

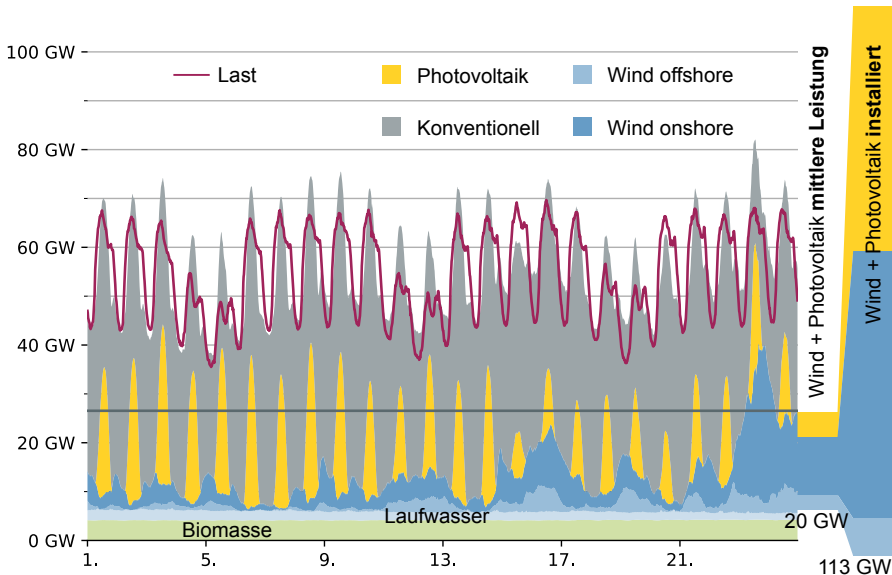
Elektrische Energiespeicherung mit Flüssigmetallen und Salzschnmelzen

Tom Weier, Gerrit M. Horstmann, Steffen Landgraf, Michael
Nimtz, Paolo Personnetaz, Frank Stefani, Norbert Weber

Institut für Fluidodynamik

27. September 2021

Elektrizitätserzeugung und -bedarf September 2021

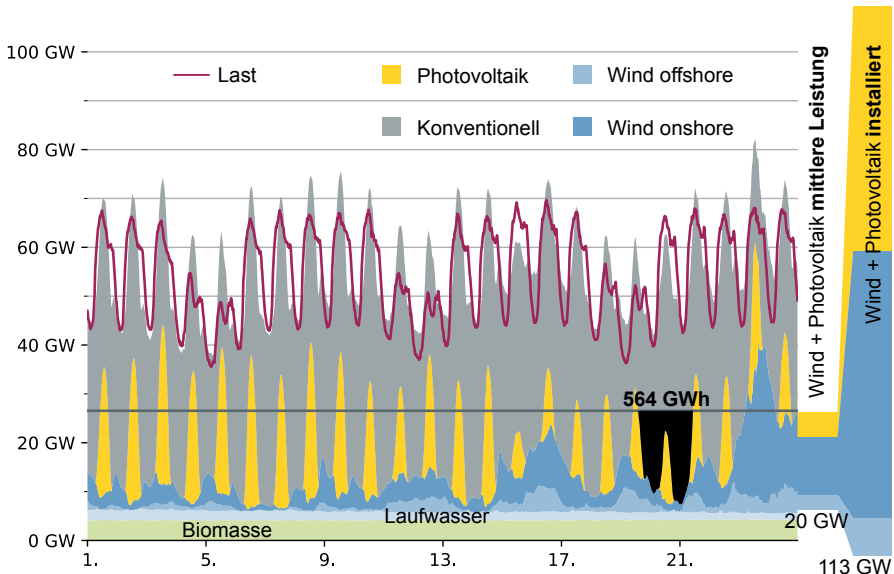


Datenquelle: Bundesnetzagentur | SMARD.de (2021)



4.0

Elektrizitätserzeugung und -bedarf September 2021



Datenquelle: Bundesnetzagentur | SMARD.de (2021)



Norsk Hydro ASA Sunndal



Norsk Hydro, 2010

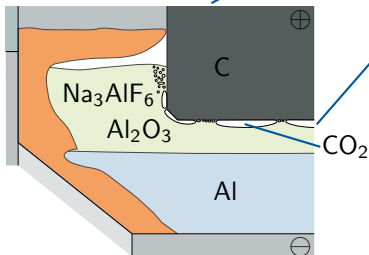
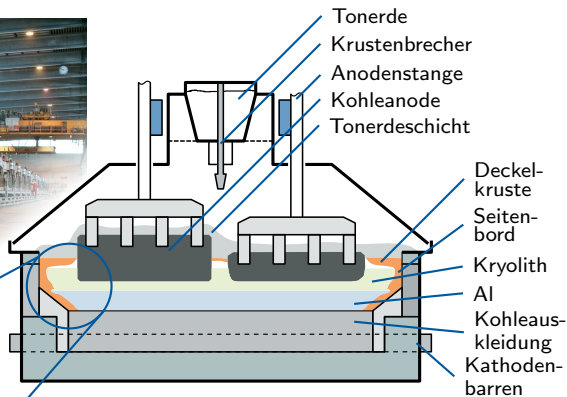
400 000 t Al/Jahr, 15.3 GWh/Tag



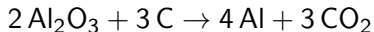
HZDR

Aluminiumelektrolyse

Norsk Hydro, 2010



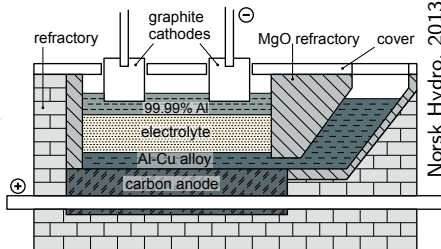
- Weltjahresproduktion 64 Millionen t
- ➔ >3% Weltstromproduktion



- Zelle:
 - $T_{\text{op}} = 960 \text{ }^\circ\text{C}$
 - 300 ... 600 kA
 - 9 ... 18 m Länge
 - 3 ... 5 m Breite

