Molten Halide Salts for Large-Scale Energy Storage

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- Introduction
  - 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**

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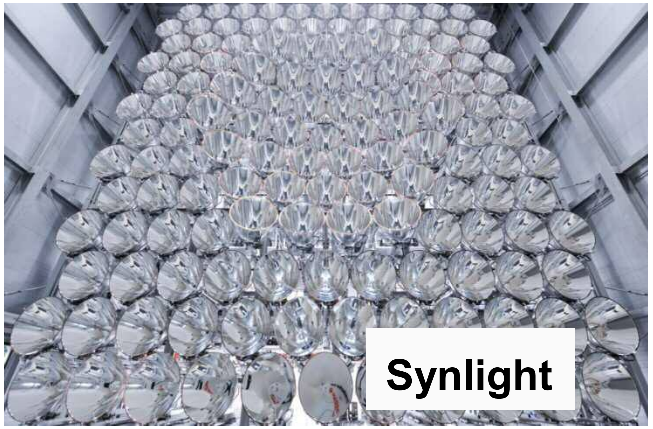
Energy Research Program Themes

- 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



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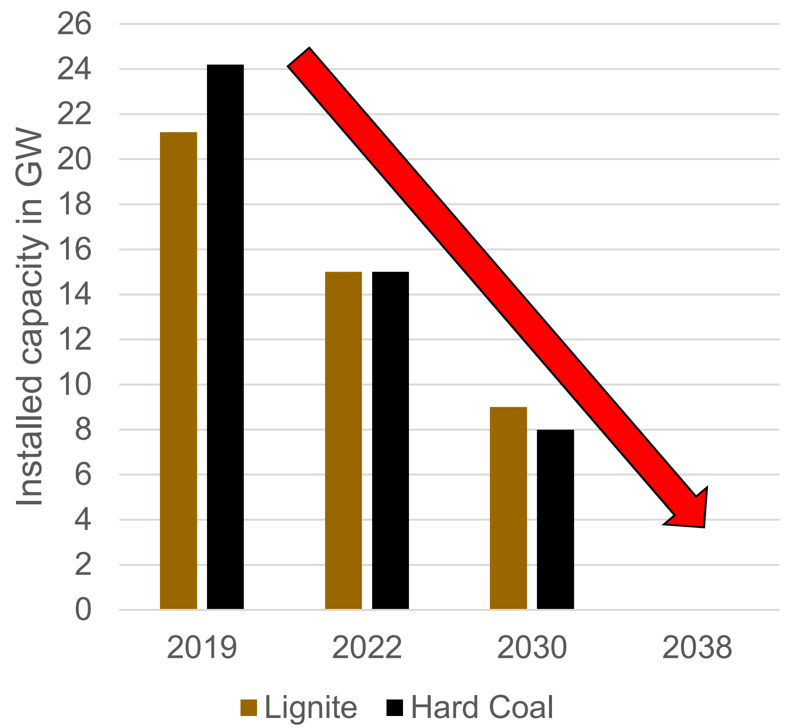
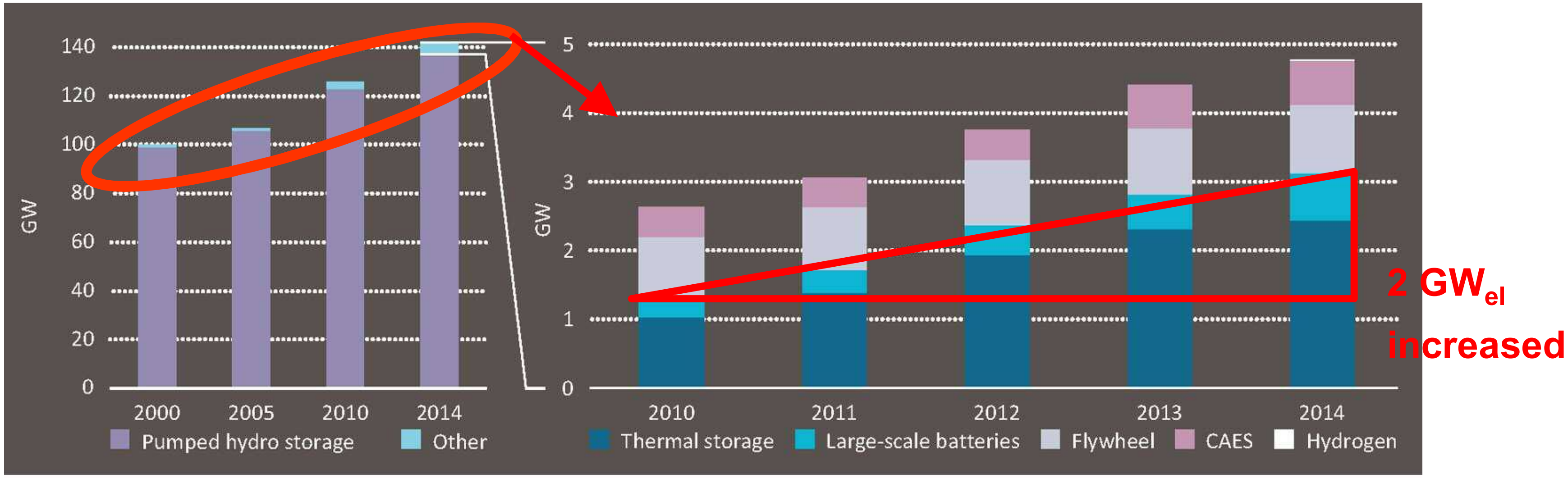
Energy Transition in Germany – Increased volatile power from PV/wind

