Progress in R&D of Molten Salt Electrolytes for Molten Salt Batteries

Wenjin Ding[1], Ralf Hoffmann[1], Thomas bauer[2]

1. Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany
2. Institute of Engineering Thermodynamics, DLR, Cologne, Germany

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BACKGROUND AND MOTIVATION

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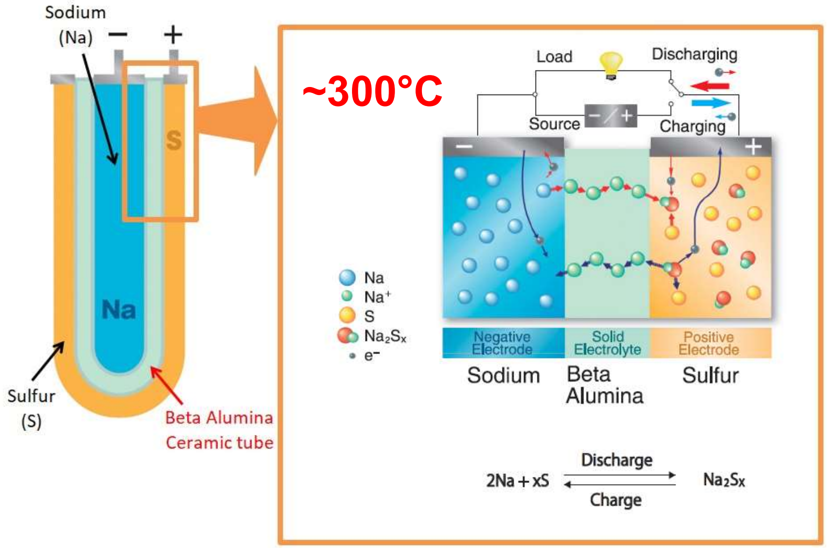
Molten salt batteries: NaS battery, liquid metal battery, ZEBRA battery, etc.

Sodium–sulfur battery (NaS battery)

- Excellent storage performance as Li-ion batteries with long lifetime of ≥10 years
- Commercial stationary grid storage plants (MWh-GWh)
- NGK Insulators (Japan): Total capacity of 700 MW/4.9 GWh in 2023
- But durability and safety issues due to beta-alumina solid electrolyte

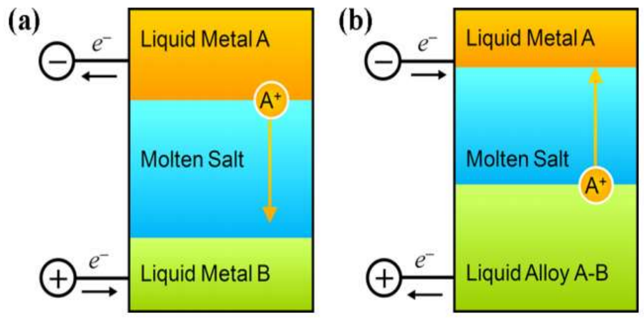


https://www.ngk-insulators.com/en/product/nas-solutions01.html

https://www.ngk-insulators.com/en/product/nas-solutions.html

Liquid metal battery (LMB battery)

- Excellent storage performance as Li-ion batteries with long lifetime of ≥20 years
- Ambri (USA): Commercialization for stationary grid storage (MWh-GWh)
- But low OCP (<1 V) and high operation temperature (≥500°C)

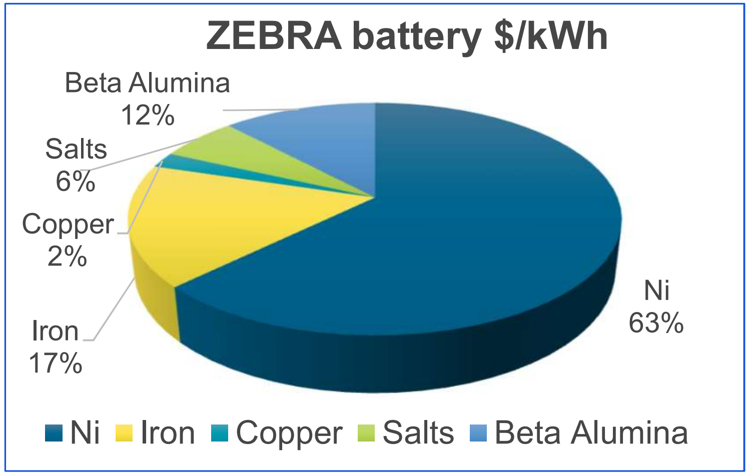


Anode $A \longleftrightarrow A^{z+} + ze^-$

Cathode $A^{z+} + ze^- + B \longleftrightarrow A(B)$

ZEBRA battery (Na-$NiCl_2$ battery)

- Excellent storage performance as Li-ion batteries with long lifetime of ≥10 years
- > 500 MWh commercial applications in automobile, cellular base station, etc.
- Suitable for stationary grid storage (MWh-GWh)
- Ni has large share of the cell material cost (more than 60%)

