Molten Salt Batteries for Grid Storage

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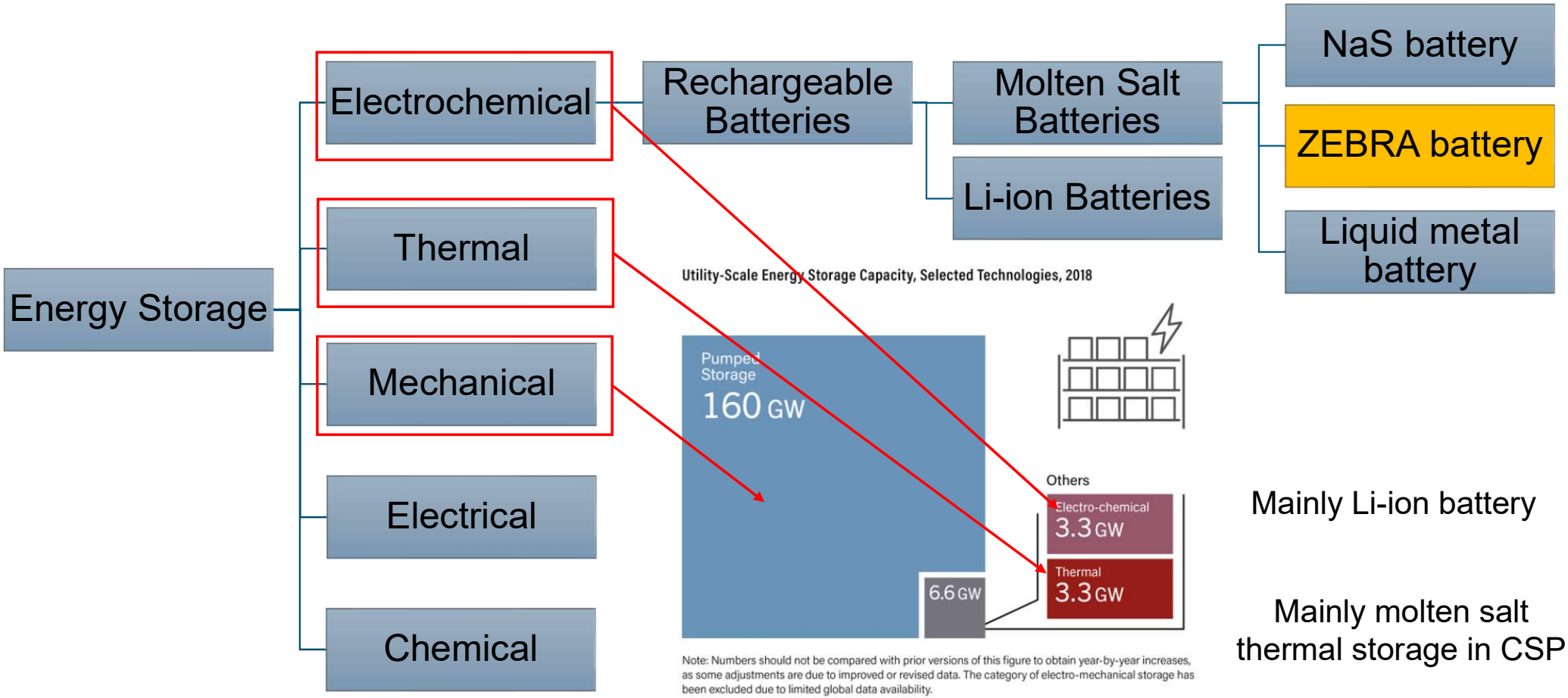
DLR

BACKGROUND AND MOTIVATION

Energy storage classification and global capacity

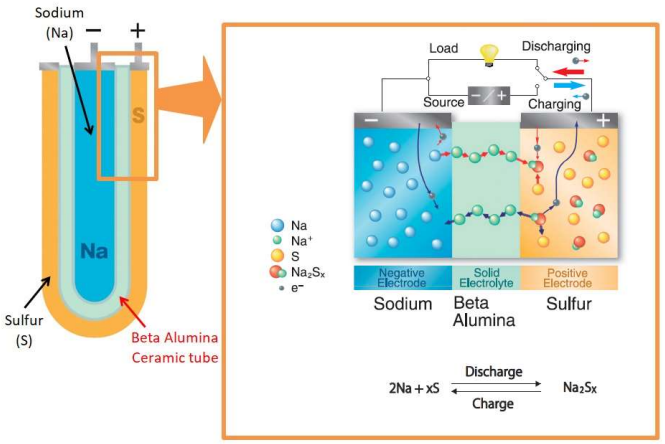


Mainly Li-ion battery

Mainly molten salt thermal storage in CSP

Sodium–sulfur battery (NaS battery)

