Research Progress of Molten Halide Salt Electrolytes in Low-Temperature Sodium Liquid Metal Batteries

Wenjin Ding[1], Qing Gong[1], Haomiao Li[2], Kangli Wang[2], Thomas Bauer[3]

[1] Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany

[2] School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan, China

[3] Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Cologne, Germany

28th EUCHEMSIL, Patras, Greece

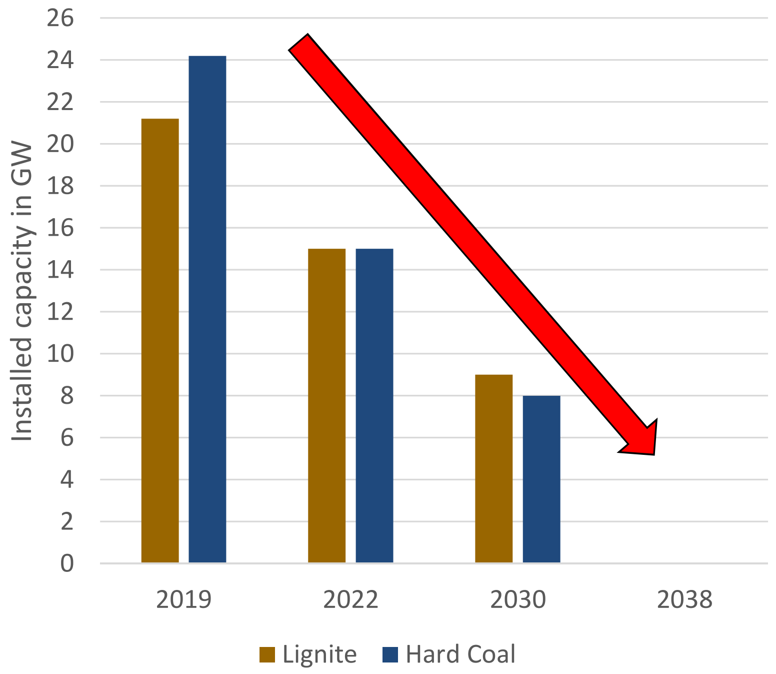
Jun. 5-10th, 2022

DLR

Contents

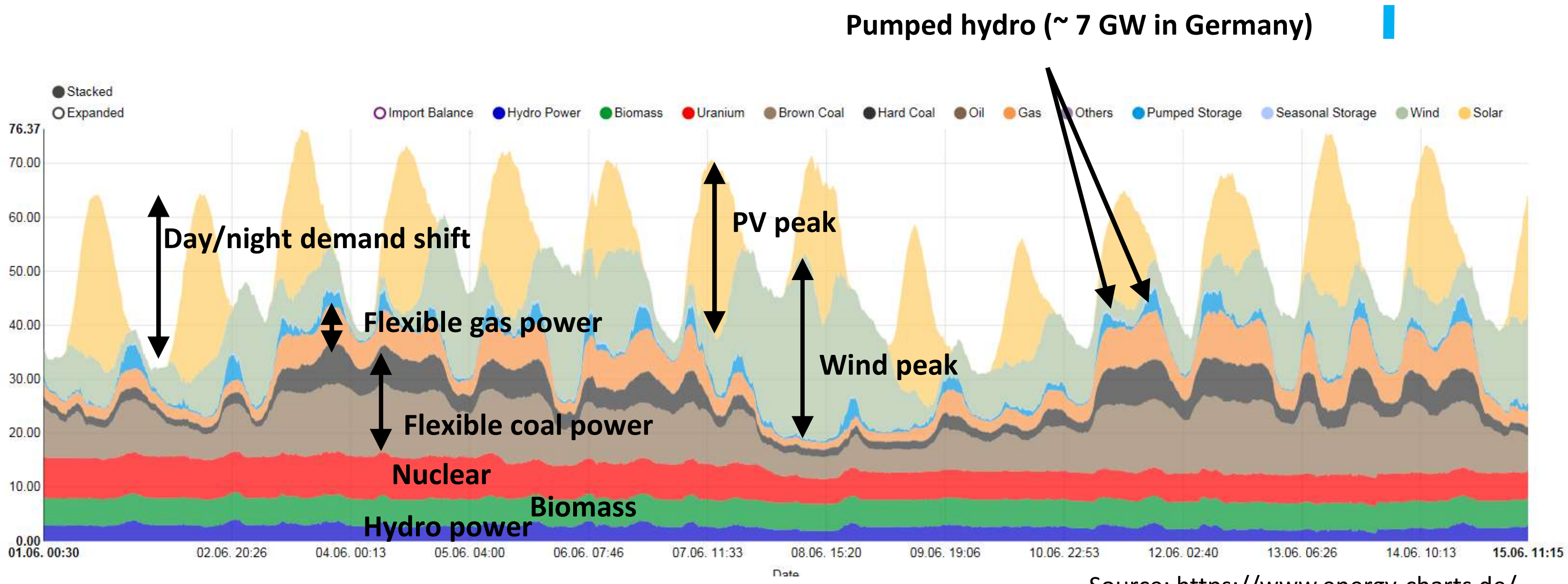
Energy Transition of electricity system in Germany