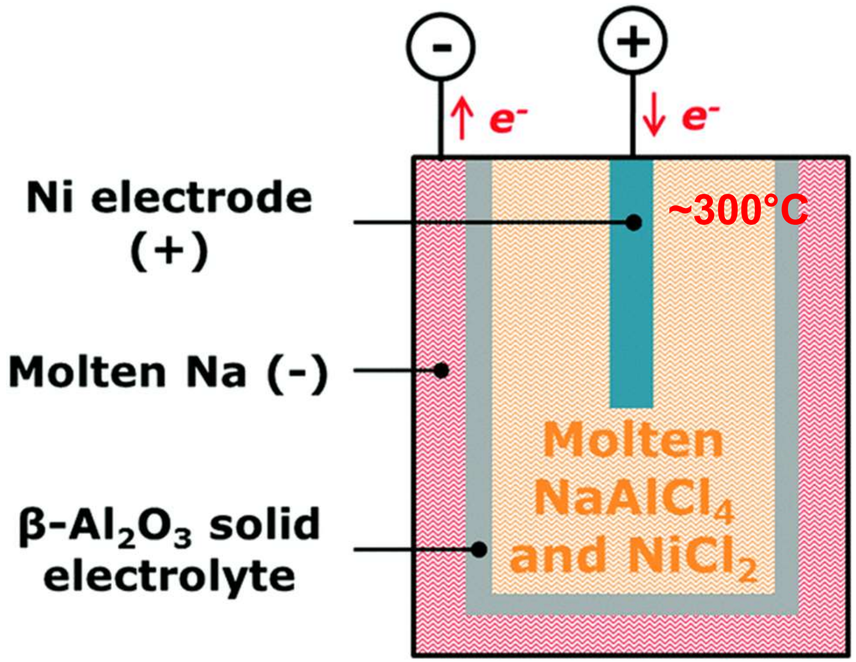


R. C. Galloway and C.-H. Dustmann, *ZEBRA Battery – Material Cost, Availability and Recycling*, MES-DEA GmbH, EVS 20, 2003

How ZEBRA battery works

- Working temperature of ~300 ℃
- Na anode, $NiCl_2$-Ni cathode
- Beta Alumina solid electrolyte (BASE) with good Na^+ ion conduction used
- Low melting point secondary electrolyte containing $AlCl_3$($NaAlCl_4$ ~155°C) for high conductivity
- Molar ratio NaCl:$AlCl_3$ >1 (basic nature*) in fully charged state for compatibility with BASE

$$2\,NaCl + Ni \underset{discharge}{\overset{charge}{\rightleftharpoons}} NiCl_2 + 2\,Na$$

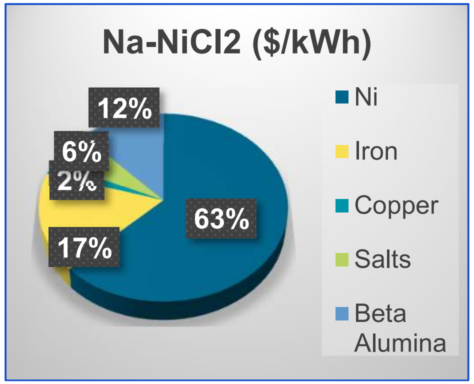


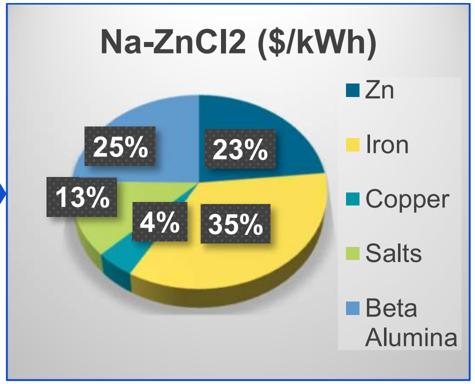
*Kim, J., et al. (2016). Journal of the Korean Electrochemical Society, 19(3), 57–62

EU H2020 project SOLSTICE: Na-$ZnCl_2$ battery

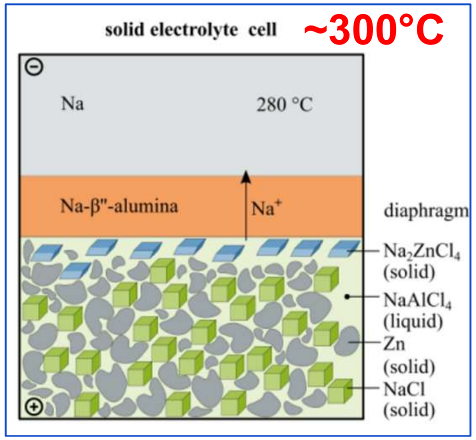
DLR

- Replacing Ni with Zn*: Cell material cost reduced by 40 %, overall battery cost by 20 %
- Promising cell performance has been shown in literature but more study on molten salt electrolyte is required to improve the cell performance*
- SOLSTICE studying on
  - $ZnCl_2$-NaCl-$AlCl_3$ salt electrolyte (melting temperature, phase change, vapor pressure, etc.) for Na-$ZnCl_2$ solid electrolyte battery (SEB)
  - Selection of molten salt electrolyte for Na-$ZnCl_2$ all liquid battery (ALB)





$$2\,NaCl + Zn \underset{discharge}{\overset{charge}{\rightleftharpoons}} ZnCl_2 + 2\,Na$$



Na-$ZnCl_2$ SEB

Na-$ZnCl_2$ ALB

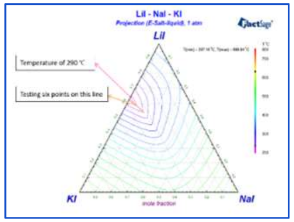
*Lu, X., et al. *Energy & Environmental Science* 6 (2013): 1837-1843.