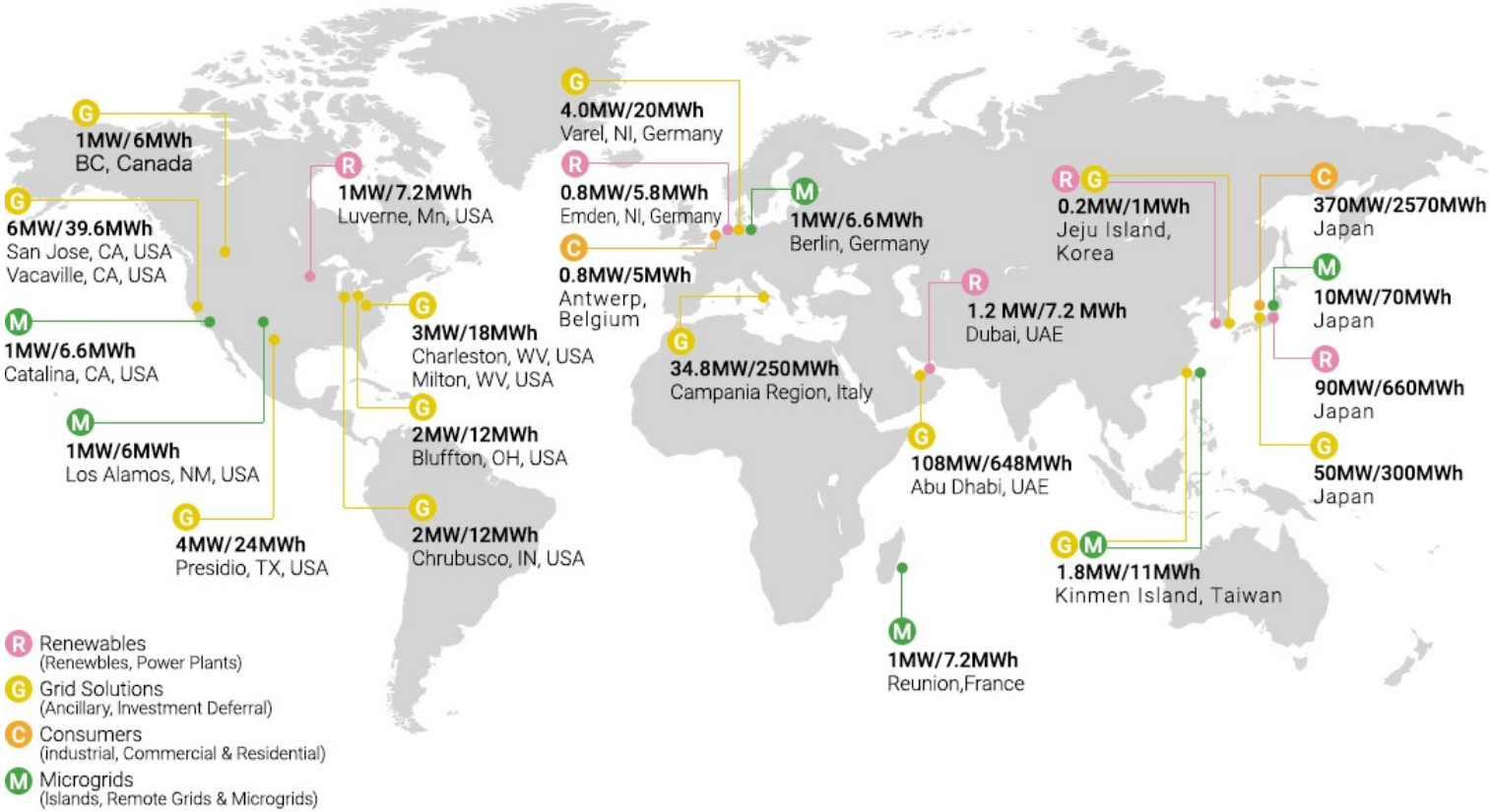
- Excellent storage performance as Li-ion batteries
- Low CAPEX cost of ≤100 USD/kWh
- Long lifetime of ≥10 years
- Commercial stationary grid storage plants (MWh-GWh)
- But durability and safety issues due to beta-alumina solid electrolyte



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

Sodium–sulfur battery (NaS battery)

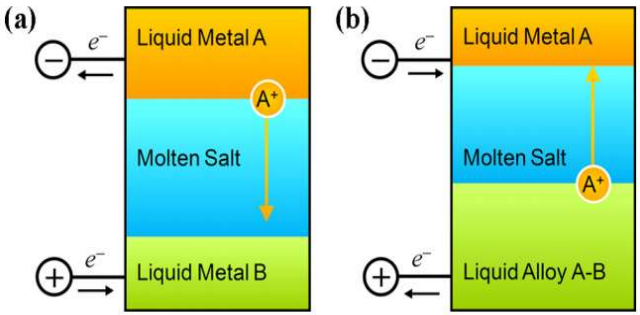
- Over 250 projects, the total capacity of 700 MW/4.9 GWh



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

Liquid metal battery (LMB battery)

- Excellent storage performance as Li-ion batteries
- Low CAPEX cost of ≤100 USD/kWh
- Long lifetime of ≥10 years
- Commercial stationary grid storage plants (MWh-GWh)
- But durability and safety issues due to beta-alumina solid electrolyte



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

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

Liquid metal battery (LMB battery)

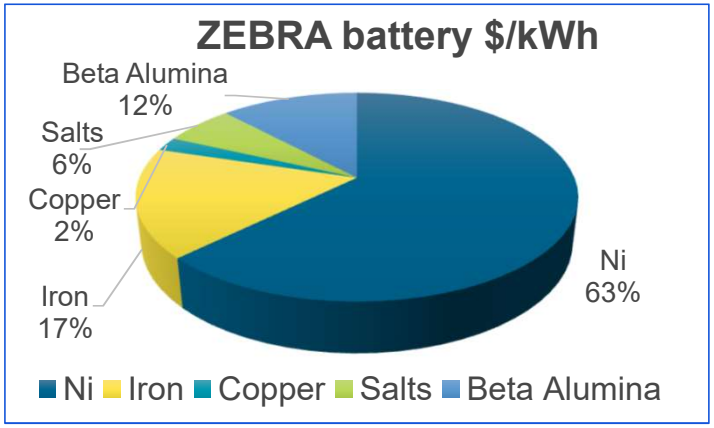
LMBs	Electrode	Electrolyte	T_m [°C]	T_w [°C]	Coulombic efficiency [%]	Energy efficiency [%]	self-discharge rate [mA/cm^2 at full charge]	Capacity loss rate [%/cycle]
Li-LMB (MIT)[1]	Anode: Li; Cathode: Sb-Sn	LiF-LiCl-LiBr	440	500	>98	70-90	NA	0.006
Ca-LMB (MIT & Ambri)[2]	Anode: Ca alloys; Cathode: Sb 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.