- 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:
https://www.iea.org/newsroomandevents/graphics/2015-06-30-installed-global-capacity-for-grid-connected-storage.html
http://www.ren21.net/wp-content/uploads/2018/06/17-8652_GSR2018_FullReport_web_final_.pdf

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)

Research Group for TES in MOLTEN SALTS

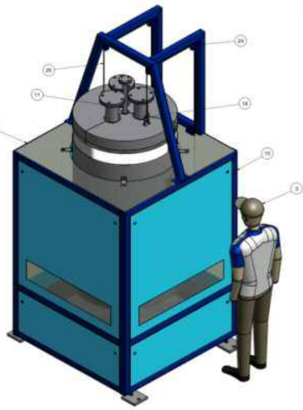
10 mg

100 ton

"... value chain research..."

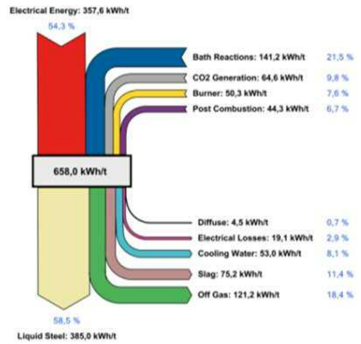
Material aspects

Process technology (Upscaling)



Components

System aspects



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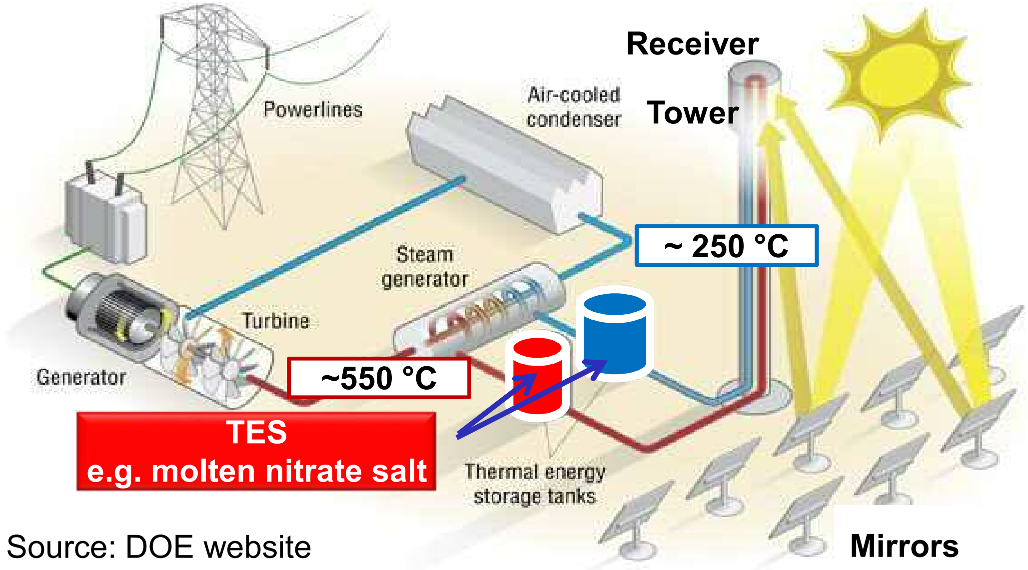
Molten Salts for Thermal Energy Storage (TES)