Aluminiumraffination

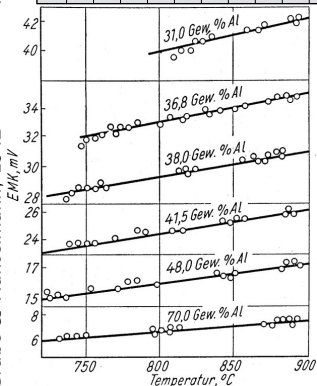
Wolstenholme, 1982



Norsk Hydro, 2013



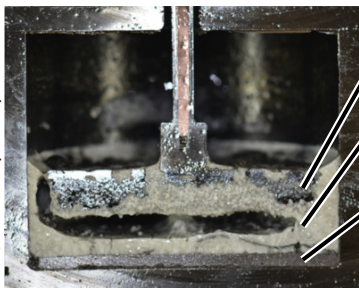
Grube & Hantelmann, 1942



- Weltjahresproduktion 70 kt
- spezifischer Energiebedarf 14 kWh/kg
- Zellstrom 30 ... 60 kA
- Zellspannung ca. 7 V
- Elektrolythöhe 8 cm ... 25 cm

Flüssigmetallbatterien

Ning et al. (2015)

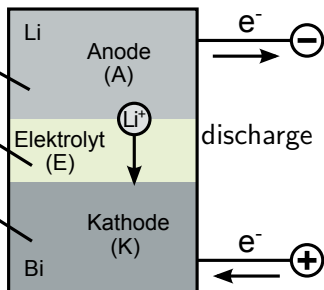


$$\rho^{(\text{Li})} = 491 \text{ kg/m}^3$$

$$\rho^{(\text{E})} = 1648 \text{ kg/m}^3$$

$$\rho^{(\text{Bi})} = 8576 \text{ kg/m}^3$$

@ 450 °C



Ambri (2016)



Vorteile

- einfache Konstruktion
- preiswerte Aktivmaterialien
- hohe Stromdichten
- gute Zyklenfestigkeit
- Skalierbarkeit

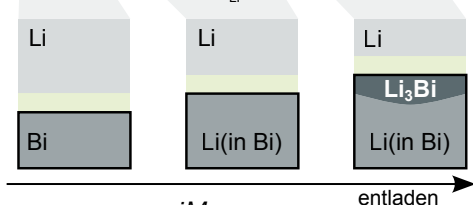
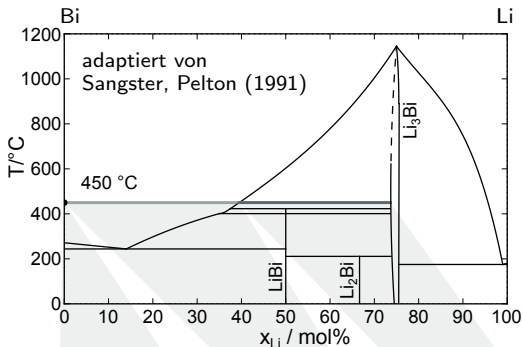
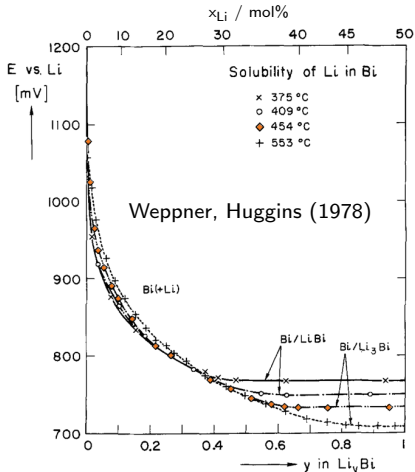
Herausforderungen

- geringe Zellspannung
- hohe Temperatur
- reaktive Medien
- **vielfältige Strömungsmechanik**

Flüssigmetallbatterien: Li||Bi

$$E_{OC} = -\frac{RT}{z_e F} \ln a_{Li(Bi)}$$

$$a_{Li(Bi)} = \gamma_{Li} x_{Li}$$



$$\dot{m}_{Li} = \frac{jM_{Li}}{z_e F}$$

Flüssigmetallzellen: Na||Bi vs. Li||Bi

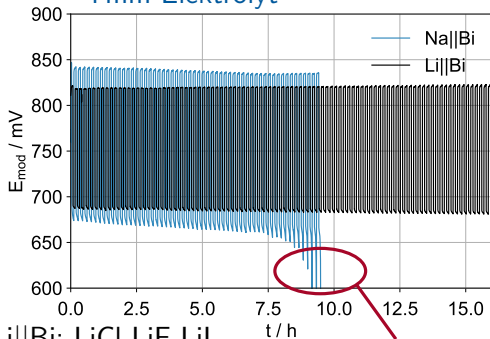


Na||Bi: KCl-LiCl-NaCl

36-55-9

450 °C

4 mm Elektrolyt



Li||Bi: LiCl-LiF-LiI

29-12-59

430 °C

4 mm Elektrolyt

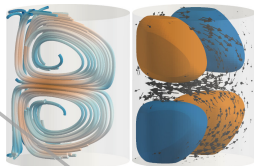


0.1 fps

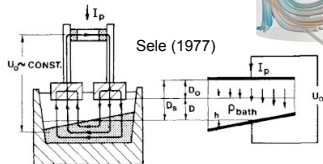
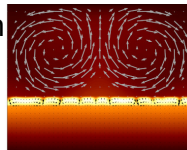
Na Verlust durch Löslichkeit

Strömungsmechanische Aspekte von FMB

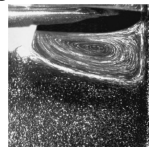
Taylor Instabilität



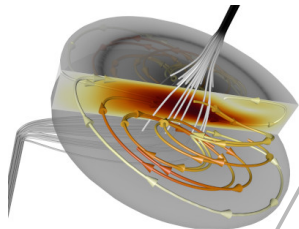
Rayleigh-Bénard Konvektion



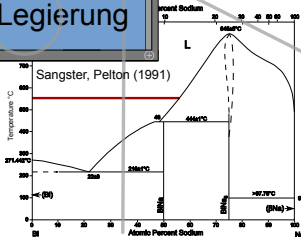
Marangonikonvektion



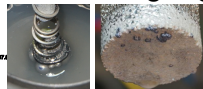
Grenzflächenwellen



Elektrowirbelströmungen



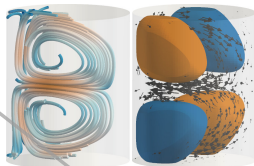
Tropfenbildung und -bewegung



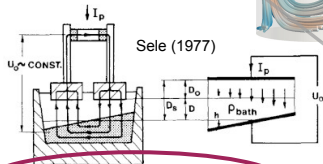
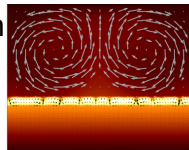
Stofftransport