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

ZEBRA battery (Na-$NiCl_2$ battery)

- Excellent storage performance as Li-ion batteries
- Low CAPEX cost of ≤100 USD/kWh
- Long lifetime of ≥10 years
- 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

ZEBRA battery (Na-$NiCl_2$ battery)

- More than 40 000 Battery systems installed
- Capacity > 500 MWh

TELECOM
> 30.000 Battery systems installed

RAILWAYS
> 1.800 Battery systems installed

OIL&GAS
> 700 Battery systems installed

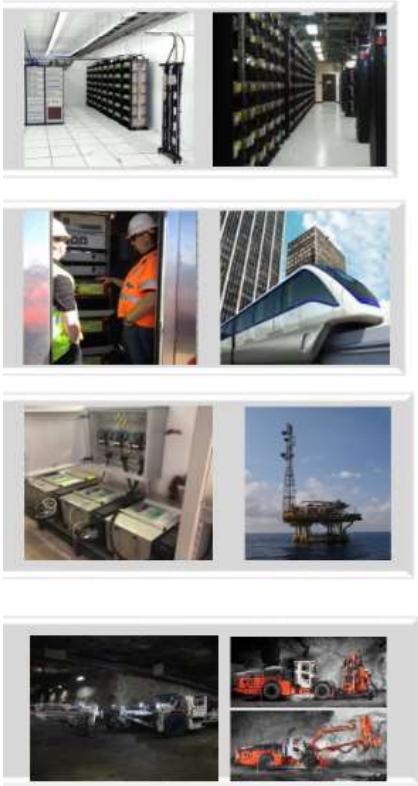
ENERGY STORAGE
> 6.000 Battery systems installed

ELECTRICAL MOBILITY
> 4.700 Battery systems installed

PRODUCTION
> 5.5 M cells (> 500 MWh) manufactured and installed

POWERED BY SALT.

FZSoNick

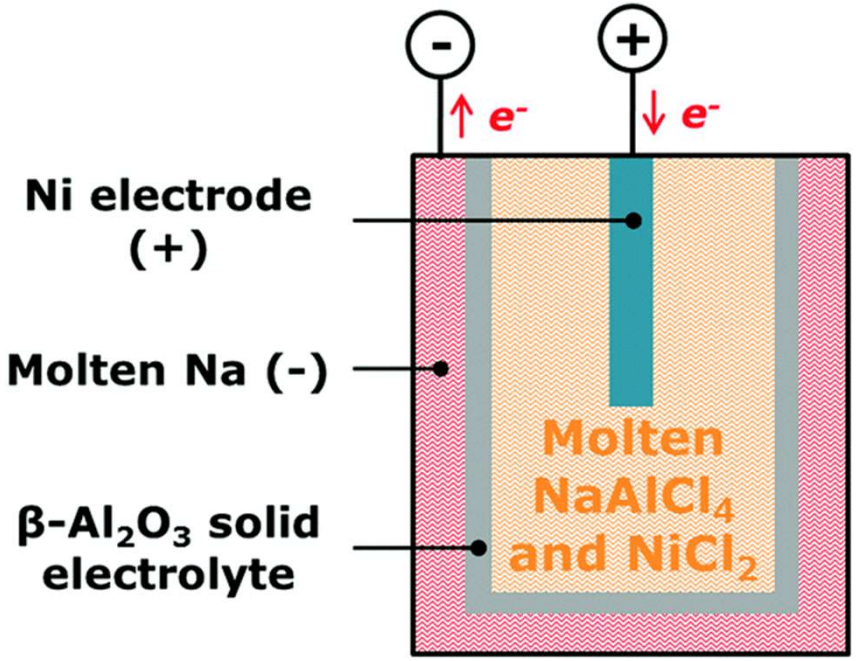


https://drive.google.com/file/d/1yrmnzXKIolegXySwIu9-E5thOUHtb72k/view

How ZEBRA battery works

- Working temperature about 280-300 ℃
- 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

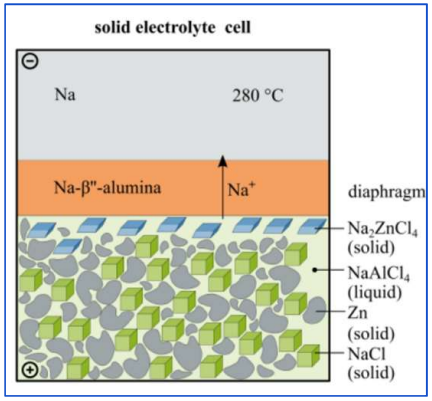
$$2\,NaCl + Ni \underset{discharge}{\overset{charge}{\rightleftharpoons}} NiCl_2 + 2\,Na$$

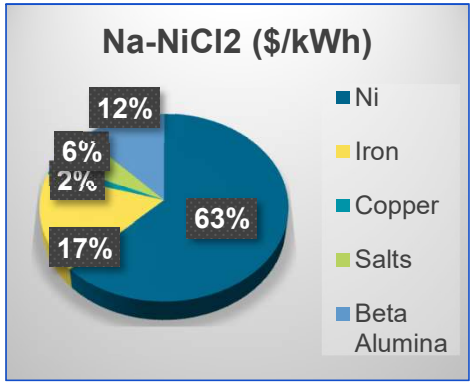


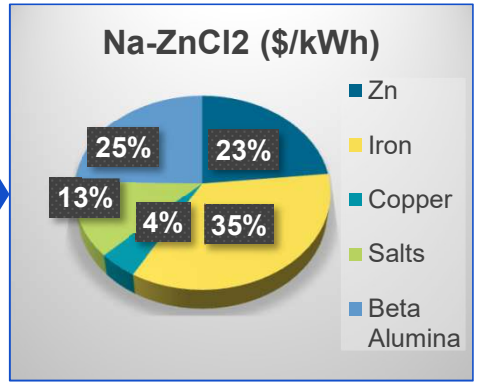
*Kim, J., et al. (2016). Journal of the Korean Electrochemical Society, 19(3), 57–62

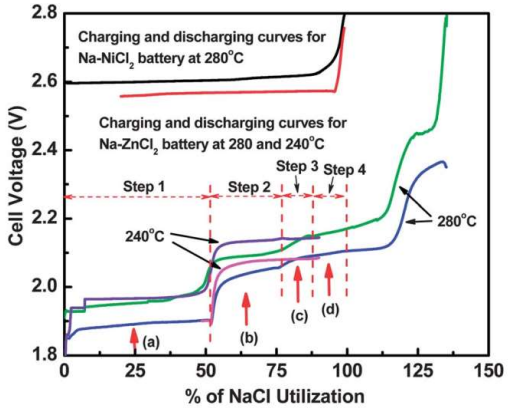
EU H2020 project SOLSTICE: Na-$ZnCl_2$ battery

- Replacing Ni with Zn*: Cell material cost reduced by 40 %, overall battery cost by 20 %
- Higher NaCl utilization: Eutectic $ZnCl_2$-NaCl (250 ℃) lower than $NiCl_2$-NaCl (550 ℃)
- Promising cell performance has been shown in literature*
- But complex reaction mechanism: Multiple reversible reactions (4 steps)
- Study on properties of $ZnCl_2$-NaCl-$AlCl_3$ salt electrolyte (melting temperature, phase change, vapor pressure, etc.) to improve the cell performance for commercial applications









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

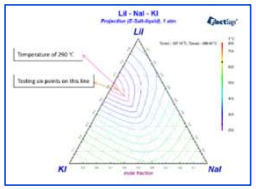
*Lu, X., et al. *Energy & Environmental Science* 6 (2013): 1837-1843.

