Molten Halide Salts for Large-Scale Energy Storage

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  – Energy research at DLR
  – Large-scale energy storage for Energy Transition

• Molten halide salts for large-scale energy storage
  – Thermal energy storage (TES)
  – Liquid metal battery (LMB)

• Summary and outlook
German Aerospace Center (DLR)

- Research Institution (six research areas)
- Space Agency
- Project Management Agency

Aeronautics  Space  Transportation  Energy  Security  Digitalization
Energy Research Program Themes

- Efficient fossil-fuel power stations (turbo machines, combustion chambers, heat exchangers)
- Solar thermal power plant technology, solar conversion
- Wind research
- Energy storage (thermal, chemical, electrical)
- High and low temperature fuel cells
- Systems analysis and technology assessment
Energy Transition in Germany –
Increased volatile power from PV/wind

- 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
  - Large-scale energy storage required to stabilize the grid

Source: Final report of the „Commission on Growth, Structural Change and Employment“ 2019
Installed Global Capacity for Grid-Connected Storage

Sources:

Grid-connected electrical storage power in 2014:
- Pumped hydro ~130 GW_{el}
- Thermal energy storage (TES) ~2.3 GW_{el}
- Batteries ~0.6 Gw_{el}

Concentrating Solar Power (CSP) grid-connected molten salt storage in 2015
- power > 1.5 GW_{el}
- capacity > 30 GWh_{th} (typically 8 h storage)

375 Mw_{el} Molten salt tanks
28 500 tons molten salt
Source: Andasol 3
Research Group for TES in MOLTEN SALTS

System aspects
Components
Process technology (Upscaling)
Material aspects

"... value chain research..."

10 mg
100 ton

DLR test facility TESIS
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Molten Salts for Thermal Energy Storage (TES)

- Large-scale hourly storage for **CSP plants** (13 GWhₑ) demonstrated
- **Inexpensive** heat storage capacity from 170 to 560 °C in molten salts (nitrate/nitrite, non-toxic, non-flammable) in large-scale **unpressurized** tanks
- Potential to transfer technology from CSP to **grid-connected storage → Carnot battery**
- **Limitation**: Thermal decomposition of nitrate/nitrite at >560°C

Next Generation CSP with Advanced-salt System

Advanced-salt system + sCO₂ power cycle for higher energy conversion and lower LCOE*

- Advanced-salt system (520-720°C)
- sCO₂ power cycle (500-700°C, efficiency > 50%)

Example: Selection of Promising Chloride Salts for TES

- Considering thermal and physical properties (Cₚ, vapor pressure, melting point), hygroscopicity (corrosiveness) and prices, MgCl₂-KCl-NaCl eutectic salt mixture (<0.35 USD/kg, thermal stability >800°C, Tₘ = 385°C) is selected [1].

- Other research: Corrosion control of structural materials in molten chlorides [2].

FactSage simulation

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Liquid Metal Battery (LMB) for Grid-scale Storage

- **LMBs:**
  - Long life > 10,000 cycles, easy to scale-up → all liquid/liquid interfaces
  - Low storage costs → materials of electrodes and electrolytes
- **Liquid metal electrodes**
  → Low cost metals, high electric conductivity, simple structure of electrodes
- **Molten salt electrolytes**
  → Cheap, high ionic conductivity, low self-discharge, …

State of the Art LMBs

- **Li-based LMB** with excellent performance in labor-scale achieved

- **Na-based LMB** with excellent performance in labor-scale still not achieved
  - **Low-melting-point** $T_m$ molten salt electrolyte is the key challenge

<table>
<thead>
<tr>
<th>LMBs</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>$T_m$ [°C]</th>
<th>$T_w$ [°C]</th>
<th>Coulombic efficiency [%]</th>
<th>Energy efficiency [%]</th>
<th>self-discharge rate [mA/cm² at full charge]</th>
<th>Capacity loss rate [%/cycle]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-LMB</td>
<td>Anode: Li; Cathode: Sb-Sn</td>
<td>LiF-LiCl-LiBr</td>
<td>440</td>
<td>500</td>
<td>&gt;98%</td>
<td>70-90</td>
<td>&lt;1</td>
<td>0.006</td>
</tr>
<tr>
<td>Na-LMB</td>
<td>Anode: Na Cathode: Bi (single-cation)</td>
<td>NaF-NaCl-NaI</td>
<td>530</td>
<td>580</td>
<td>82</td>
<td>59</td>
<td>~20</td>
<td>NA</td>
</tr>
</tbody>
</table>

R&D of Low-temperature Na-based LMB

- **Sino-German project funded by DFG-NSFC:**
  - Prof. K. Wang, Dr. H. Li, Huazhong University of Science and Technology (HUST), China
  - Dr. A. Weisenburger, Dr. A. Jianu, Karlsruhe Institute of Technology (KIT), Germany