Strömungsmechanische Aspekte von FMB

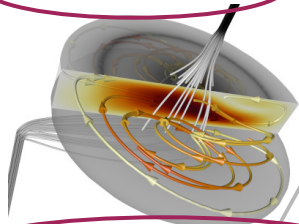
Taylor Instabilität



Rayleigh-Bénard Konvektion



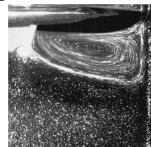
Grenzflächenwellen



Elektrowirbelströmungen

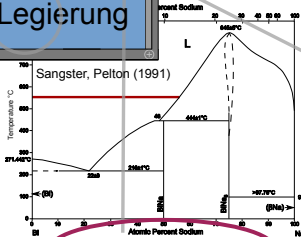


Marangonikonvektion



Cramer et al. (2011)

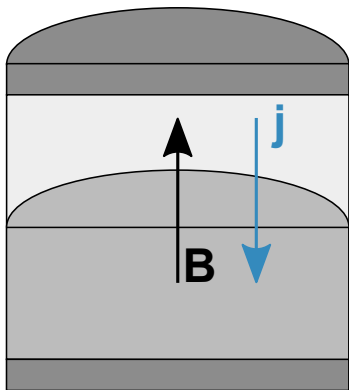
Tropfenbildung und -bewegung



Stofftransport

Langwellige Instabilitäten/Schwappen

Zweischichtsystem/Aluminiumelektrolyse

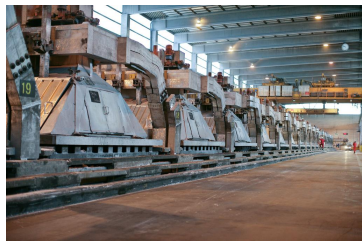


Graphit-
elektrode
 $\sigma \approx 10^5 \text{ S/m}$

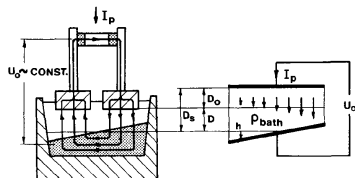
Kryolit
 $\sigma \approx 10^2 \text{ S/m}$

Aluminium
 $\sigma \approx 10^6 \text{ S/m}$

Stromsampler
 $\sigma \approx 10^6 \text{ S/m}$



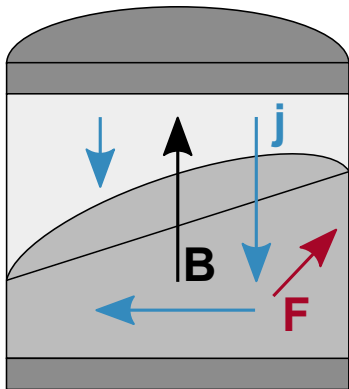
Hydro (2017)



Sele (1977)

Langwellige Instabilitäten/Schwappen

Zweischichtsystem/Aluminiumelektrolyse

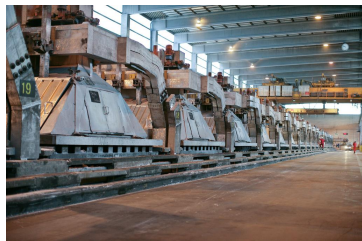


Graphit-
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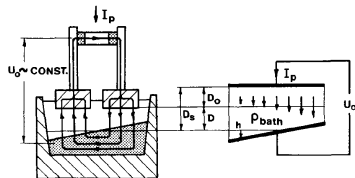
Kryolit
 $\sigma \approx 10^2 \text{ S/m}$

Aluminium
 $\sigma \approx 10^6 \text{ S/m}$

Stromsamm-
ler
 $\sigma \approx 10^6 \text{ S/m}$



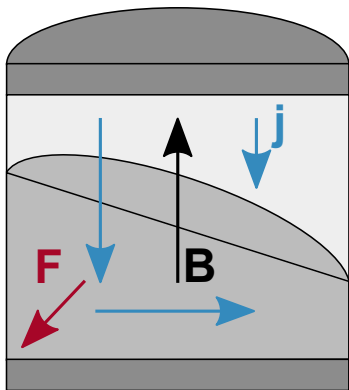
Hydro (2017)



Sele (1977)

Langwellige Instabilitäten/Schwappen

Zweischichtsystem/Aluminiumelektrolyse

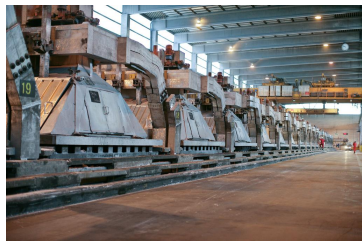


Graphit-
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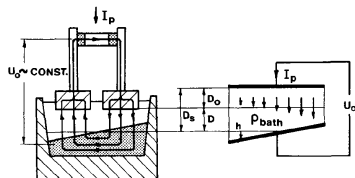
Kryolit
 $\sigma \approx 10^2 \text{ S/m}$

Aluminium
 $\sigma \approx 10^6 \text{ S/m}$

Stromsammeler
 $\sigma \approx 10^6 \text{ S/m}$

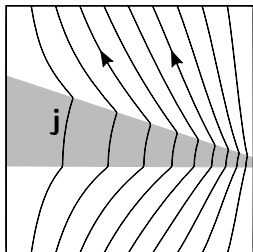


Hydro (2017)



Sele (1977)