METHODS AND RESULTS

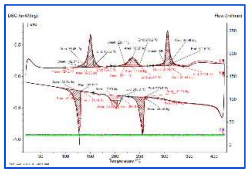
Methods

- Target: To understand and optimize the $ZnCl_2$-NaCl-$AlCl_3$ salt electrolyte
  - Phase diagram (melting temperature, phase change) simulated with FactSage™ and verified with Differential Scanning Calorimetry (DSC) & OptiMelt™
  - Phase diagram for salt electrolyte optimization and better cell performance
  - Salt vapor pressure for battery safety issue

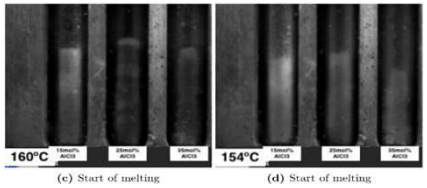
Phase diagram for battery operation & electrolyte improvement



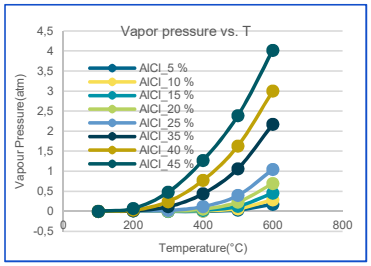
Thermoanalysis via DSC



Thermoanalysis via OptiMelt

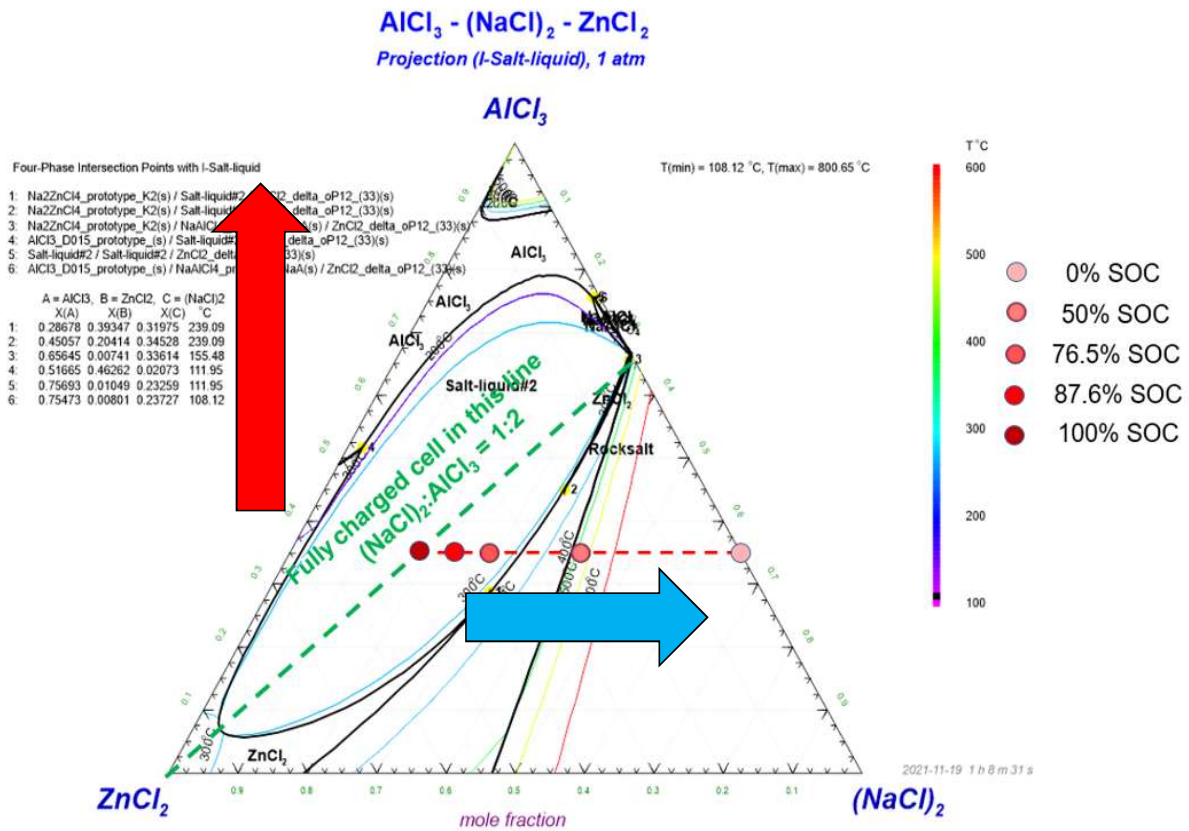


Salt vapor pressure vs. composition & T for safe operation



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

- Increasing $AlCl_3$, melting temperature of the salt electrolyte decrease 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