METHODS AND RESULTS

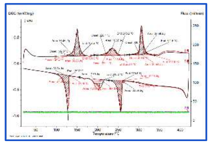
Methods

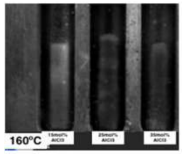
- Simulation-assisted molten salt electrolyte selection for all molten salt batteries
- FactSage simulation, DSC measurements, key salt properties determination and material cost analysis are used for selection
- Battery cell tests

1. Screening of salt mixtures via phase diagram simulation (T_m)



2. Measurements of melting temperatures T_m

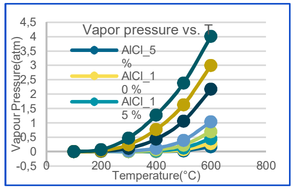


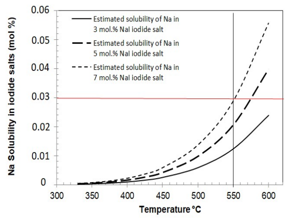


(c) Start of melting

3. Pre-selection of molten salt electrolytes

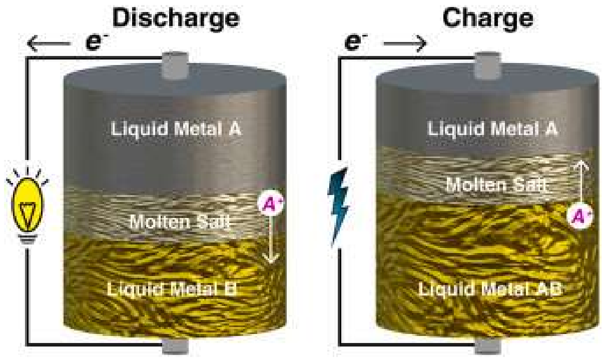
4. Determination of key salt properties as electrolytes





5. Cost analysis of materials

6. Battery cell Tests with selected molten salt electrolytes



https://doi.org/10.1016/j.rser.2022.112167

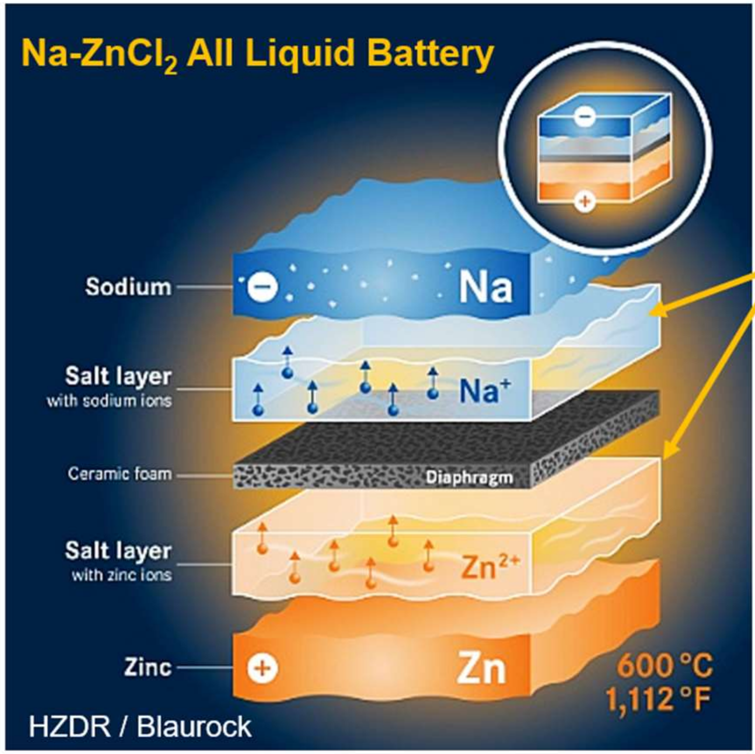
Liquid metal battery (LMB battery)

LMBs	Electrode	Electrolyte	T_m [°C]	T_w [°C]	Coulombic efficiency [%]	Energy efficiency [%]	self-discharge rate [mA/cm^2 at full charge]	Capacity loss rate [%/cycle]
Li-LMB (MIT)[1]	Anode: Li; Cathode: Sb-Sn	LiF-LiCl-LiBr	440	500	>98	70-90	NA	0.006
Ca-LMB (MIT & Ambri)[2]	Anode: Ca alloys; Cathode: Sb alloys	LiCl-NaCl-$CaCl_2$	450	500	~100	>80	NA	<0.01
Na-LMB (ANL)[3]	Anode: Na Cathode: Bi	NaF-NaCl-NaI (single-cation)	530	580	82	59	~20	NA
Na-LMB (HUST, DLR, KIT)[4]	**Anode: Na Cathode: Bi-Sb**	**LiCl-KCl-NaCl (59:5:36 mol%)**	**350**	**450**	**>97**	**~80**	**<1**	**Over 700 cycles no fade, estimated lifetime >15 000 cycles**