- Currently ~45 GW installed coal power plants in Germany to be shut down stepwise until 2038
- After 2038 no coal power plants in operation anymore
- Additional aspects:
    - The last 9.5 GW of nuclear power plants also to be shut down until 2022
    - Significant increase of volatile power from PV/wind



Source: Final report of the „Commission on Growth, Structural Change and Employment" 2019

Electricity generation in Germany (Example)



Source: https://www.energy-charts.de/

In future the situation will be marked by

- Large share of volatile PV & wind power with limited operation hours
- Large installed PV & wind power compared to power demand

→ Flexibility requirement, such as storage in batteries, power-to-X, hybrid operation, …

Liquid metal batteries (LMBs)

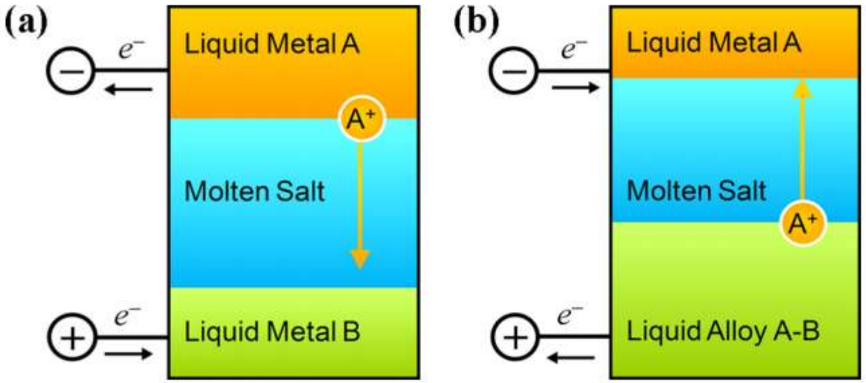
- Molten chloride salt electrolytes in high temperature batteries for kW-MW (kWh-GWh) storage
- **Commercialization of liquid metal batteries**
  - MIT spin-off Ambri in 2010
  - Ca-based liquid metal battery using $CaCl_2$-containing molten chloride salt electrolyte
  - Ambri secures $144 million for liquid metal battery commercialization from Bill Gates in 08.2021

A liquid metal battery cell of Ambri

A MW-scale liquid metal battery in a container

DLR

Liquid metal battery for grid-scale electricity storage



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

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

H. Kim, et al., Chem. Rev. 113, 2075 (2013).

Liquid metal electrodes

- Low cost metals, high electric conductivity, simple electrode structure

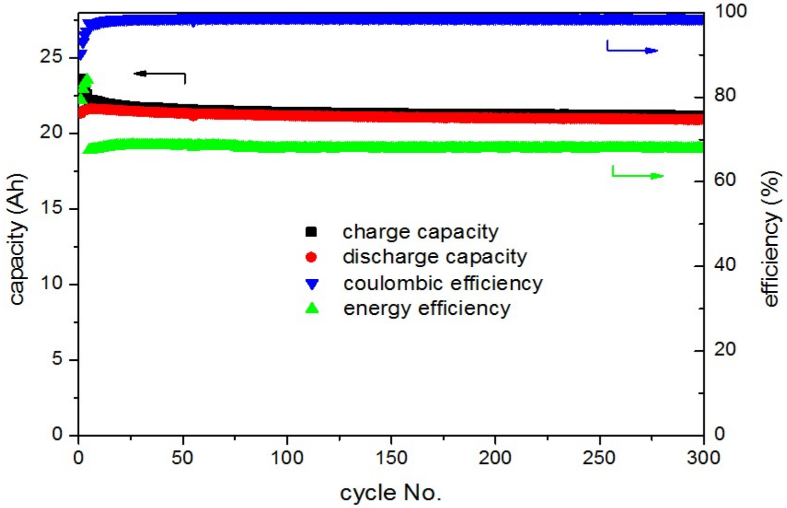
Molten salt electrolytes

- Cheap inorganic salts (e.g., halide salts), high ionic conductivity, high thermal and electrochemical stability

Advantages compared to conventional batteries such Li-ion battery

- Liquid-liquid interfaces → low activation overvoltage
- All-liquid construction → high charging/discharging rate and long service life
- Low material costs → low storage cost

State of the knowledge: Li-based LMB



- Anode: Li metal
- electrolyte: LiF-LiCl-LiBr (T_m=440°C)
- cathode: Sb-Pb alloy
- working temperature: 500 °C
- Inert atmosphere

Wang, Sadoway, et al.. ***Nature***, 2014, 514(7522): 348-350.

Excellent performance:

- High discharge voltage: ~0.7 V
- Low self-discharge: <0.6 mA/cm²
- High Coulombic efficiency: >98 %
- Round-trip energy efficiency: ~70%
- Low fade rate: <1/20 000 capacity loss per cycle (>20 years life-time)

But high electrodes cost including Li anode (>60 USD/kWh) → using Na anode?