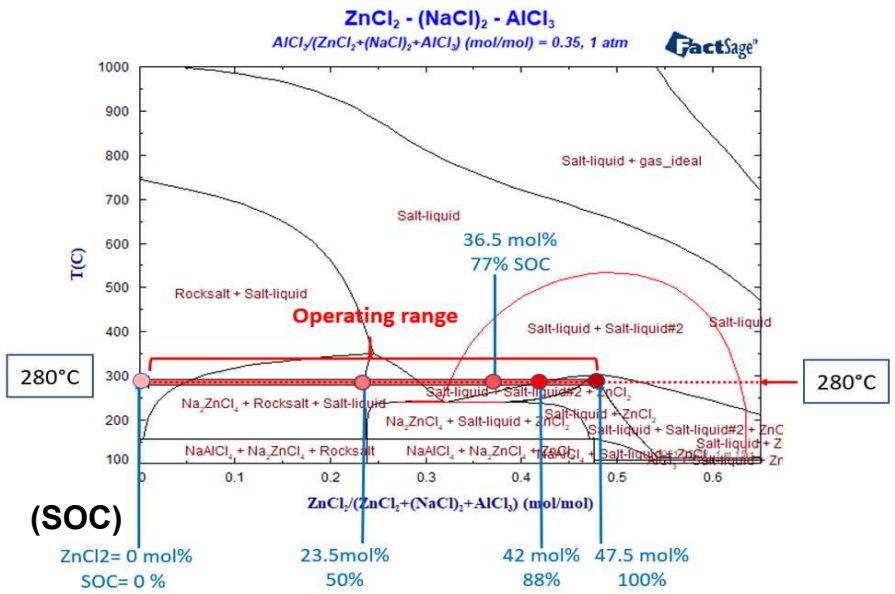


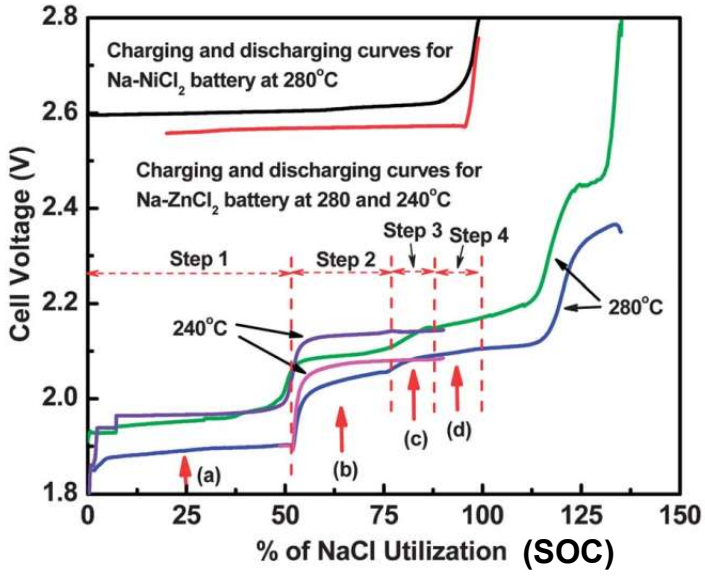
Overall reaction

$2NaCl + Zn \longleftrightarrow 2Na + ZnCl_2$

Binary phase diagram simulation

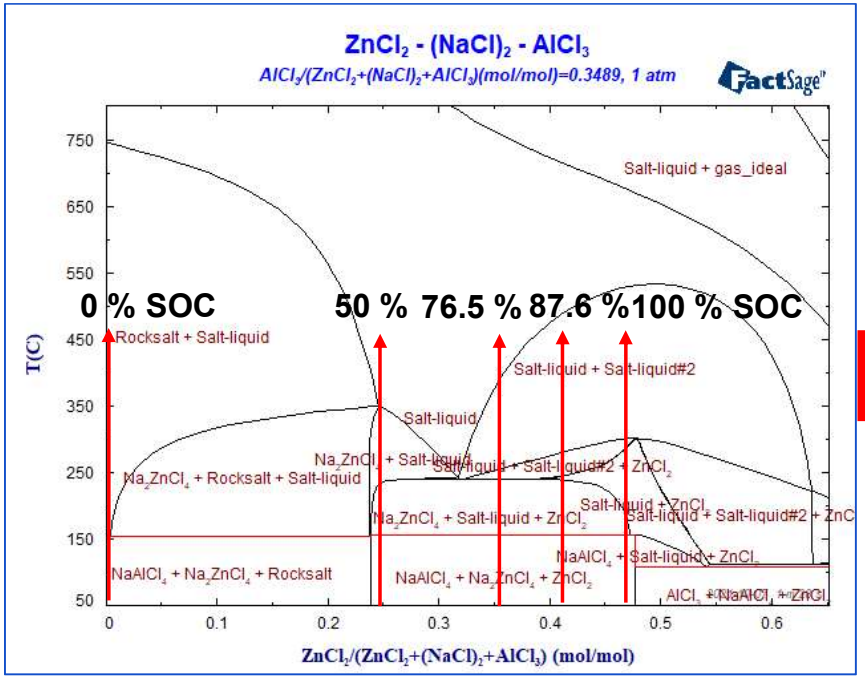
- Binary phase diagrams of $AlCl_3$ = 0-50 mol% simulated
- Phase changes with SOC change simulated
- Voltage change with SOC change in the cell test could be explained with the phase changes
- Next step: DSC & OptiMelt to experimentally verify simulation results

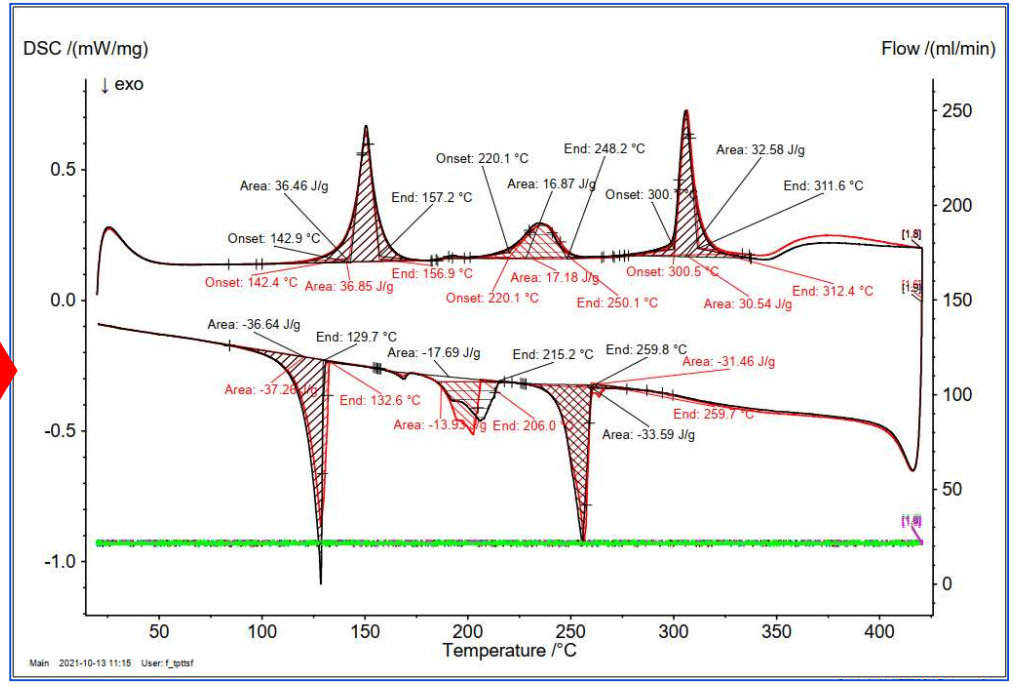




*Lu, X., et al. *Energy & Environmental Science* 6 (2013): 1837-1843.