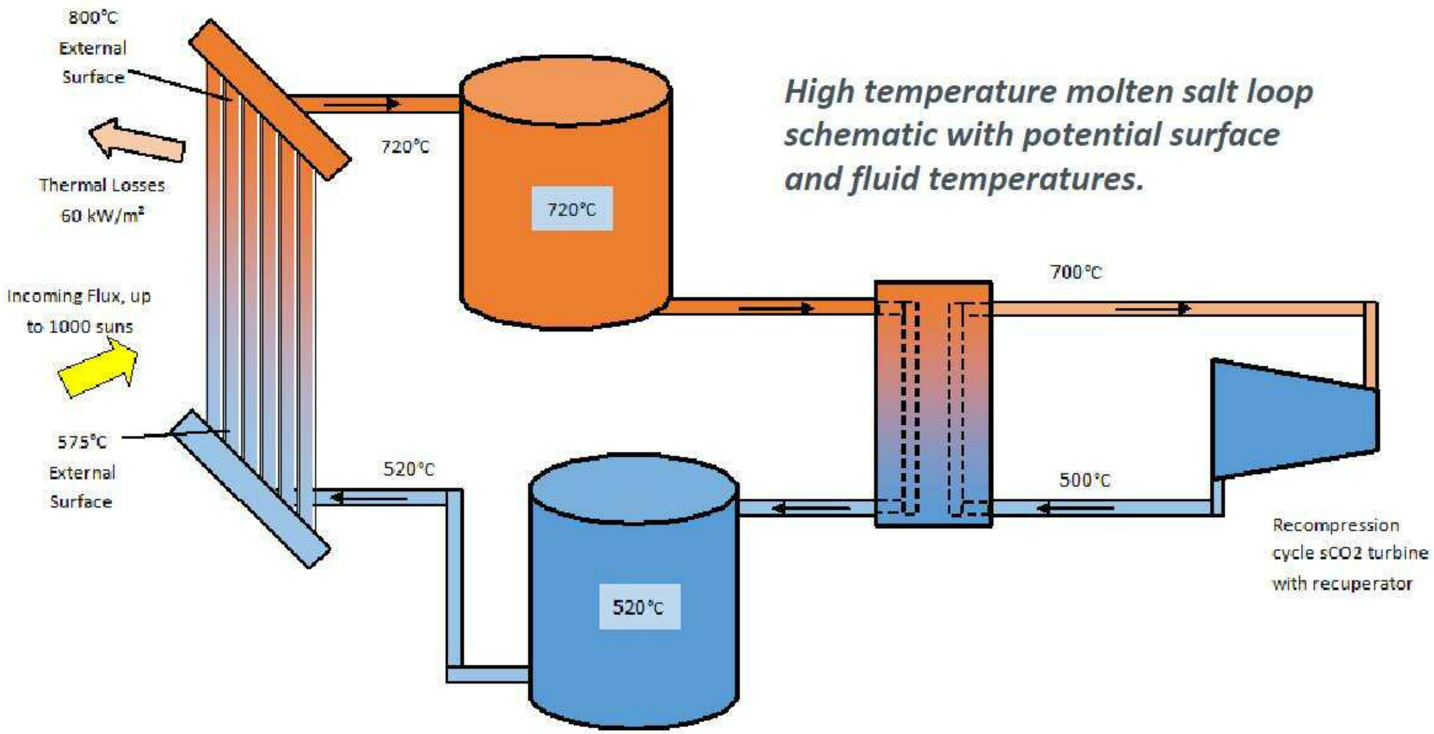
- Large-scale hourly storage for **CSP plants** (13 GWh_{el}) demonstrated
- **Inexpensive** heat storage capacity from 170 to 560 ° C in molten salts (**nitrate/nitrite**, non-toxic, non-flammable) in large-scale **unpressurized** tanks
- Potential to transfer technology from CSP to **grid-connected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