Contents

DFG-NSFC research project on Na-LMB

Research topic: **Study on Corrosion Control and Low-Temperature Electrolytes for Low-Cost Na-Based Liquid Metal Batteries (Na-LMB)**

Partners:

- *Karlsruhe Institute of Technology* (KIT), Germany
- *Huazhong University of Science and Technology* (HUST), China

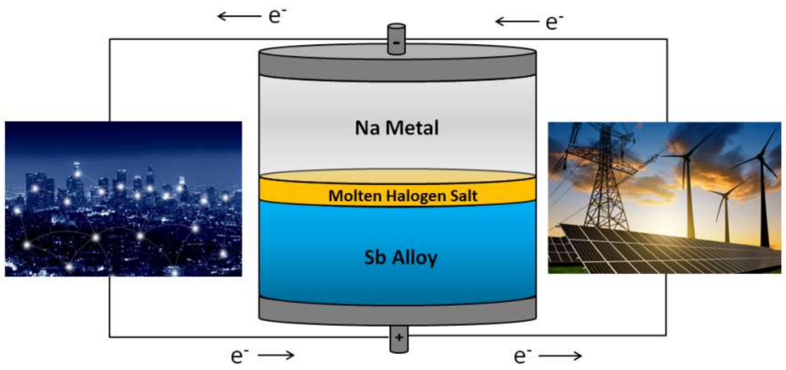
Main targets: Na-based LMBs (Na//Sb-Sn or Na//Sb-Bi) with

- High discharge voltage > 0.5 V and low self-discharge (low solubility of Na in electrolyte)
- long-life >20 years (Low cycling loss, low corrosion rates of structural materials)
- Low operating temperatures <450°C (mainly for the electrolyte)

Key work of DLR :

Selection of a molten salt electrolyte with Na^+

- Essential requirements (low melting point <450°C, Low solubility of Na <0.5 mole%, …)
- Additional requirements (high ionic conductivity, low corrosiveness, …)



Simulation-assisted R&D of molten halide salts for Na-LMBs

1. Screening of salt mixtures via phase diagram simulation

2. Experimental measurements of melting temperatures

3. Determination of key molten salt properties as electrolyte

4. Cost pre-analysis of materials

5. Battery pre-tests with selected molten salt electrolytes

Q. Gong, Master thesis, TU Ilmenau/DLR, (2020).

H. Zhou, et al. *Energy Storage Materials*, 2022, accepted.

Q. Gong, W. Ding, K. Wang, A. Weisenburger, et al., ***J. Power Sources*** 475 (2020) 228674.

1. Simulation-assisted screening of molten halide salts for Na-LMBs

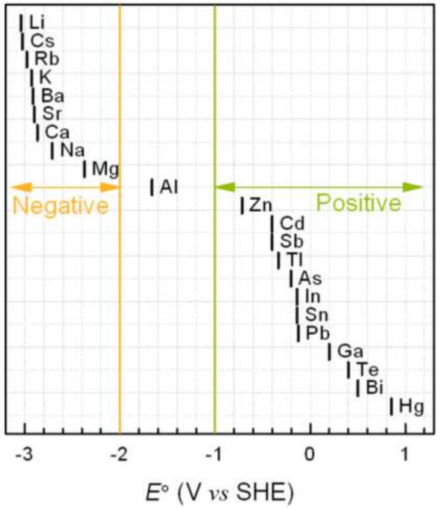
Salts Screening *via* thermodynamic modelling (FactSage^{TM}) and reviewing literature:

- Potential electrolyte salts: **Na, Li, K//Cl, Br, I**

Regarding salt stability, Na-solubility, salt cost and simplicity, following ternary systems are selected for further study:

- **Na-K-Li//Cl (starting salt system)**
- **Na-K-Li//Br**
- **Na-K-Li//I**

Salt system	Example	lowest Tm / °C	mol.%	T(Na 30%) / °C	mol.%	T (Na 40%) / °C	mol.%	T (Na 50%) / °C	mol.%
Binary	Na//Cl, I	573	40.1-59.9						
	Na//Cl, Br	740	25.3-74.7						
	Na//Br, I	645	30.8-69.2						
	Na, Li//Cl	554	27.3-72.7	560	30-70	590	40-60	620	50-50
	Na, Li//Br	509	25.8-74.2	525	30-70	550	40-60	575	50-50
	Na, Li//I	450	20.8-79.2	460	30-70	480	40-60	510	50-50
Ternary	Na, Li//Cl, I	421	43.8(Na/(Na+Li))-53.1					435	50-55
	Na, Li//Cl, Br	417	31.3(Na/(Na+Li))-43.9	425	30-42	465	40-45	530	50-45
		425	32.4(Na/(Na+Li))-42.7						
	Na, Li//Br, I	352	32.5(Na/(Na+Li))-48.9	355	30-50	400	40-40	440	50-30
		351	31.5-48.0						
	Na//Cl, Br, I	573	61.2-0.0-38.8						
	Na, Li, K//Cl			450	30-30-40	525	40-20-40	580	50.0-50.0-0.0
	Na, Li, K//Br			490	30-50-20	540	40-60-0	580	50.0-50.0-0.0
	Na, Li, K//I			410	30-40-30	460	40-30-30	505	50.0-16.0-34.0
Quaternary	Na, K, Ba, Ca//Cl	435	34-7-17-42						