1. K. Wang, K. Jiang, B. Chung, et al.. ***Nature***, 2014, 514(7522): 348-350.
2. T. Ouchi, et al., ***Journal of ECS***, 2014, 161(12): A1898-A1904, and Technology: Ambri
3. H. Kim, K. Wang, K. Jiang, D. Sadoway, et al., ***Chem. Rev.*** 113, 2075 (2013).
4. H. Zhou, W. Ding, A. Weisenburger, K. Wang, K. Jiang, et al., Ener. Stor. Mater., 2022, 50: 572-579.
5. W. Ding, Q. Gong, et al., Journal of Power Sources 553, 232254

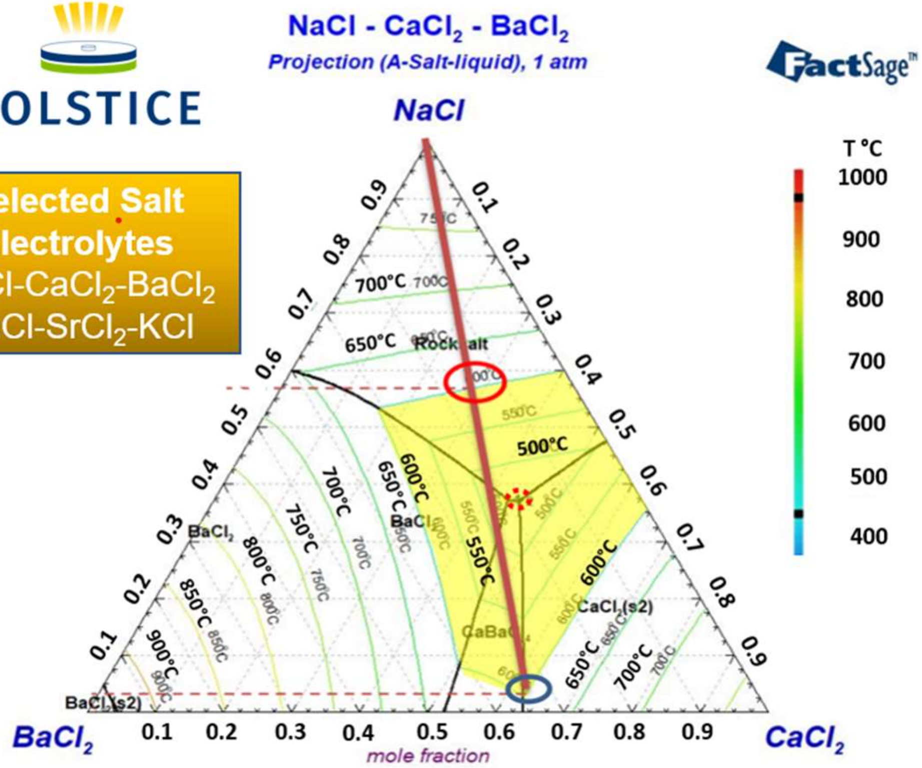
DFG-NSFC research project (2019-2023): Study on Corrosion Control and Low-Temperature Electrolytes for Low-Cost Na-Based Liquid Metal Batteries (Na-LMB)

Na-ZnCl$_2$ all liquid battery (ALB)