- **Na-based liquid metal batteries with $T_w < 450^\circ C$:**
  - Liquid metal electrodes (Na//SbSn and Na//BiSb)
  - $Na^+$-containing molten salt electrolyte with $T_m < 400^\circ C$ and low solubility of Na metal for low self-discharge
  - Excellent performance as Li-LMB but lower costs and lower $T_w$

- **Molten halide salts are promising electrolytes**
  - High electrochemical stability (>2.5 V)
  - High thermal stability (>500°C)
  - High conductivity
  - Low costs
  - **But much higher $T_m$ than electrodes**
Selection Process of Molten Salt Electrolyte

1. Screening of salt mixtures via phase diagram simulation ($T_m$)
2. Experimental measurements of melting temperatures $T_m$
3. Determination of key molten salt properties as electrolyte
4. Cost pre-analysis of materials
5. Battery pre-tests with selected molten salt electrolytes

1 Screening of Halide Salt Mixtures Regarding $T_m$

- Salt mixture containing:
  - Cation: $\text{Li}^+$, $\text{K}^+$, $\text{Ba}^{2+}$, $\text{Ca}^{2+}$, $\text{Na}^+$
  - Anion (halide): $\text{F}^-$ (not selected due to high $T_m$), $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$

- Screening via thermodynamic modelling (FactSage) and literature review

- Potential electrolyte salts:
  - $\text{Li}^+$-containing: $\text{Na-Li-K//Cl-Br-I}$ (e.g. $\text{Na-Li-K//I}$: $T_m = 290°C$, $\text{Na-Li-K//Cl}$: $T_m = 350°C$)
  - Not $\text{Li}^+$-containing: $\text{Na-K-Ba-Ca//Cl-Br-I}$ (e.g. $\text{Na-K-Ba-Ca//Cl}$: $T_m = 435°C$)

- $\text{Na-Li-K//I}$ (starting salt system) due to lowest $T_m$
1 Screening of Halide Salt Mixtures Regarding $T_m$

- **Eutectic Na-Li-K/I:**
  - Pseudo-binary salt with $T_m = \sim290 \ ^\circ\text{C}$
  - Eutectic Li-K/I: 63-37 mol%
  - Solubility of NaI in the eutectic LiI-KI is $\sim12$ mol%

- **Na-K-Li/I** is promising:
  - Melting temperature $T_m < 300\ ^\circ\text{C}$
  - But which Na$^+$ concentration regarding:
    - Low Na metal solubility
    - Sufficient Na$^+$ conductivity

- Six eutectic salt compositions are selected for further investigation:
  - NaI: 0, 3, 5, 7, 9, 12 mol%

2 Experimental measurements of $T_m$

- **Methods:**
  - Thermal: Differential scanning calorimetry (DSC)
  - Optical: Melting point measurement apparatus (OptiMelt™)

- **Na-K-Li//I:**
  - Solubility of NaI in the eutectic LiI-KI (64-36 mol%) is 7-9 mol%.
  - 12 mol% NaI: not eutectic, secondary peaks besides main peaks at ~309-330°C.

3 Determination of Molten Salt Properties as Electrolyte

- **Estimation of Na solubility** in NaI-LiI-KI based on literature data [1]:
  - Dissolution reaction $Na + Na^+ \rightarrow Na^+_2$
  - $< 0.03$ mol% at $< 550$ °C (estimated self-discharge $< 1$ mA/cm$^2$)
  - Underestimated due to dissolution reactions with other cations (i.e., Li$^+$, K$^+$)
  - Experiments in progress

- **Estimation of Na$^+$ conductivity** based on [2]:
  - 28 mS/cm for $T>350$°C for 3-7 mol% NaI
  - Higher than that of electrolyte in conventional Li-ion battery (~10 mS/cm)

4 Cost Pre-analysis of Materials

- Salt costs:
  - NaI-LiI-KI > NaCl-LiCl-KCl > NaF-NaCl-NaI
  - Small effect on battery costs due to thin molten salt electrolyte

- Salt corrosivity against structural materials:
  - Not a critical issue due to inert atmosphere of LMB and inhibition effect of Na
  - Conventional stainless steels allowed (KIT: Selection of structural materials)