Langwellige Instabilitäten/Schwappen

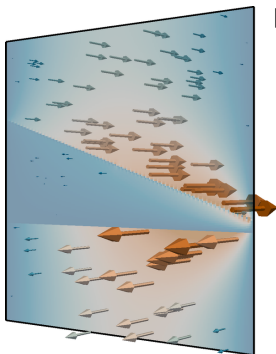


$$\sigma = 10^6 \text{ S/m}$$

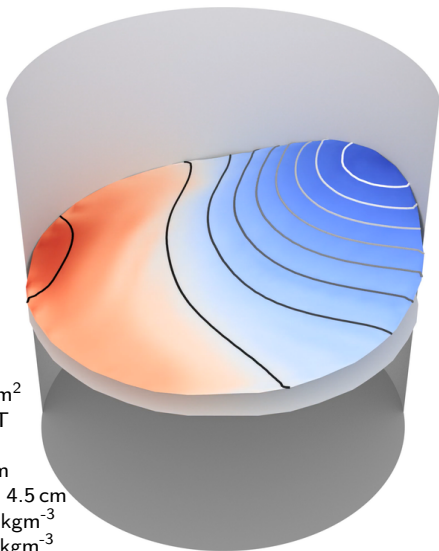
$$\sigma = 1 \text{ S/m}$$

$$\sigma = 10^6 \text{ S/m}$$

F

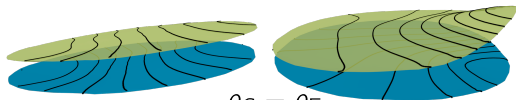


$$\begin{aligned} I &= 120 \text{ A} \\ A &= 78.5 \text{ cm}^2 \\ B_z &= 10 \text{ mT} \\ \mathbf{Mg} \parallel \mathbf{Sb} \\ h_E &= 1.0 \text{ cm} \\ h_A &= h_C = 4.5 \text{ cm} \\ \rho_A &= \mathbf{1577} \text{ kgm}^{-3} \\ \rho_E &= \mathbf{1715} \text{ kgm}^{-3} \\ \rho_C &= \mathbf{6270} \text{ kgm}^{-3} \end{aligned}$$

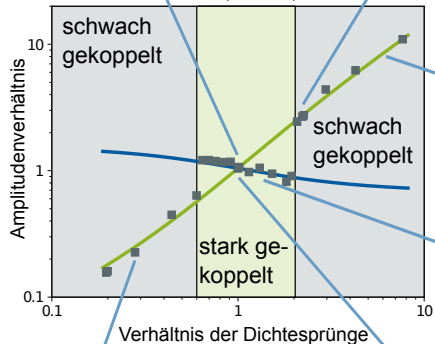


Weber et al. (2017) Phys. Fluids

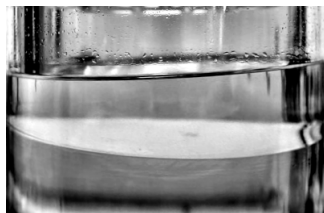
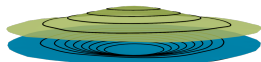
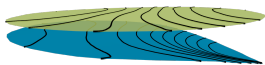
Grenzflächenwellen in Dreischichtsystemen



$$\mathcal{A} = \frac{\rho_C - \rho_E}{\rho_E - \rho_A}$$

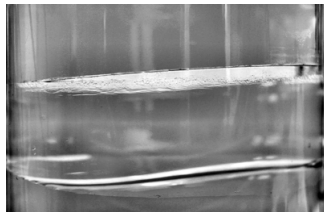


\mathcal{A}



gegenphasig, schwach gekoppelt

gleichphasig, stark gekoppelt



Nore et al. (2021) Phys. Rev. Lett.

Kopplungsbereiche für verschiedene FMB

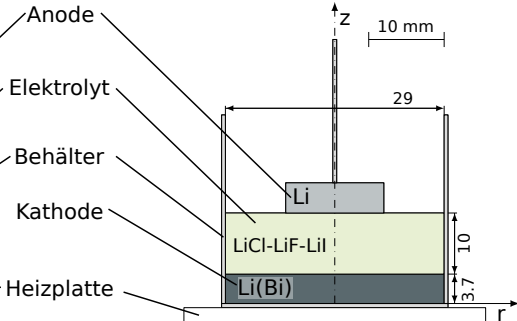
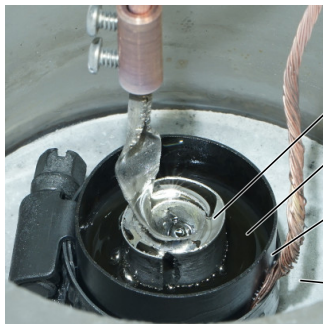
Elektroden	Elektrolyt	T_{op} (°C)	ρ_A	ρ_E (kg m ⁻³)	ρ_C	A_g	
Li Se	LiCl-LiF-LiI	375	497	2690	3814	0.51	stark gekoppelt
Al Al-Cu	AlF ₃ -NaF-CaCl ₂ -NaCl	800	2300	2700	3140	1.1	
Li Te	LiCl-LiF-LiI	475	489	2690	5782	1.41	
Na Sn	NaCl-NaI	625	801	2420	6740	2.67	schwach gekoppelt
Li Bi	LiCl-LiF-LiI	485	488	2690	9800	3.22	
Na Bi	NaCl-NaI-NaF	550	831	2549	9720	4.18	
K Hg	KBr-KI-KOH	250	640	2400	12992	6.02	nicht gekoppelt
Ca Sb	CaCl ₂ -LiCl	700	1401	1742	6270	13.28	
Ca Bi	CaCl ₂ -LiCl	550	1434	1803	9720	21.43	
Mg Sb	KCl-MgCl ₂ -NaCl	700	1577	1715	6270	33.06	

Kopplungsbereiche für verschiedene FMB

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Mg Sb	KCl-MgCl ₂ -NaCl	700	1577	1715	6270	33.06	

Frary (1925): „Care must be taken to maintain an adequate metal thickness in the cathode layer; otherwise the heavy currents and powerful magnetic fields set up a swirling motion so violent that the anode and cathode layers can come into contact in spots.“