*https://www.solarpaces.org/make-carnot-batteries-with-molten-salt-thermal-energy-storage-from-ex-coal-plants/



Source: DOE website

Next Generation CSP with Advanced-salt System



Advanced-salt system + sCO_2 power cycle for higher energy conversion and lower LCOE*

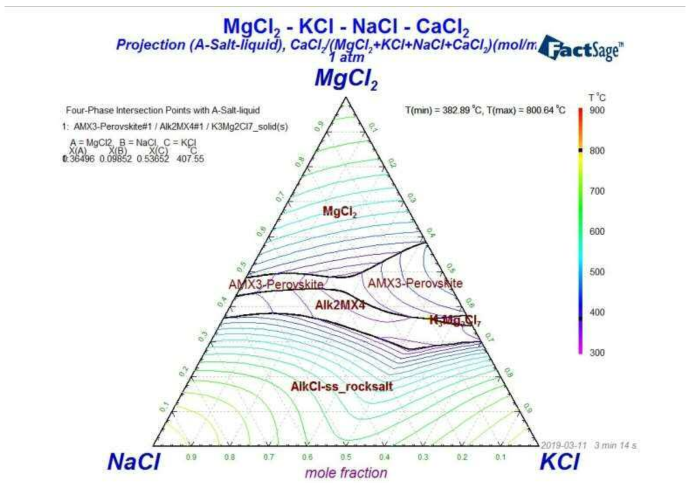
- Advanced-salt system (520-720°C)
- sCO_2 power cycle (500-700°C, efficiency > 50%)

*M. Mehos et al., Technical Report: NREL/TP-5500-67464, NREL, Golden, CO, 2017.

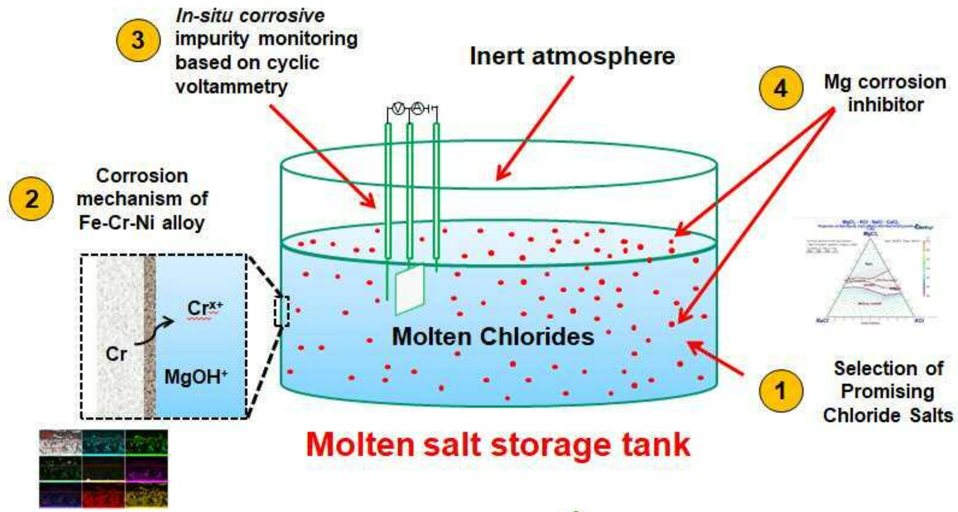
Example: Selection of Promising Chloride Salts for TES

- Considering thermal and physical properties (C_p, vapor pressure, melting point), hygroscopicity (corrosiveness) and prices, $MgCl_2$-KCl-NaCl eutectic salt mixture (<0.35 USD/kg, thermal stability >800°C, T_m = 385°C) is selected [1].