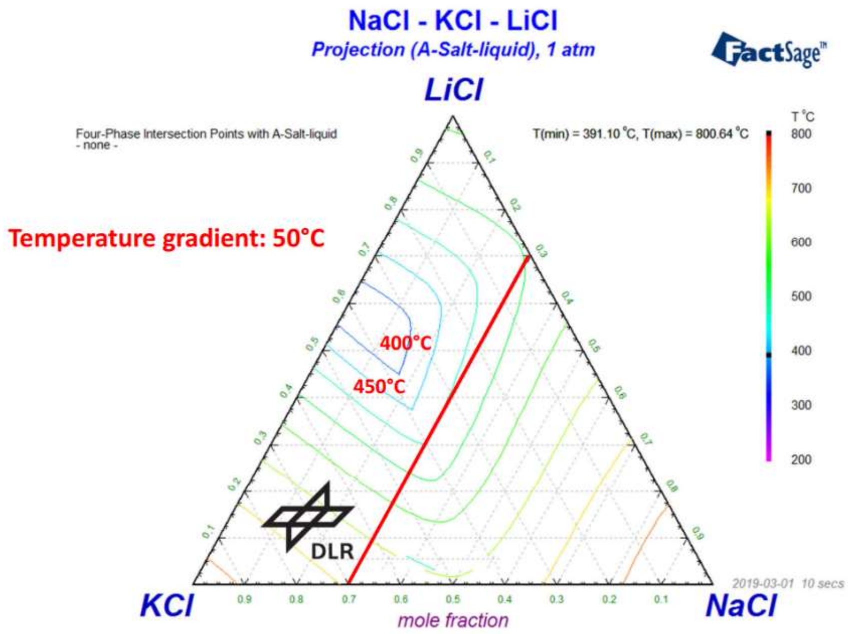
H. Kim, et al., Chem. Rev. 113, 2075 (2013).

Phase Diagram of Na-Li-K//Cl

- **Eutectic Na-Li-K//Cl:**
  - **Pseudo-binary salt** with T_m = ~350 °C
  - Eutectic Li-K//Cl: 59-41 mol%
  - Solubility of NaCl in the eutectic LiCl-KCl is ~10 mol%

- **Compared to Na-Li-K//I:**
  - Higher melting temperature (50°C higher)
  - Higher thermal and electrochemical stability (~3 V vs. ~2.5 V)
  - Low costs (15%)

- Six eutectic salt compositions are selected for further investigation:
  NaCl: 0, 5, 9, 12.5, 15, 19 mol%

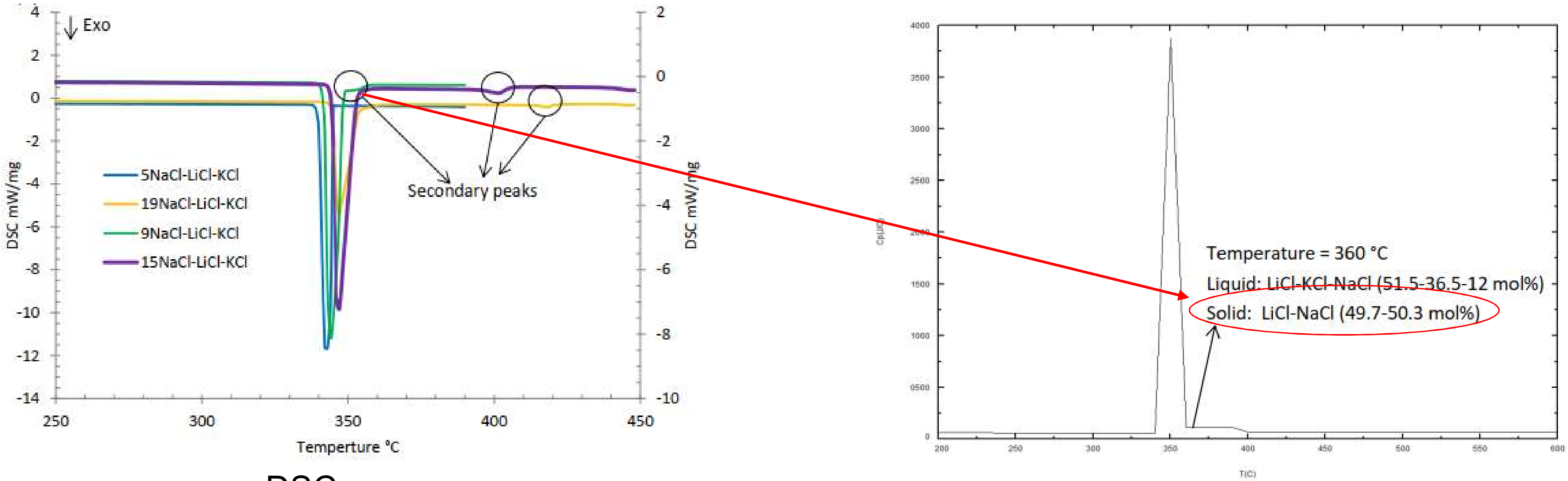


Simulated phase diagram of Na-Li-K//Cl

Q. Gong, Master thesis, TU Ilmenau/DLR, (2020).

2 Na-Li-K//Cl: Experimental measurements of T_m

- **Na-K-Li//Cl:**
  - Solubility of NaCl in the eutectic LiCl-KCl (59-41 mol%) is **~9 mol%**
  - **15 mol%** NaCl: not eutectic, secondary peaks besides main peaks at **~400°C**
  - **12.6 mol%** NaCl: not eutectic, secondary peaks besides main peaks at ~372°C
  - Secondary peak represents dissolution of **excess LiCl-NaCl**