Zyklieren mit Ruhephasen



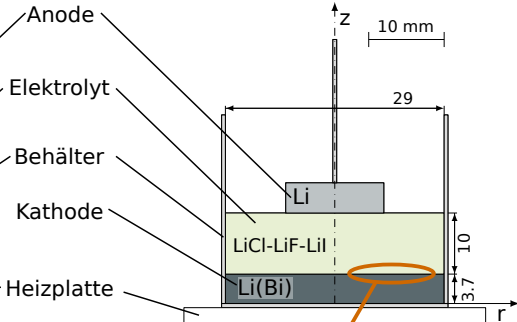
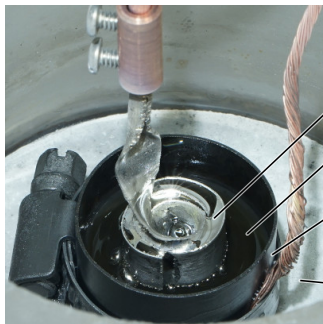
$$T_{\text{op}} = 460\text{ }^{\circ}\text{C}$$

$$A_{\text{A}} = 1\text{ cm}^2$$

$$\text{LiCl-LiF-LiI: } 29.1-11.7-59.2, T_{\text{m}} = 341\text{ }^{\circ}\text{C}$$

$$E = E_{\text{OC}} \pm (IR_{\text{E}} + \eta_{\text{a,A}} + \eta_{\text{a,C}} + \eta_{\text{c,A}} + \eta_{\text{c,C}})$$

Zyklieren mit Ruhephasen



$$T_{\text{op}} = 460 \text{ } ^\circ\text{C}$$

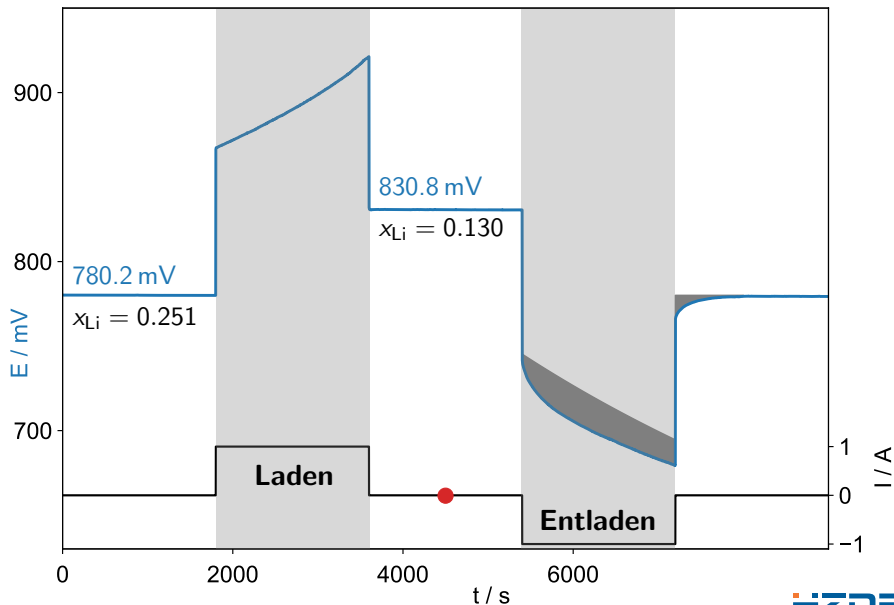
$$A_A = 1 \text{ cm}^2$$

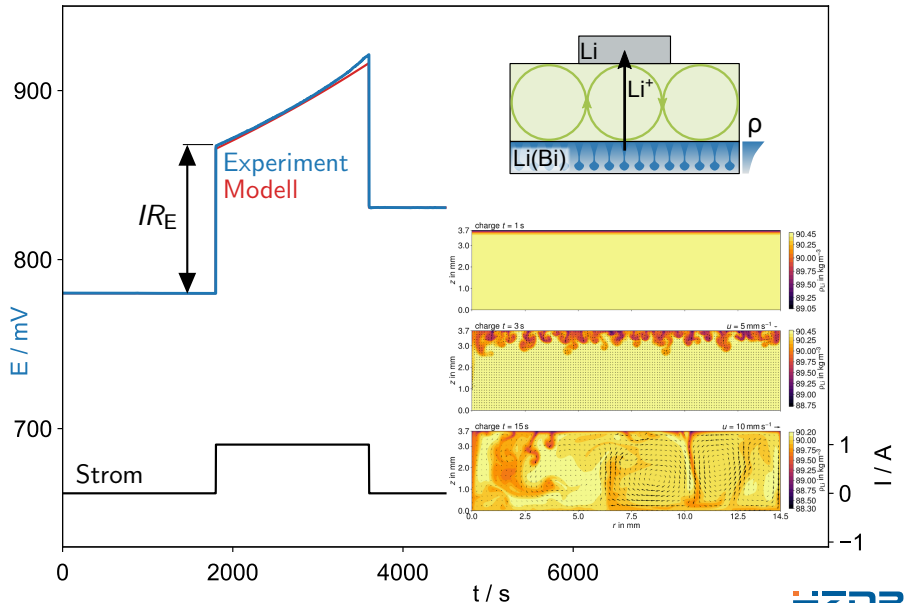
$$\text{LiCl-LiF-LiI: } 29.1\text{-}11.7\text{-}59.2, T_m = 341 \text{ } ^\circ\text{C}$$

$$E = E_{\text{OC}} \pm (IR_E + \cancel{\eta_{a,A}} + \cancel{\eta_{a,C}} + \cancel{\eta_{c,A}} + \eta_{c,C})$$

$$\underbrace{-\frac{RT}{z_e F} \ln a_{\text{Li(Bi)}}}_{\text{an der Elektrolyt|Li(Bi) Grenzfläche}}$$

