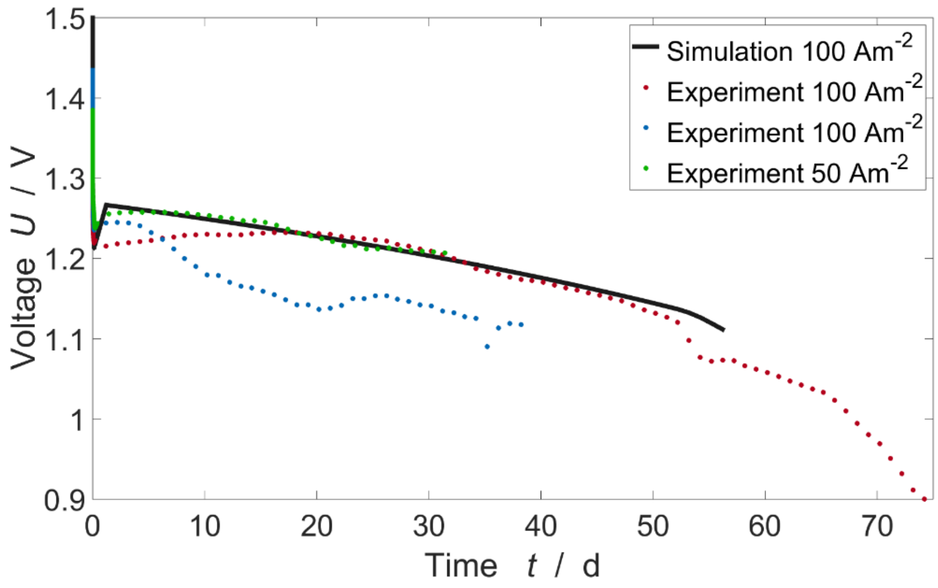


Alkaline Coin Cell: Volume Fractions



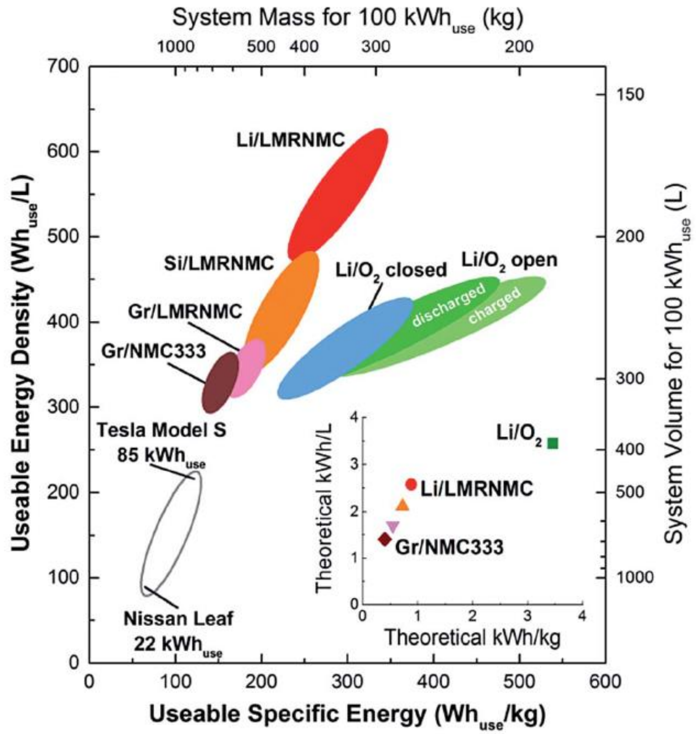
Alkaline Coin Cell: Lifetime Analysis

- Absorption of **atmospheric CO_2**, consumption of OH^-
- Linear decay in cell voltage
  - Daily measurements of cell voltage
  - Initial galvanostatic discharge to reach voltage plateau



Summary and Outlook

- Metal air batteries: **high risk / high gain**
- Applications: stationary, mobile, portable
- Various metal ions
  - **Lithium** air batteries: lightweight
  - Sodium air batteries: cheap
  - **Zinc** air batteries: commercial
- Various electrolytes



Thank you!

European Commission

Bundesministerium für Bildung und Forschung

DAAD Deutscher Akademischer Austausch Dienst German Academic Exchange Service

HIU for Electrochemical Energy Storage

- Center of Excellence for research in electrochemical energy storage
- Founded in Jan. 2011
- New building on University Ulm campus for 100 scientists (September 2014)
- DLR battery modeling activities are integrated into HIU

Karlsruher Institut für Technologie

Universität Ulm

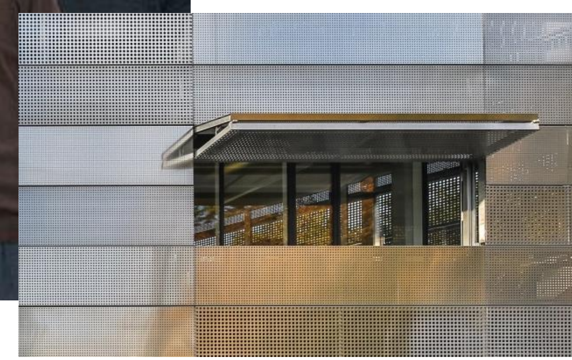
Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg

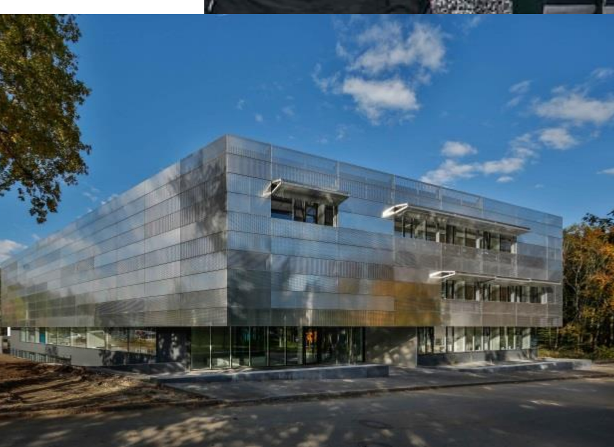
Deutsches Zentrum für Luft- und Raumfahrt

HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

Thank you for your attention

Johannes Stamm
Simon Clark
Timo Danner
Martin Bazant
Arnulf Latz





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