SOLSTICE

Selected Salt Electrolytes
NaCl-CaCl$_2$-BaCl$_2$
NaCl-SrCl$_2$-KCl

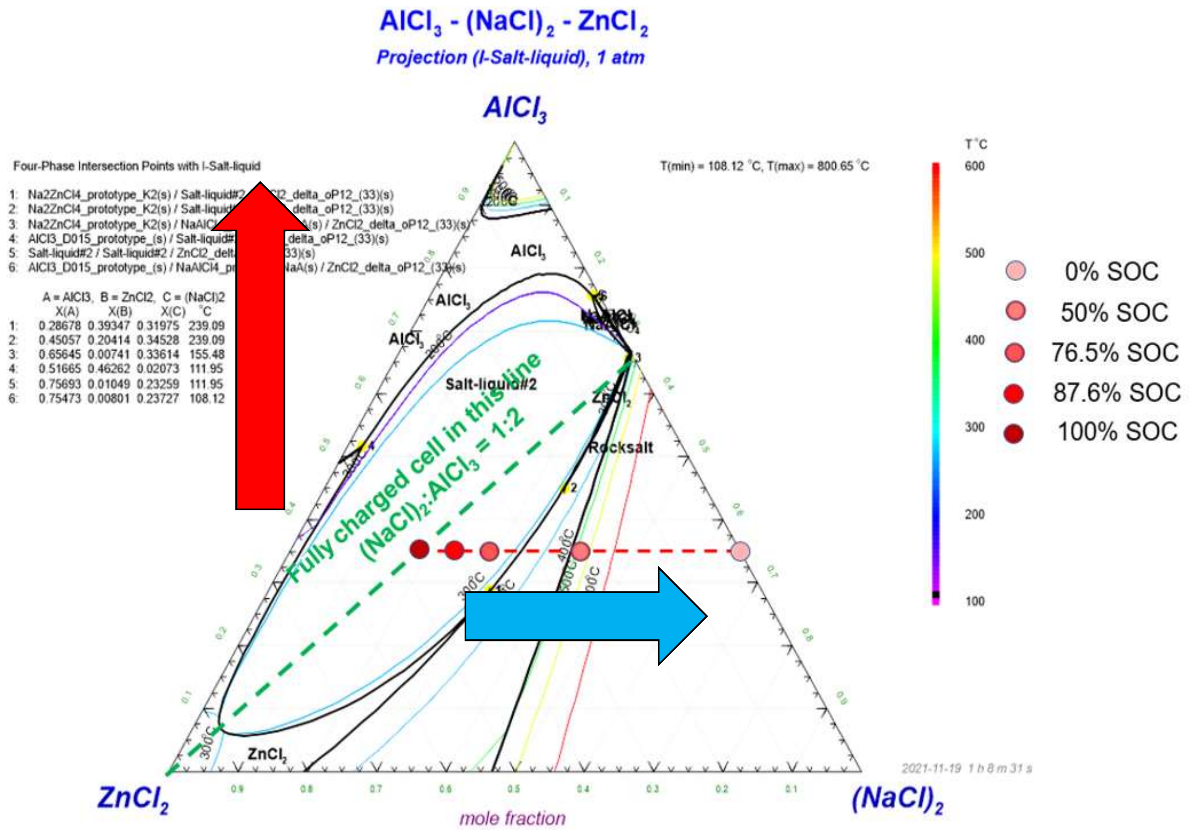


https://doi.org/10.3390/batteries11050177

Molten salt electrolyte for Na-ZnCl2 solid electrolyte battery

- Simulated phase diagram of $ZnCl_2$-$(NaCl)_2$-$AlCl_3$

- Increasing $AlCl_3$, melting temperature of the salt electrolyte decreases fast
- Increasing NaCl during discharging (SOC from 100% to 0%), melting temperature decreases fast
- Next step: Cutting ternary phase diagram at constant $AlCl_3$ mol.% for analysis of phase changes with SOC change



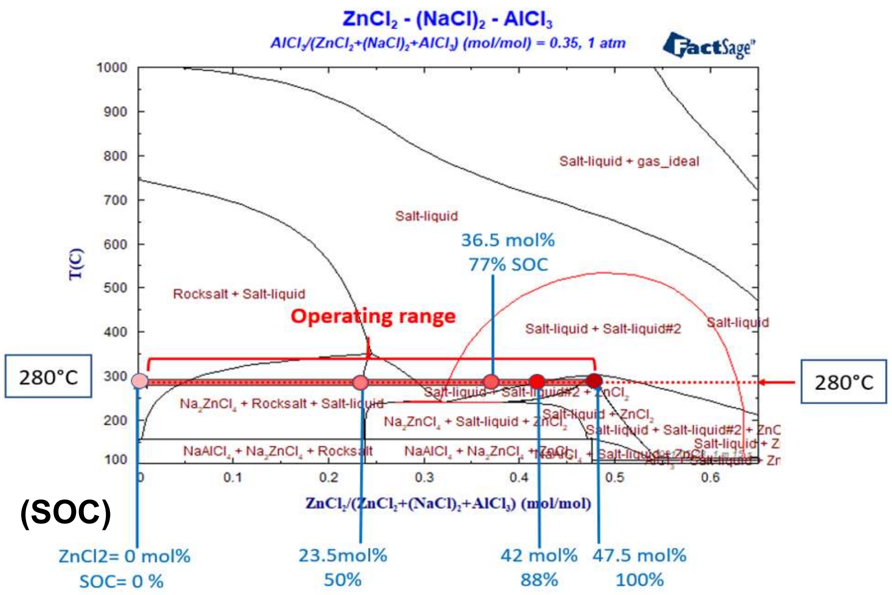
Overall reaction

2NaCl+Zn ⟷ 2Na+$ZnCl_2$

https://doi.org/10.3390/batteries9080401

Binary phase diagram simulation

- Binary phase diagrams of $AlCl_3$ = 0-50 mol% simulated
- Phase changes with SOC change simulated
- Voltage change with SOC change in the cell test could be explained with the phase changes
- Next step: DSC & OptiMelt to experimentally verify simulation results