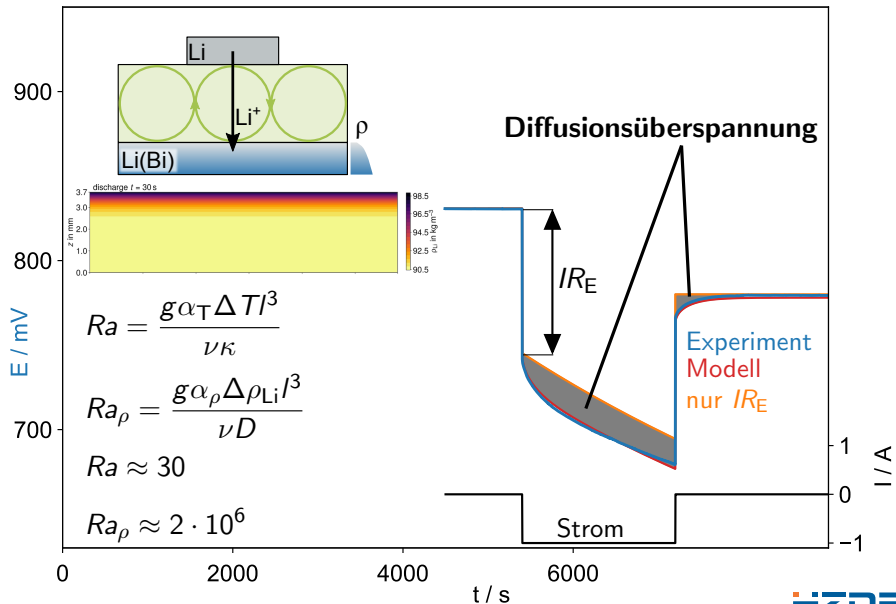
Asymmetrie der Lade-/Entladespannung



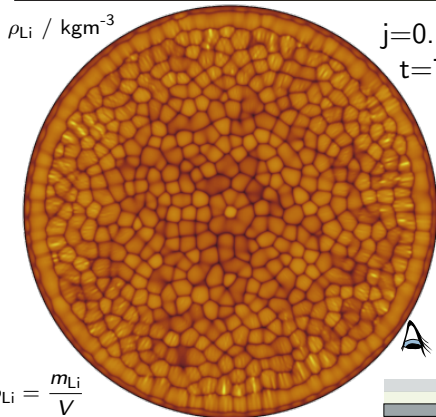
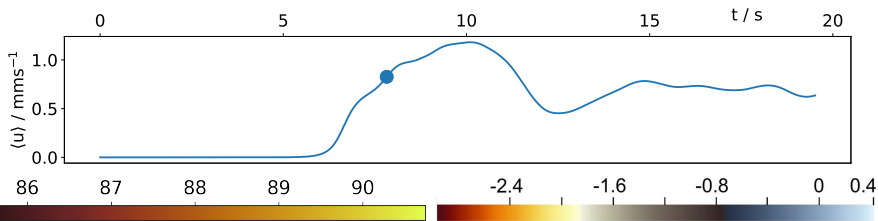


Entladen

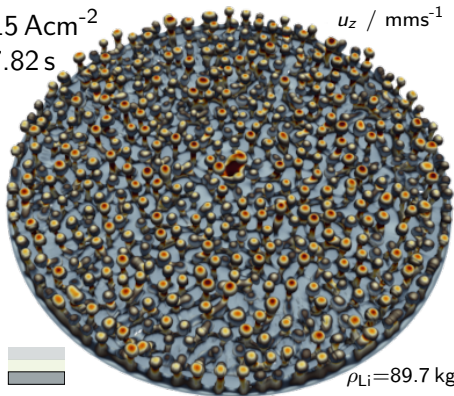
Personnetaz et al. (2019) Electrochem. Comm.
Kelley, Weier (2018) Appl. Mech. Rev.



Laden: solutale Konvektion in der Kathode



$j=0.15 \text{ Acm}^{-2}$
 $t=7.82 \text{ s}$



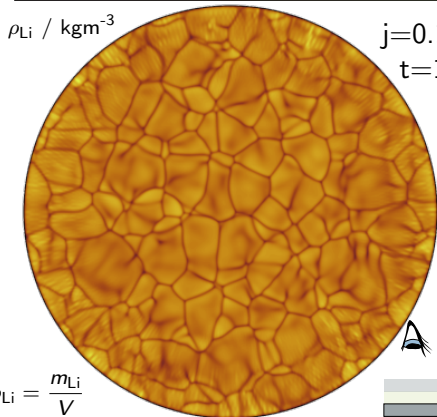
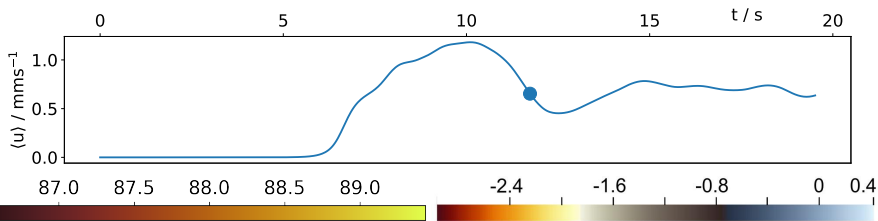
$$\rho_{\text{Li}} = \frac{m_{\text{Li}}}{V}$$



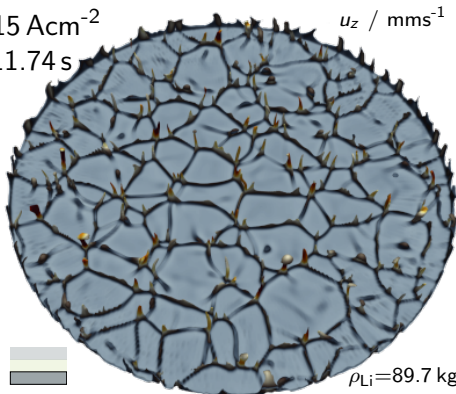
$\rho_{\text{Li}}=89.7 \text{ kgm}^{-3}$