DSC™ results

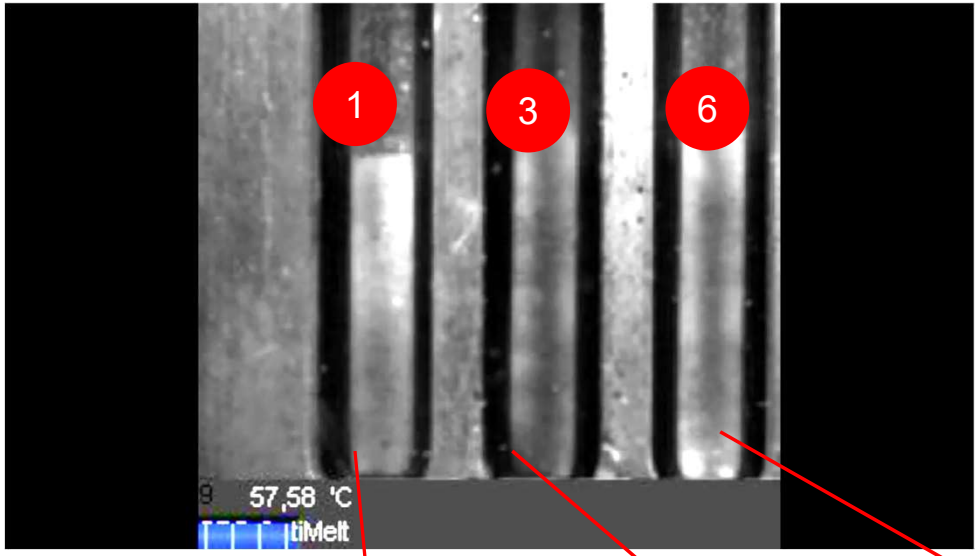




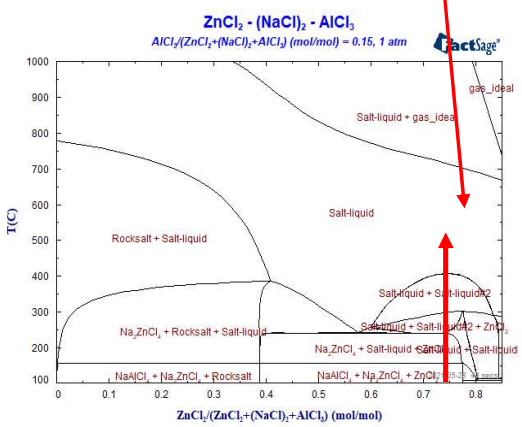
DSC results complying with simulation results

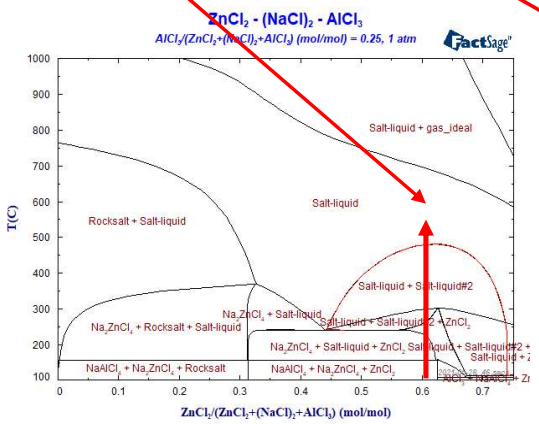
SOC(%)	$AlCl_3$	$ZnCl_2$	2NaCl	Factsage	DSC
	mol%	mol%	mol%	Transition Temperature(°C)	Start(°C)
100	34.89	47.67	17.44	155	152
				200	204
				300	303.7

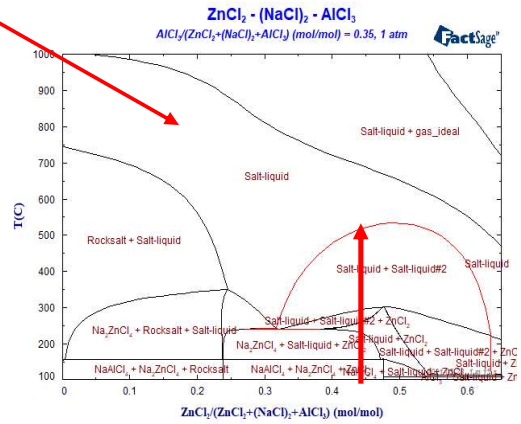
OptiMelt™ results



- Visual observation on salt melting
- OptiMelt results complying with DSC results
- More $AlCl_3$ containing, more is the liquid secondary electrolyte at 160°C (above melting temperature of $NaAlCl_4$), but higher salt vapor pressure