DSC

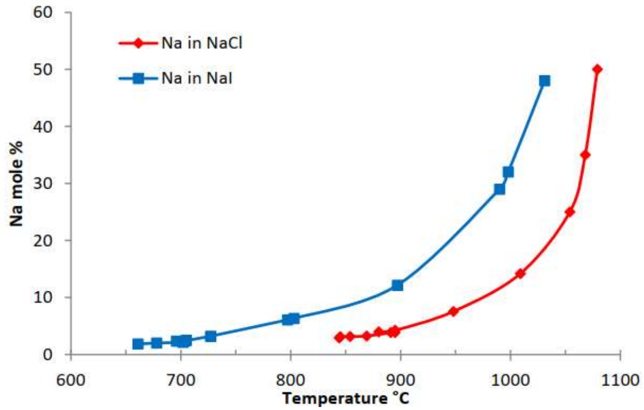
FactSage simulation

Q. Gong, Master thesis, TU Ilmenau/DLR, (2020).

3 Na-Li-K//Cl: Determination of Molten Salt Properties

- **Estimation of Na solubility** in Na-Li-K//Cl based on literature data [1]:
  <u>**< 0.01 mol%**</u> at < 500 °C (estimated self-discharge <u>**< 0.5 mA/cm²**</u>)
  Underestimated due to dissolution reactions with other cations (i.e., Li^+, K^+)

- **Estimation of Na^+ conductivity** based on [2]:
  - <u>116 mS/cm</u> for T=400°C for 9 mol% NaCl



Na solubility

Electrolyte	Battery	Operating temperature °C	Viscosity (at operating temperature) mPa·s	Effective ionic concentration mol%	Effective ionic conductivity mS·cm⁻¹
LiCl-KCl-NaCl	Na-LMB	~400	~2.0	9	~116
LiPF6 in PC	LIB	~30	8.03	~10	6.0
β-alumina (Na_2O·(9~11)Al_2O_3)	NaS	~300	solid	~10	200-400
HNO_3	Lead-acid battery	~30	~1	9	301

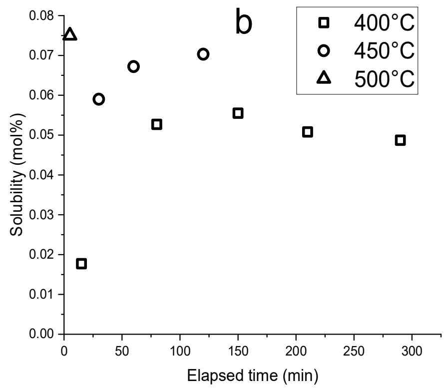
Na^+ conductivity

1) G.J. Janz, et al. The Journal of Physical Chemistry 62 (1958): 1479-1482.
2) G.J. Janz, et al. Physical properties data compilations relevant to energy storage. II. Molten salts: data on single and multi-component salt systems. No. NSRDS-NBS-61-PT-2. NATIONAL STANDARD REFERENCE DATA SYSTEM, 1979.

Experimental Results: Na solubility in NaCl-LiCl-KCl

- Measured with titration method
- Low Na solubility (<0.14 mol%) for acceptable self-discharge rate (<0.4 mA/cm^2)

NaCl / mol%	T / °C	C(Na) / mol%	Self-discharge / mA/cm^2
0	400 450 500	0.102 0.132 0.136	<0.4
3	400 450 500	0.055 0.072 0.075	<0.2
6	400 450 500	0.032 0.052 0.041	<0.2



NaCl(3 mol%)-LiCl-KCl

4 Cost Pre-analysis of Materials: Na-Li-K//Cl

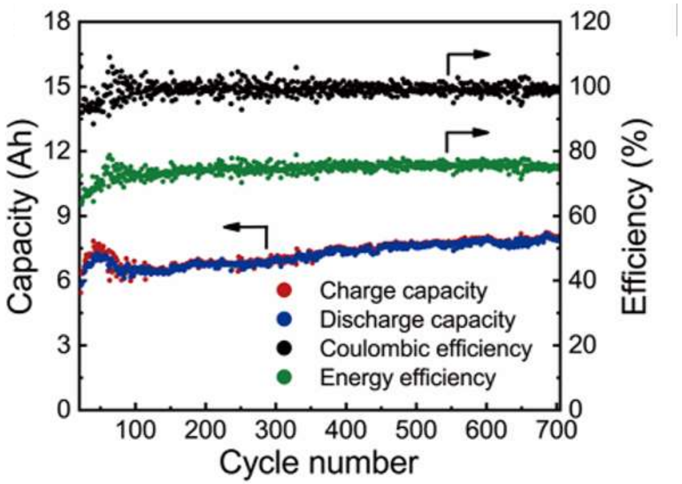
- **Salt costs**:
  - NaCl-LiCl-KCl has similar cost as NaF-NaCl-NaI
  - Small effect on battery costs due to thin molten salt electrolyte
- **Salt corrosivity to structural materials**:
  - Not a critical issue due to inert atmosphere of LMB and inhibition effect of Na
  - Conventional stainless steels allowed