HZDR

Laden: solutale Konvektion in der Kathode



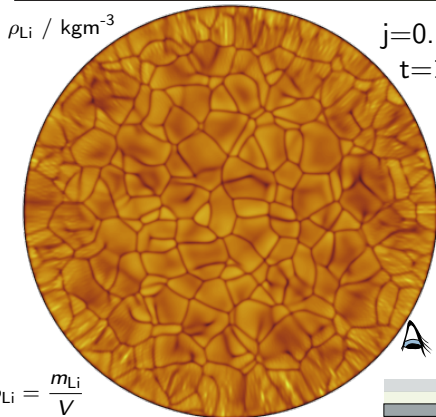
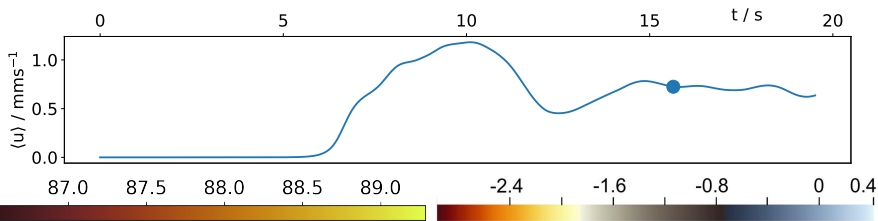
$j = 0.15 \text{ Acm}^{-2}$
 $t = 11.74 \text{ s}$



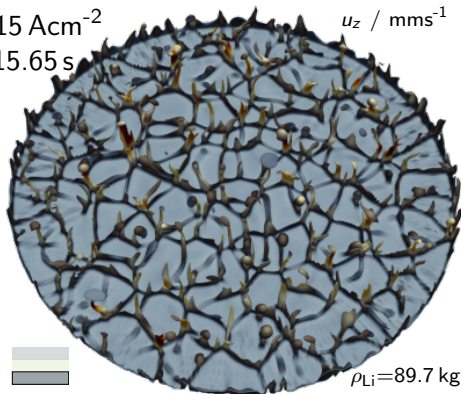
$$\rho_{\text{Li}} = \frac{m_{\text{Li}}}{V}$$

$\rho_{\text{Li}} = 89.7 \text{ kgm}^{-3}$

Laden: solutale Konvektion in der Kathode



$j = 0.15 \text{ Acm}^{-2}$
 $t = 15.65 \text{ s}$

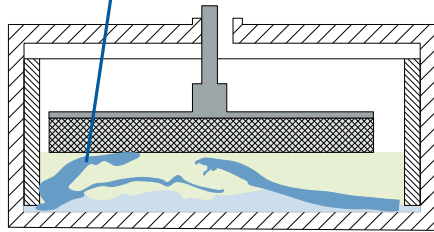
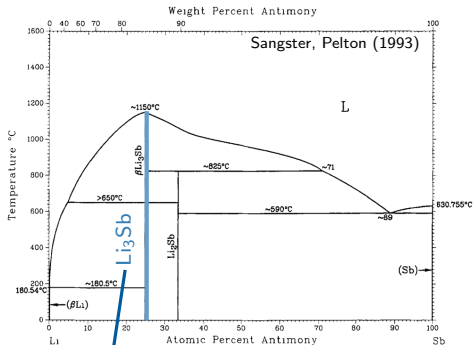


Entladen: Bildung intermetallischer Phasen

- Li||Sb Zelle
- beim Entladen Li-Anreicherung Nähe Kathodenoberfläche
- ➔ Bildung von Li_3Sb
- ➔ mechanische Spannungen in der intermetallischen Deckschicht
- ➔ Aufwölbung
- ➔ Kurzschluss

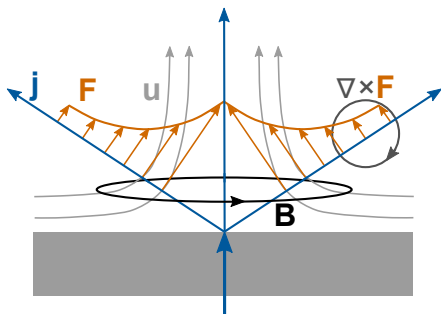


Kelley (2017)



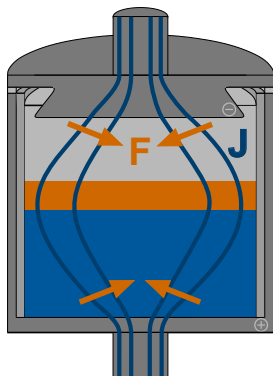
Elektrowirbelströmungen

Beispiel: Punktquelle



- radiale Stromdichtekomponenten
- Lorentzkraft **rotationsbehaftet**

Flüssigmetallbatterie



- Querschnittsänderungen
- rotationsbehaftete Lorentzkraft

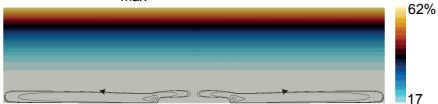
Schichtung, Vermischung & Elektrowirbelströmungen



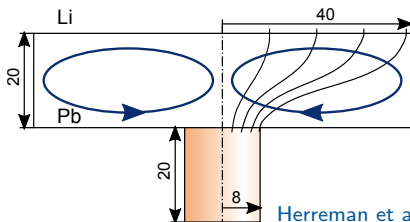
$t = 322$ s, $u_{max} = 3.9$ mm/s



$t = 1167$ s, $u_{max} = 3.0$ mm/s



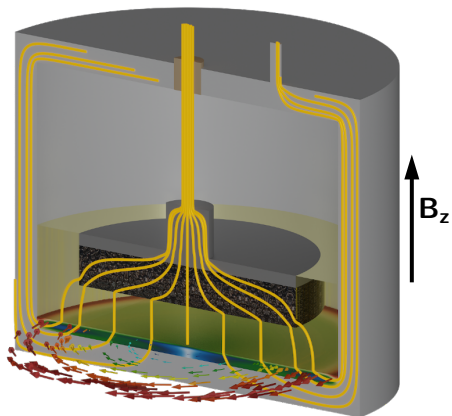
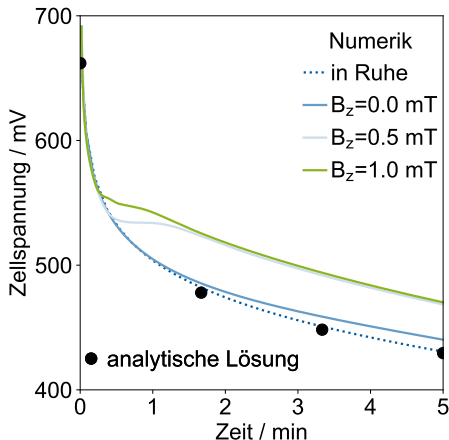
$t = 2944$ s, $u_{max} = 0.2$ mm/s