<table>
<thead>
<tr>
<th>Salts</th>
<th>Large-scale prices / USD/kg</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaI</td>
<td>~3</td>
<td>Current price (CP)*</td>
</tr>
<tr>
<td>KI</td>
<td>~4</td>
<td>CP</td>
</tr>
<tr>
<td>LiI</td>
<td>~40</td>
<td>CP</td>
</tr>
<tr>
<td>NaI-LiI-KI eutectic</td>
<td>~20</td>
<td>Calculated with CPs of single salts</td>
</tr>
<tr>
<td>NaCl-LiCl-KCl eutectic</td>
<td>~3</td>
<td>Calculated with CPs of single salts</td>
</tr>
<tr>
<td>NaF-NaCl-NaI eutectic</td>
<td>~2</td>
<td>Calculated with CPs of single salts</td>
</tr>
</tbody>
</table>


5 Battery Pre-tests with Selected Molten Salt Electrolytes

- **Test conditions:**
  - ~1 cm thick NaCl(9 mol%)-LiCl-KCl (similar as NaI-Lil-KI) electrolyte,
  - $T_w = 450^\circ C$, 100 discharge/charge cycles, current up to 1000 mA/cm$^2$

- **Results:**
  - Higher Coulombic efficiency >95%
  - $T_w$ reduced by >100$^\circ C$ → low costs for structural and isolation materials
  - But unacceptable capacity loss rate → to be improved by battery optimization

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</thead>
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<tr>
<td>Na-LMB</td>
<td>Anode: Li; Cathode: Bi-based alloy</td>
<td>NaCl-LiCl-KCl</td>
<td>350</td>
<td>450</td>
<td>&gt;95%</td>
<td>To be measured</td>
<td>0.1</td>
</tr>
<tr>
<td>(HUST, KIT, DLR)</td>
<td></td>
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<td>(ANL)</td>
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</tbody>
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Summary and Outlook

- Next generation TES technology based on molten chloride salts is being developed
  - MgCl₂-NaCl-KCl is selected
  - Focusing on corrosion control of structural materials

- Molten halide salts as electrolyte in LMB:
  - Process for selection of salt mixtures is proposed
  - Li-K-Na halide salt mixtures as promising electrolytes of Na-LMB
  - Battery pre-tests show promising results
  - Other halide salt mixtures will be studied
  - Battery optimization will be performed
Thank you for your attention!

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Acknowledgement:
Locations and employees

Approx. 8700 employees with 40 institutes and facilities at 20 sites.


And a research site of concentrated solar power (CSP) in Almeria/Spain
Electricity generation in Germany (Example)

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**: Large-scale energy storage, power-to-X, demand side management, hybrid operation,…
Carnot Battery

- Electricity- heat (stored) - electricity
- Round-efficiency ~50%
- A conventional coal power plant is being transformed to Carnot battery plant
Advanced-Salt System – Chlorides or Carbonates

- Chloride/carbonate (>800 °C)
- Salt costs: Chloride < Nitrate < Carbonate
- Tank costs (corrosion, T): Nitrate < Carbonate < Chloride

Estimated costs of various TES systems*

J. Gomez-Vidal, A. Kruizenga, Technology Pathway Molten Salt, Project of CSP Gen 3 Roadmap, 02. 2017
SunShot Initiative is a federal government program run by DOE.

Reducing corrosiveness of chlorides → Reducing tank (TES) costs by using cheaper alloys
R&D of Molten Chlorides for Thermal Energy Storage

1. Selection of Promising Chloride Salts
2. Corrosion mechanism of Fe-Cr-Ni alloy
3. In-situ corrosive impurity monitoring based on cyclic voltammetry
4. Mg corrosion inhibitor

Inert atmosphere

Molten Chlorides

Molten salt storage tank

2 Corrosion Mechanism of Commercial Fe-Cr-Ni Alloys

Molten Chlorides

Molten salt storage tank

2 Proposed Corrosion Mechanisms

- Large amount of Mg and O detected in holes in corrosion layer
- MgCr$_2$O$_4$ and MgO detected in oxides on surface

SS 310 in MgNaK chloride (700°C, 500 h)

3 In-situ Monitoring of Corrosive Impurities

In-situ corrosive impurity monitoring based on cyclic voltammetry

Inert atmosphere

Molten Chlorides

Molten salt storage tank

3 Cyclic Voltammetry (循环伏安法)

MgCl₂/KCl/NaCl (60/20/20 mole%) at 500 °C, Tungsten as working, counter and reference electrode

Most stable corrosive impurity MgOH⁺

Reaction B: MgOH⁺ + e⁻ = MgO + ½ H₂

4 Mg Corrosion Inhibitor

Mg corrosion inhibitor

Inert atmosphere

Molten Chlorides

Molten salt storage tank

4 Reduced Corrosion Rates by Mg

Adding Mg as corrosion inhibitor can significantly reduce the corrosion rate in case of Fe-Cr-Ni based alloys, to ~10% compared with the case without Mg addition.

Inhibition mechanism: Adding Mg reduces redox potential of molten chloride salts.