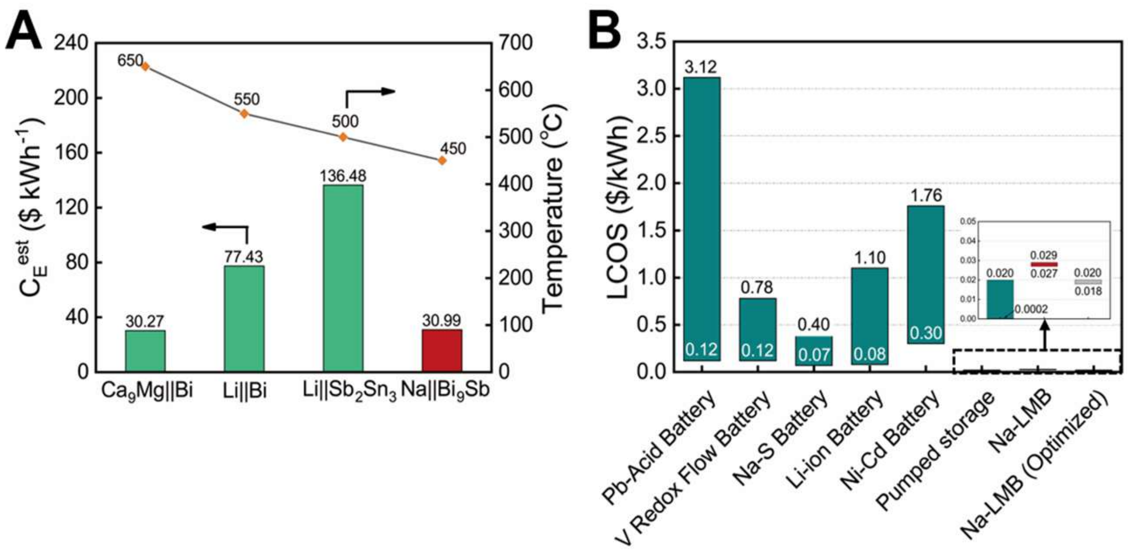
Salts	Large-scale prices / USD/kg	Sources
NaCl-LiCl-KCl eutectic	~3	Calculated with CPs of single salts
NaF-NaCl-NaI eutectic	~2	Calculated with CPs of single salts

*CP: current large-scale price of the single salt from www.alibaba.com [Accessed on May 9th of 2020].

Q. Gong, W. Ding, K. Wang, A. Weisenburger, et al. ***J. Power Sources*** 475 (2020) 228674.

5 Battery Tests with Selected Na-Li-K//Cl Electrolyte





LiCl-KCl-NaCl(5mol%) electrolyte
Coulombic efficiency >95%
Energy efficiency >75%
Measured capacity: 80% of theoretical capacity
Estimated lifetime: at least 15 000-16 000 cycles

Na-LMBs developed in this project

- Low electrode couple cost: 31 USD/kWh
- Low operating temperature: 450°C
- Low LCOS: 2.8 US Cent/kWh

H. Zhou, et al. *Energy Storage Materials*, 2022, accepted.

Contents

Summary

- Molten salt electrolyte selection is one of the key issues in R&D of Na-based LMB
- Optimal composition determined: LiCl-NaCl-KCl: 55-(<9)-36 mol%
- Na solubility in selected salts will be measured to ensure low self discharge of LMB
- LMB test cells with selected electrolyte show promising results at T=450°C

Thank you for your attention!

Dr. Wenjin Ding
Institute of Engineering Thermodynamics (ITT), Stuttgart
German Aerospace Center (DLR)
Email: wenjin.ding@dlr.de