Herreman et al. (2020) Phys. Rev. Fluids

- Kann eine Elektrowirbelströmung die Bildung einer stabilen Dichteschichtung beim Entladen verhindern?
- **SFEMaNS** (TAMU/UH/LIMSI)
- Li||Pb Zelle, Entladen, 500°C
- homogene Stromdichte 0.5 A/cm^2 an Kathodenoberseite
- ➔ Ringwirbel
- elektrischer und Stoffstrom gekoppelt (Faraday'sches Gesetz):
$$m = \frac{M}{z_e F} I t$$
- ➔ ungenügende Vermischung für moderate Zellengrößen

Vermischung durch Drallströmung



- 100 Ah Zelle von Ning et al. (2015) simuliert (Li||Bi)
- Stromdichte 1 A/cm^2 , komplett geladen ($x_{\text{Li}}=0.02$)
- Drallströmung: Überspannungen $\sim 60\% \downarrow$, einfache EVF: nur $\sim 10\% \downarrow$

TerraScale: Energos Reno mit Ambri Speichern

TerraScale: „Energos Reno project“

- Churchill County
- ca. 1500 Hektar
- 500 MW EE
- Mischnutzung,
Rechenzentren
- Projektstart 2020
- Nutzungsbeginn 2022 mit 20 MW



Ambri (2019)

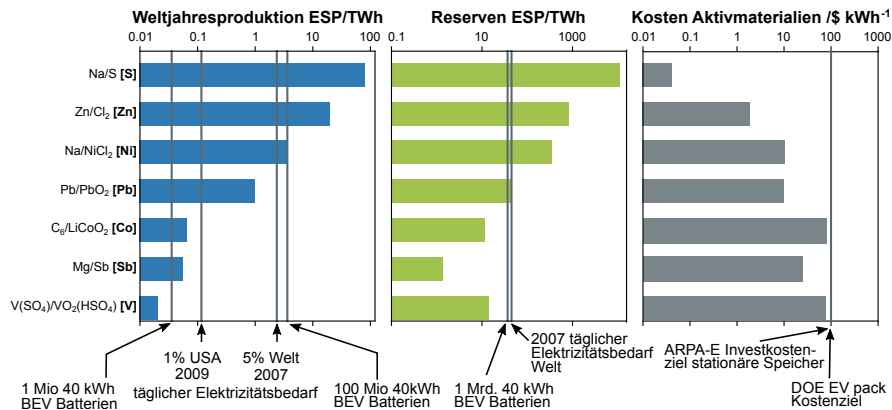


Ambri (2020)

Speicher von Ambri

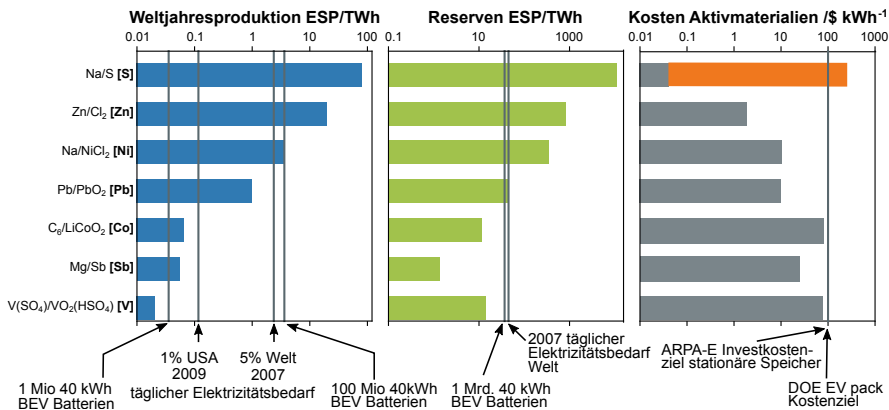
- 250 MWh
- 20 Jahre Lebensdauer
bei 100% DOD
- 500 °C
- Ca-Sb

Energiespeicherpotential (ESP)



adaptiert von Wadia et al. (2011)

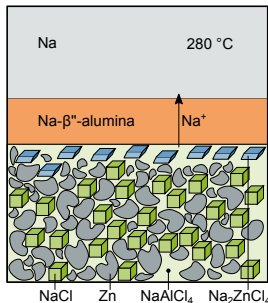
Energiespeicherpotential (ESP)



adaptiert von Wadia et al. (2011)

Horizon 2020 Projekt SOLSTICE: Na||ZnCl₂

„Sodium-Zink molten salt batteries for low-cost stationary storage“



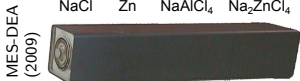
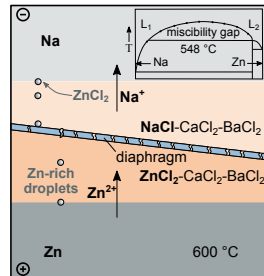
eine Aktivmaterialkombination

$$2 \text{Na} + \text{ZnCl}_2 \rightarrow 2 \text{NaCl} + \text{Zn}$$

zwei Systeme:

Standardbedingungen: 1.95 V
 theo. Kapazität: 570 Wh/kg
 Aktivmaterialien: ~4€/kWh

Projektlaufzeit: 2021-2024
 12 Partner, ~ 8 Mio. €



Das Projekt SOLSTICE wird im Rahmen des Horizon 2020 Programms der Europäischen Union unter der Finanzhilfvereinbarung Nr. 963599 gefördert.



Zusammenfassung

- Flüssigmetallbatterien als stationäre Großspeicher
- wichtiger Aspekt: Skalierung auf Zellebene
- vollständig flüssiges Inventar → Strömungsmechanik
- facettenreiche Dynamik der Oberflächenwellen
- Konzentrationsgradienten bestimmen Konvektion in der Kathode
- EVF: Vermischung beim Entladen, Drall hilft

und Ausblick

- Erweiterung Numerik
- Mehrkomponenten-Kathoden
- Na||Zn Zellen im Rahmen von SOLSTICE