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



FactSage simulation



1) W. Ding, et al., *AIP Conference Proceedings* , 2019, 2126: 200014
2) W. Ding, et al., *Frontiers of Chemical Science and Engineering*, 2018, 12(3): 564–576

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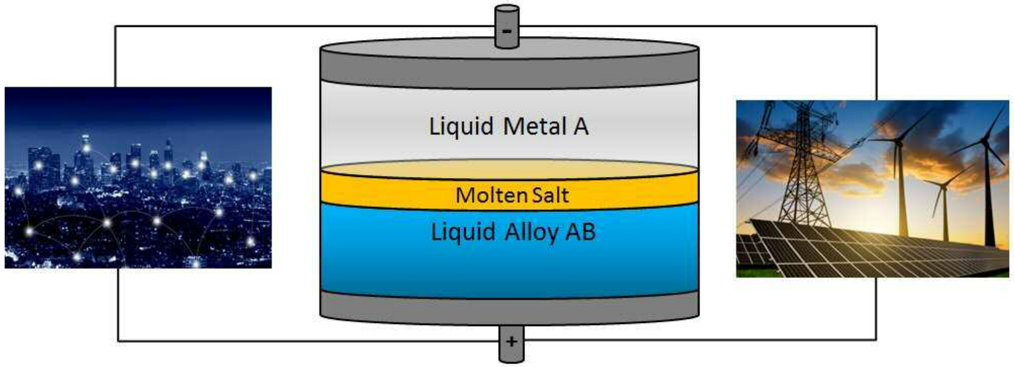
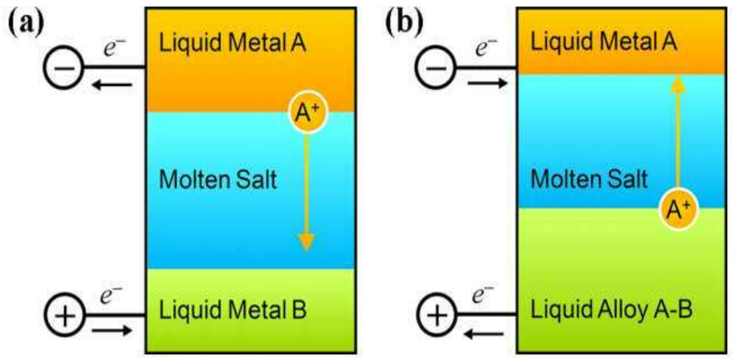
Liquid Metal Battery (LMB) for Grid-scale Storage

- **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, …



H. Kim, K. Wang, K. Jiang, D. Sadoway, et al., ***Chem. Rev.*** 113, 2075 (2013).



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

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

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

LMBs	Electrode	Electrolyte	T_m [°C]	T_w [°C]	Coulombic efficiency [%]	Energy efficiency [%]	self-discharge rate [mA/cm²] at full charge]	Capacity loss rate [%/cycle]
Li-LMB (MIT) [1]	Anode: Li; Cathode: Sb-Sn	LiF-LiCl-LiBr	440	500	>98%	70-90	<1	0.006
Na-LMB (ANL) [2]	Anode: Na Cathode: Bi	NaF-NaCl-NaI (single-cation)	530	580	82	59	~20	NA

1) K. Wang, K. Jiang, B. Chung, et al.. ***Nature***, 2014, 514(7522): 348-350.
2) H. Kim, K. Wang, K. Jiang, D. Sadoway, et al., ***Chem. Rev.*** 113, 2075 (2013).

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°C :**
  - Liquid metal electrodes (Na//SbSn and Na//BiSb)
  - Na^+-containing molten salt electrolyte with T_m<400°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**

Karlsruhe Institute of Technology

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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

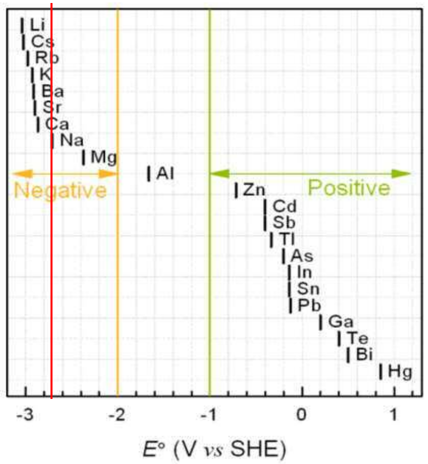
Q. Gong, W. Ding, K. Wang, A. Weisenburger, et al. **Molten iodide salt electrolyte for low-temperature low-cost sodium-based liquid metal battery**, *J. Power Sources*, accepted.