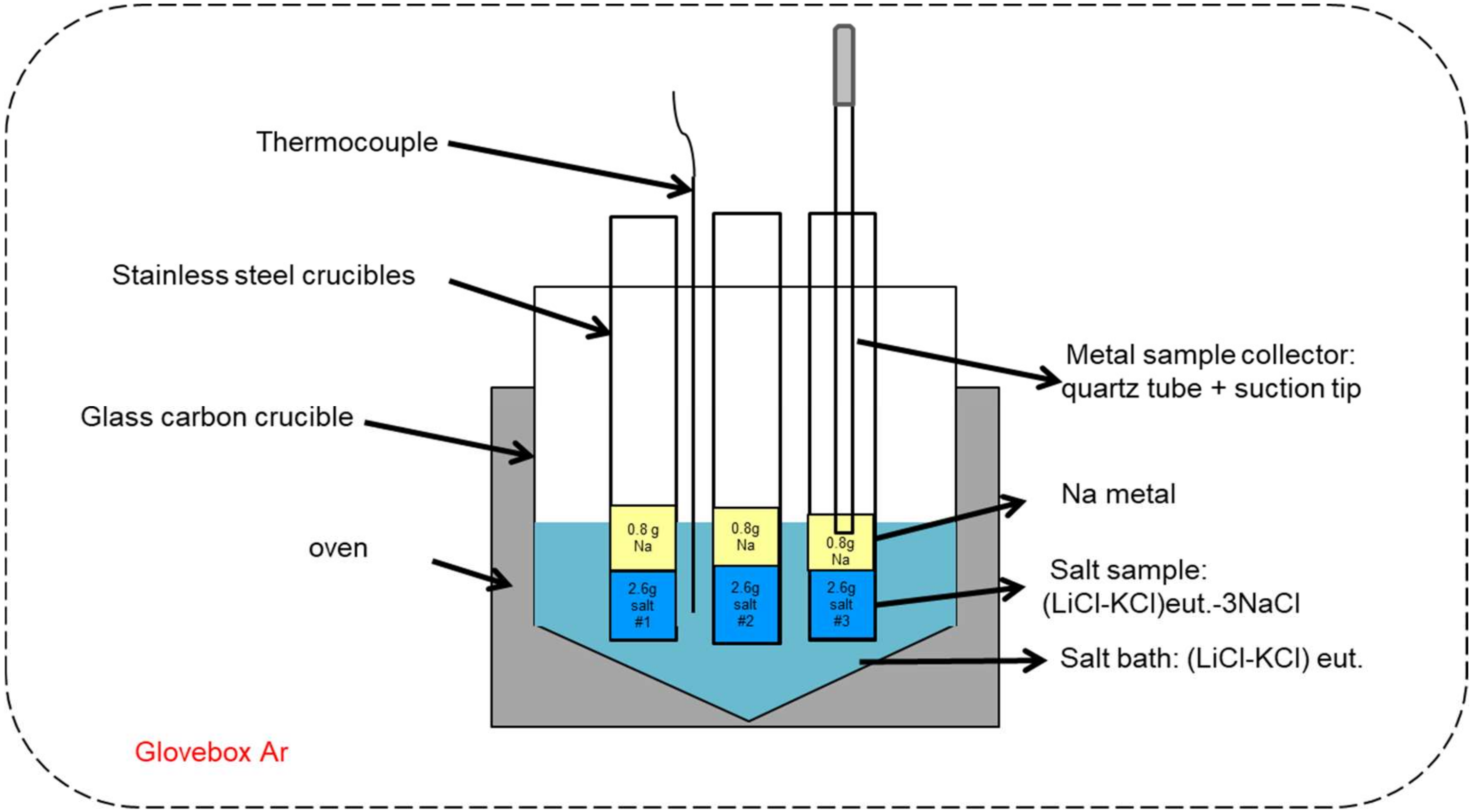
Acknowledgement:

DFG Deutsche Forschungsgemeinschaft
German Research Foundation

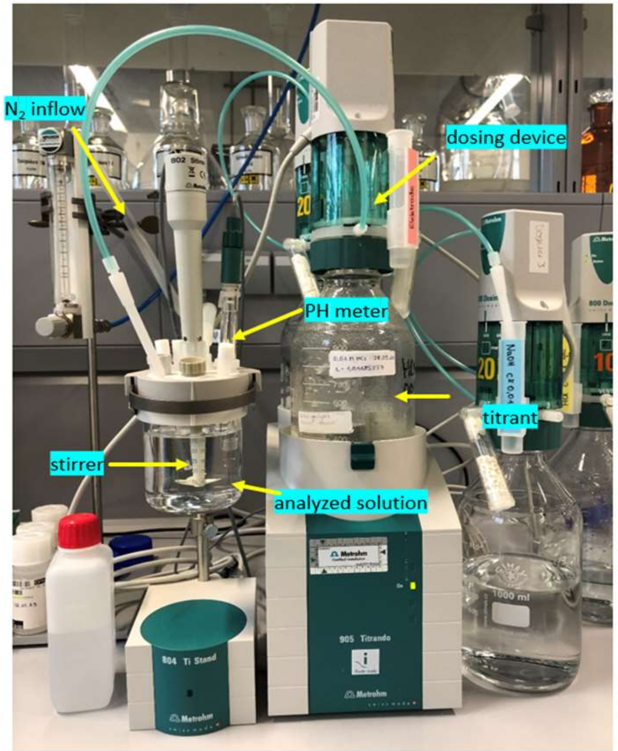
国家自然科学基金委员会
NSFC

DLR

Experimental set-up



Analysis: Titration & Ion chromatography (IC)



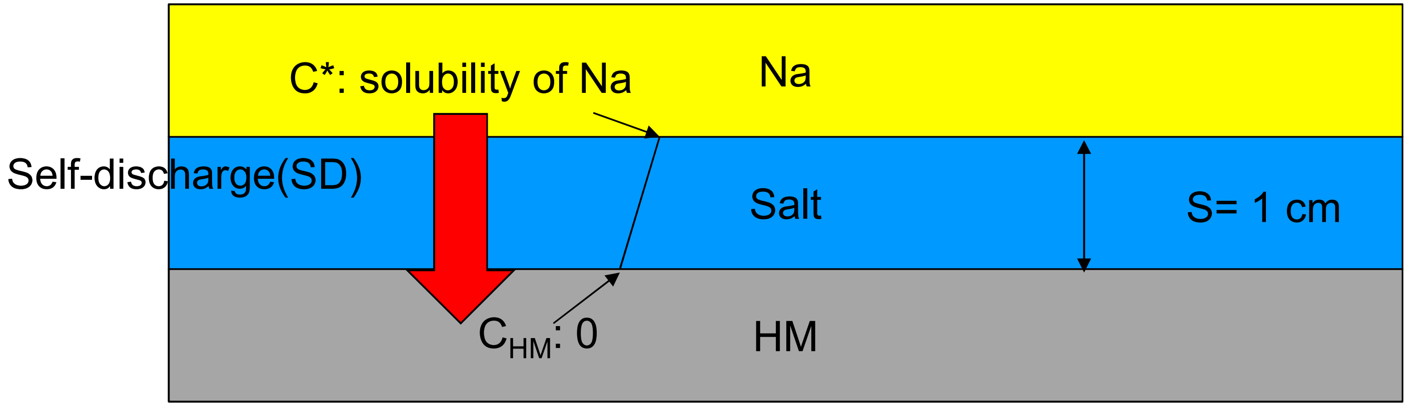
Automated Titrator of Metrohm™
Measurement limit: <0.0001 mol.% Na