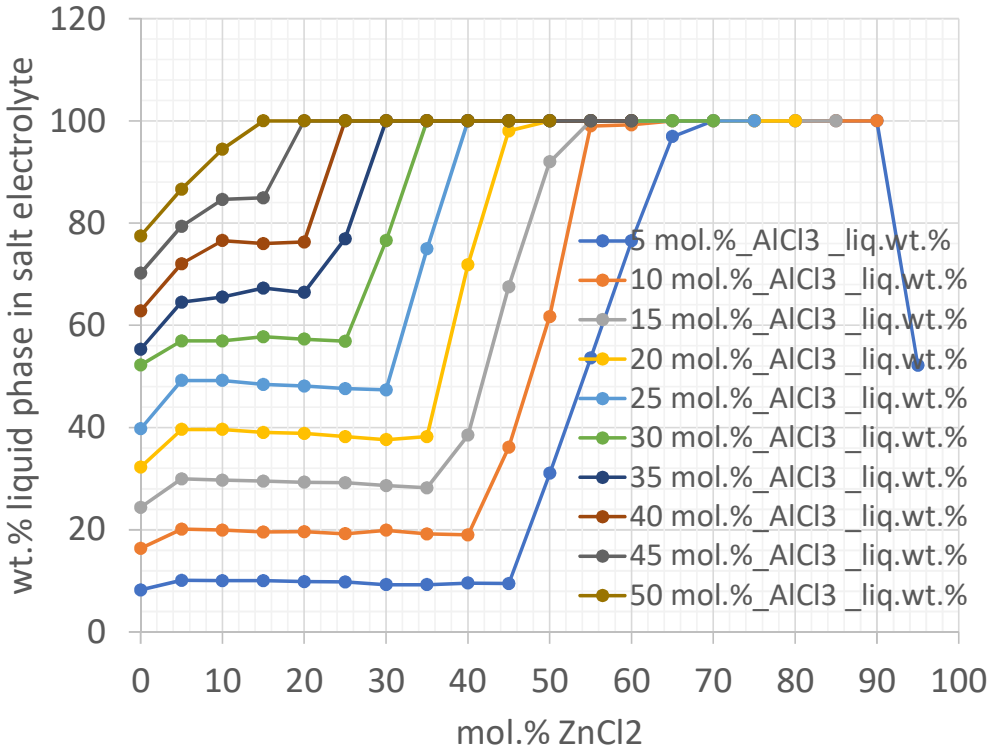


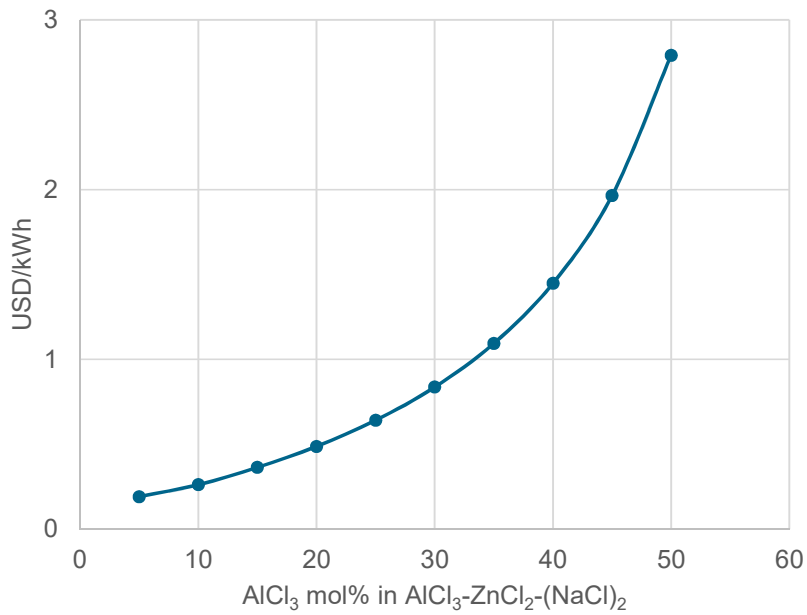


Sr.No.	$AlCl_3$	$ZnCl_2$	2NaCl
	mol%	mol%	mol%
1	15	77.5	7.5
3	25	62.5	12.5
6	35	45	20

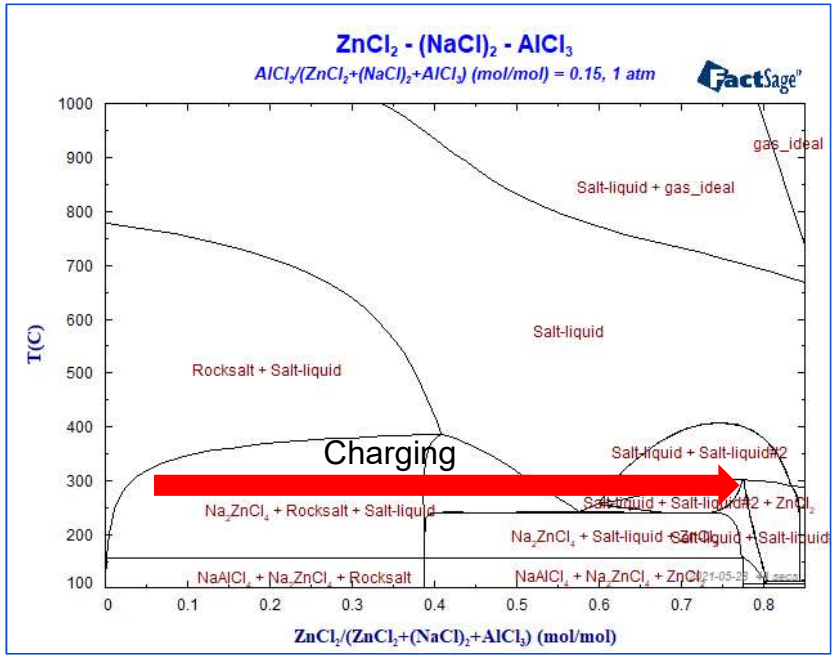
Liquid phase in salt electrolyte at 300°C (simulation)