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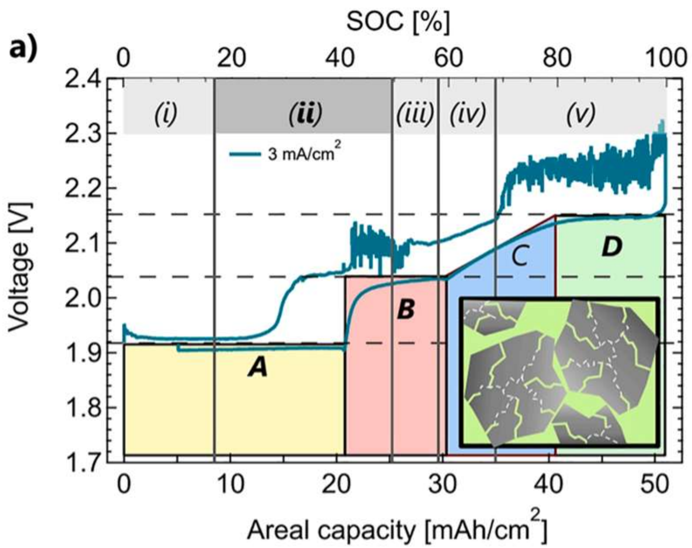
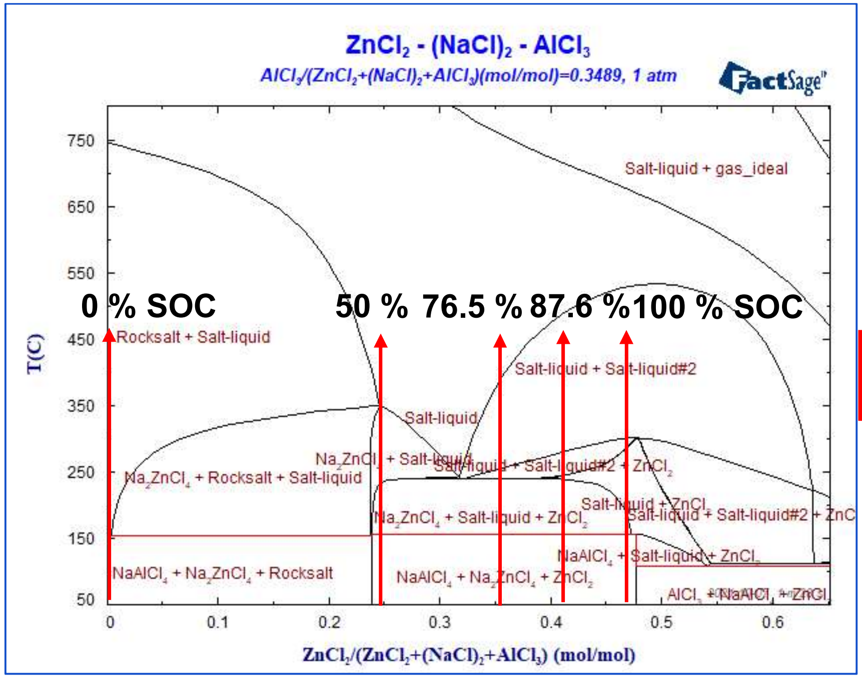
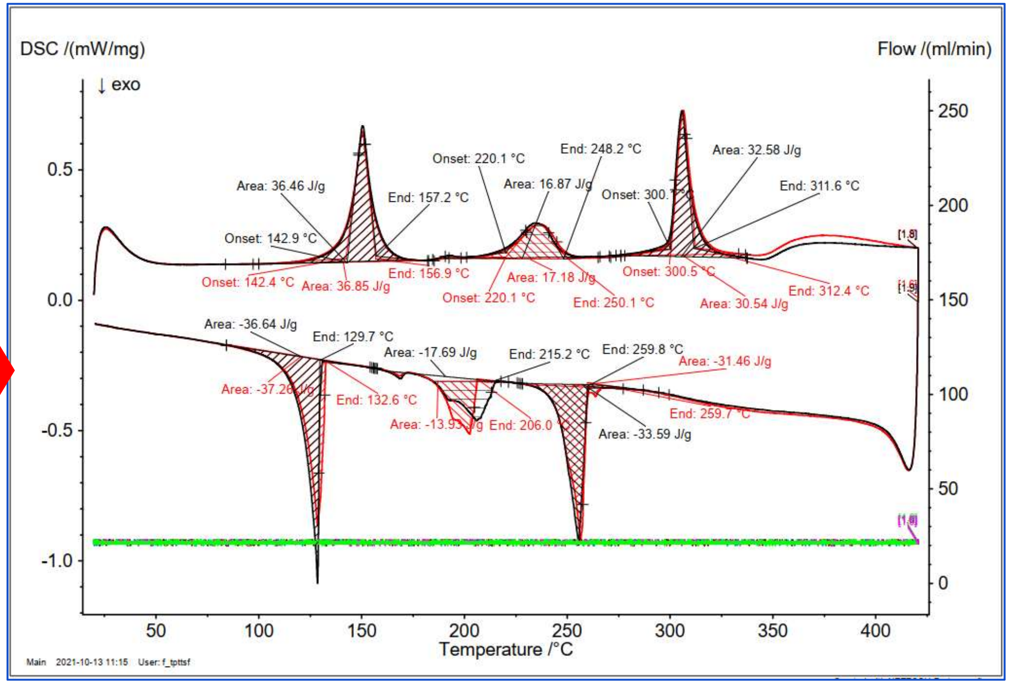