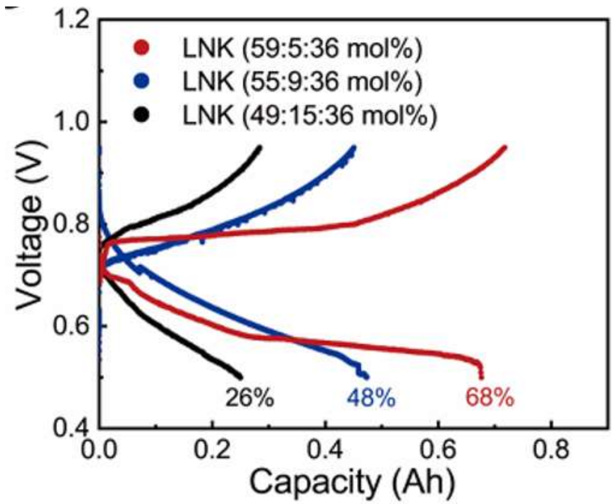
IC Metrohm: Na+, Li+, K+, Cl-

Titration reactions:
Na_2O (impurity) + 2HCl ↔ 2NaCl + H_2O
2Na (dissolved) + 2HCl ↔ 2NaCl + H_2

Molten NaCl salt: dissolved Na (literature 1.6-3.0 mol%) >> Na_2O (literature 0.01-1 mol%) at 500°C

Estimated self-discharge based on titration





Self-discharge(SD) = $F*D*(C^{*}-C_{HM})/S$

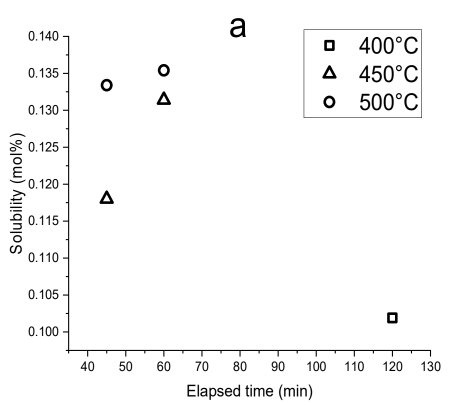
F=96485 A s/mol, D=~10^{-4} cm^2/s [1], C: mol/cm^3, S = 1 cm

[1] Borucka Alina Z., et al., Proc. R. Soc. Lond. A 241 (1957) 554–567

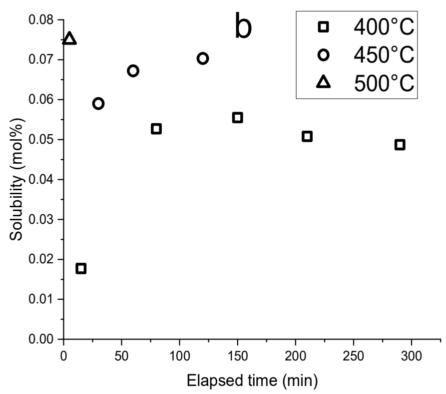
Titration Results: Na solubility

NaCl / mol%	T / °C	C(Na) / mol%	Self-discharge / mA/cm²
0	400	0.102	
	450	0.132	<0.4
	500	0.136	
3	400	0.055	
	450	0.072	<0.2
	500	0.075	
6	400	0.032	
	450	0.052	<0.2
	500	0.041	

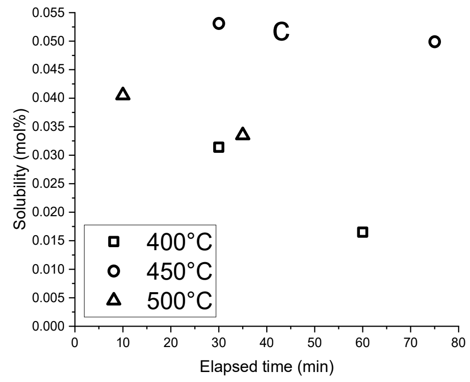
Na solubility (<0.14 mol%) is low enough for acceptable self-discharge rate (<0.4 mA/cm²).



NaCl(0 mol%)-LiCl-KCl



NaCl(3 mol%)-LiCl-KCl



NaCl(6 mol%)-LiCl-KCl

DLR