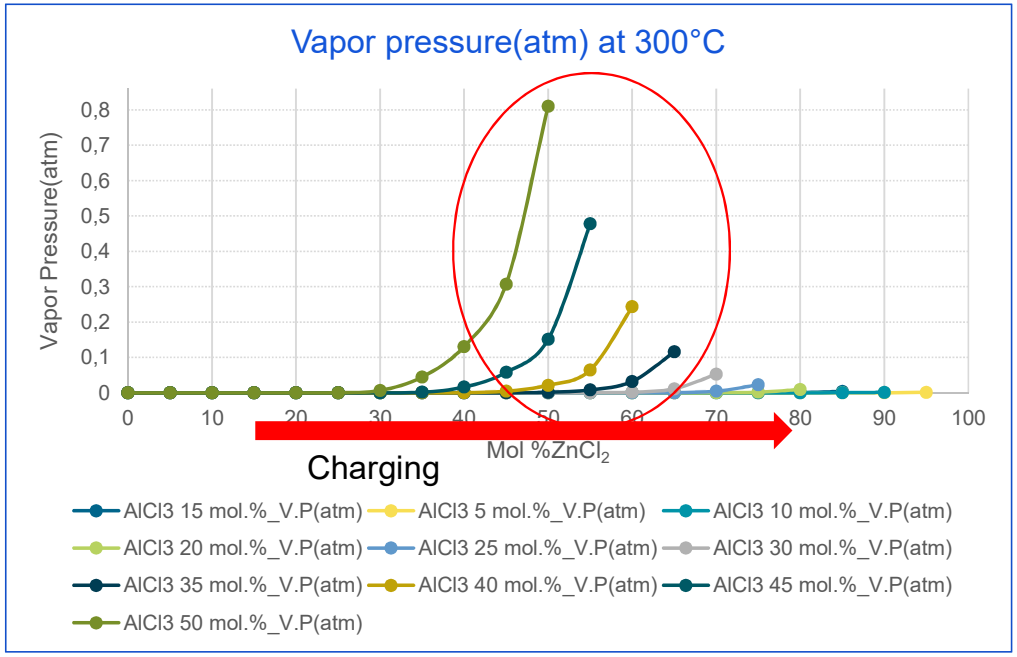
- Fully discharged state: 0 mol% $ZnCl_2$
- Full charge state: basic nature ($NaCl:AlCl_3 \geq 1:1$ or $(NaCl)_2:AlCl_3 \geq 1:2$)
- Salt cost for 1 kWh storage increases with increasing $AlCl_3$
- But low $AlCl_3$ concentration leads to low conductivity (low liquid phase wt.%) in fully discharged state





Vapor pressure vs. Salt composition

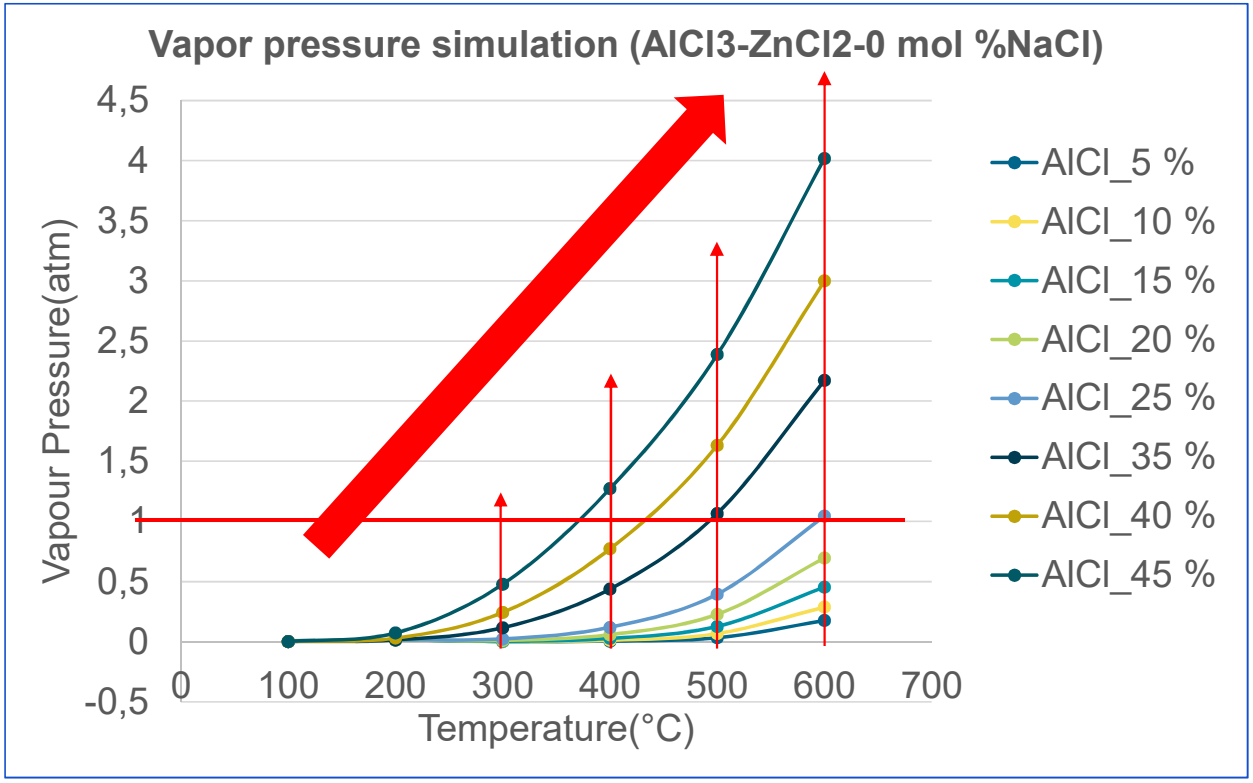




- High salt vapor pressure can lead to failure of e.g., BASE, sealing (safety issue)
- Maximum vapor pressure at high $ZnCl_2$ and $AlCl_3$ concentration
- Vapor pressure is below 1 atm for 300 °C at increasing mol% of $AlCl_3$ till 50 mol%
- Pay attention on $AlCl_3$ concentration, cell overcharge and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

Vapor pressure vs. operating temperature

- Based on the worst-case scenario inside the battery (0 mol% NaCl in overcharged state, salt vapor pressure below 1 bar), allowed max. operating temperatures for batteries with different mol% $AlCl_3$ are suggested.



Max. allowed temp (°C)	$AlCl_3$ mol%
300	>45
400	40
500	35
600	30

Summary

- $Na\text{-}ZnCl_2$ battery has similar structure as ZEBRA battery, but potentially **lower battery cost**
- To assist the battery improvement on e.g. battery operation and salt electrolyte composition, **key salt properties** such as melting temperature, phase changes, vapor pressure were studied with simulation and/or experiments.
- The experimental results with **thermoanalysis** are comparable to the simulation results.
- **Voltage change** with SOC change in the cell test could be explained with the phase changes.
- **Battery safe operation**: $AlCl_3$ in the $ZnCl_2$-$(NaCl)_2$-$AlCl_3$ salt electrolyte is suggested to not above 45 mol% (vapor pressure below 1 bar at 300°C). Pay attention on $AlCl_3$ concentration, cell overcharge and temperature runaway
- **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

Thanks for your Attention!

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Acknowledgement:

This Master thesis is part of the 'SOLSTICE' project which received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 963599.

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

Binary phase diagram simulation ($AlCl_3$ = 0-50 mol%)