https://doi.org/10.1016/j.ensm.2023.103077

DSC^{TM} results





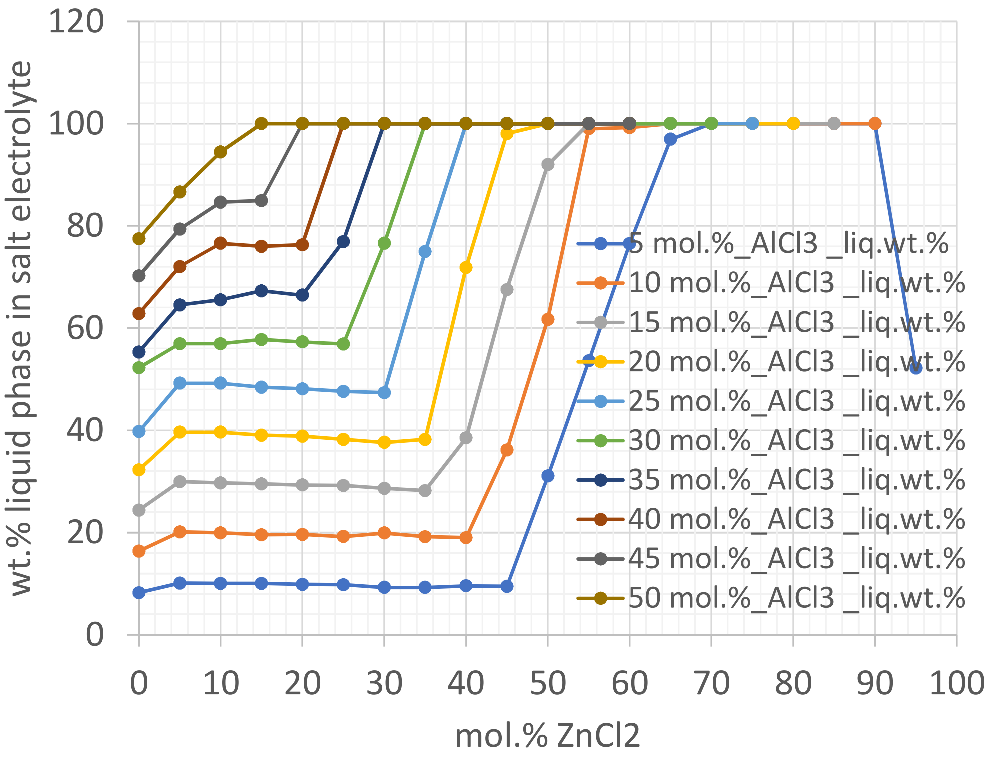
DSC results complying with simulation results

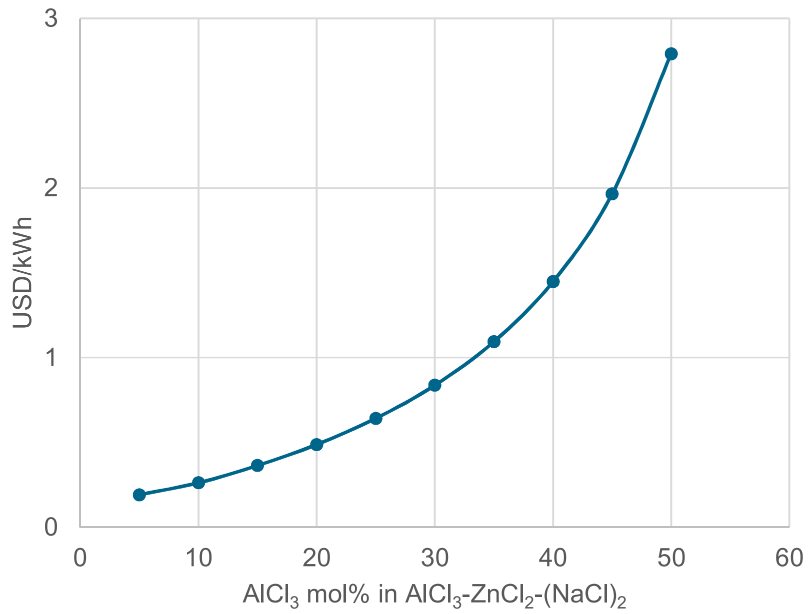
https://doi.org/10.3390/batteries9080401

SOC(%)	$AlCl_3$	$ZnCl_2$	2NaCl	Factsage	DSC
	mol%	mol%	mol%	Transition Temperature(°C)	Start(°C)
100	34.89	47.67	17.44	155	152
				200	204
				300	303.7

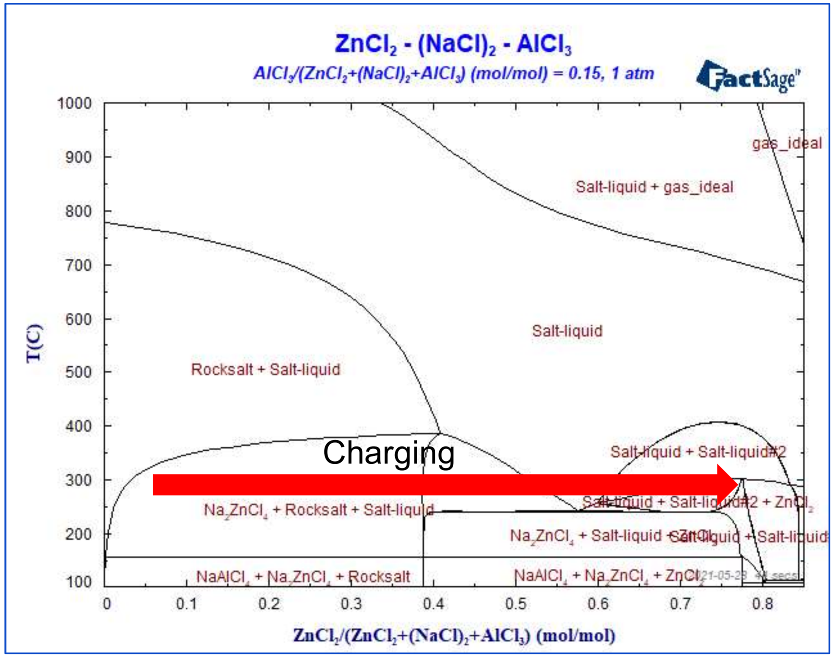
Liquid phase in salt electrolyte at 300°C (simulation)

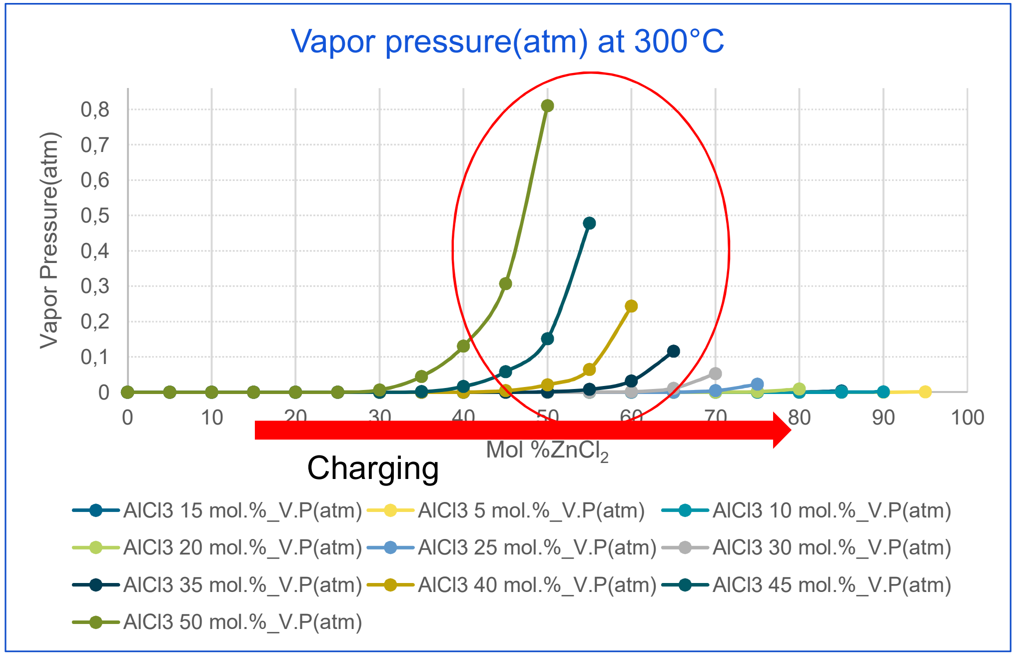
- Fully discharged state: 0 mol% $ZnCl_2$
- Full charge state: basic nature ($NaCl:AlCl_3 \geq 1:1$ or $(NaCl)_2:AlCl_3 \geq 1:2$)
- Salt cost for 1 kWh storage increases with increasing $AlCl_3$
- But low $AlCl_3$ concentration leads to low conductivity (low liquid phase wt.%) in fully discharged state





Vapor pressure vs. salt composition





- High salt vapor pressure can lead to failure of e.g., BASE, sealing (safety issue)
- Maximum vapor pressure at high $ZnCl_2$ and $AlCl_3$ concentration
- Vapor pressure is below 1 atm for 300 °C at increasing mol% of $AlCl_3$ till 50 mol%
- Pay attention on $AlCl_3$ concentration, cell overcharge and temperature runaway

Summary

- This method has been successfully used for liquid metal battery, Na-$ZnCl_2$ SEB and ALB batteries.
- Obtained phase diagrams, phase behaviours and vapor pressures could be used for battery cell operation and optimization.
- Simulation-assisted method for molten salt electrolyte selection in this study could be used for all molten salt batteries.

Thanks for your Attention!

Dr. Wenjin Ding: Wenjin.Ding@dlr.de

Dr. Thomas Bauer: Thomas.Bauer@dlr.de

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https://www.solstice-battery.eu/