1 Screening of Halide Salt Mixtures Regarding T_m

- Salt mixture containing:
  - Cation: Li^+, K^+, Ba^{2+}, Ca^{2+}, Na^+
  - Anion (halide): F^- (not selected due to high T_m), Cl^-, Br^-, I^-
- Screening *via* thermodynamic modelling (FactSage) and literature review
- Potential electrolyte salts:
  - Li^+-containing: Na-Li-K//Cl-Br-I (e.g. Na-Li-K//I: T_m = 290°C, Na-Li-K//Cl: T_m = 350°C)
  - Not Li^+-containing: Na-K-Ba-Ca//Cl-Br-I (e.g. Na-K-Ba-Ca//Cl: T_m = 435°C)

- **Na-Li-K//I (starting salt system) due to lowest T_m**

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).

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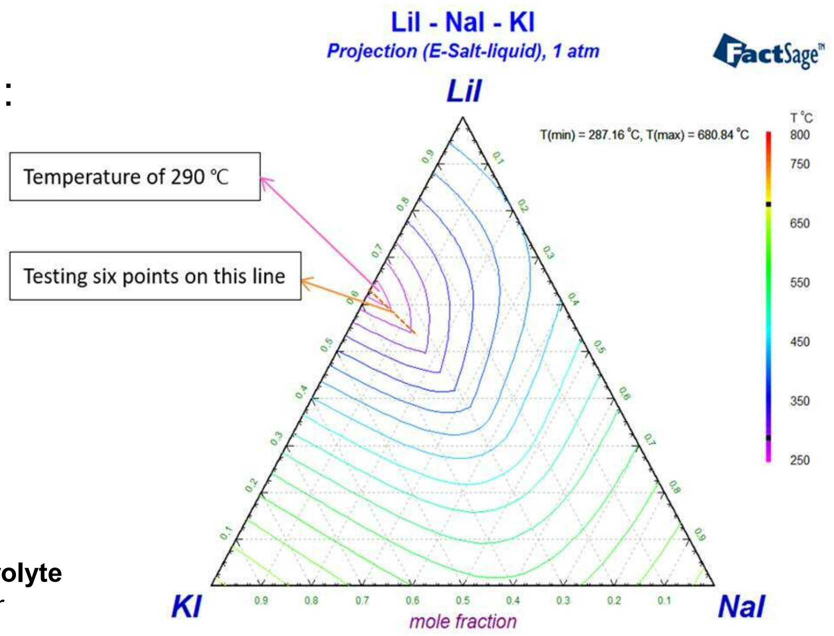
1 Screening of Halide Salt Mixtures Regarding T_m

- **Eutectic Na-Li-K//I:**
  - **Pseudo-binary salt** with T_m = ~290 °C
  - Eutectic Li-K//I: 63-37 mol%
  - Solubility of NaI in the eutectic LiI-KI is ~12 mol%

- **Na-K-Li//I is promising**:
  - Melting temperature T_m < 300°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%



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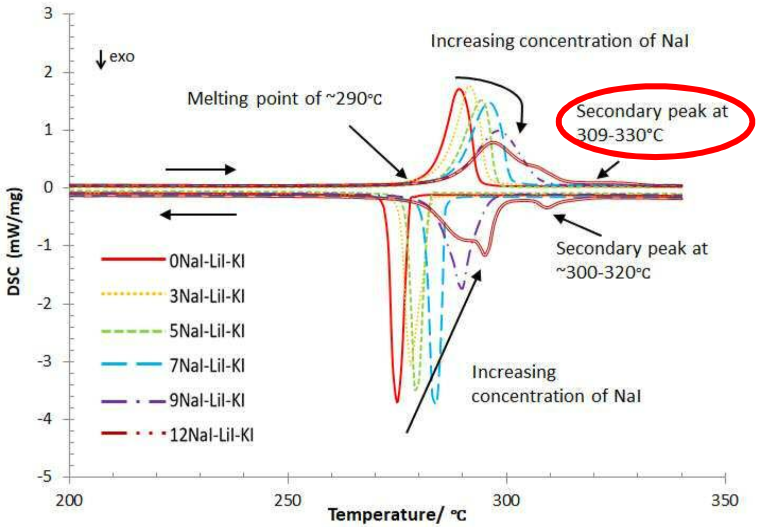
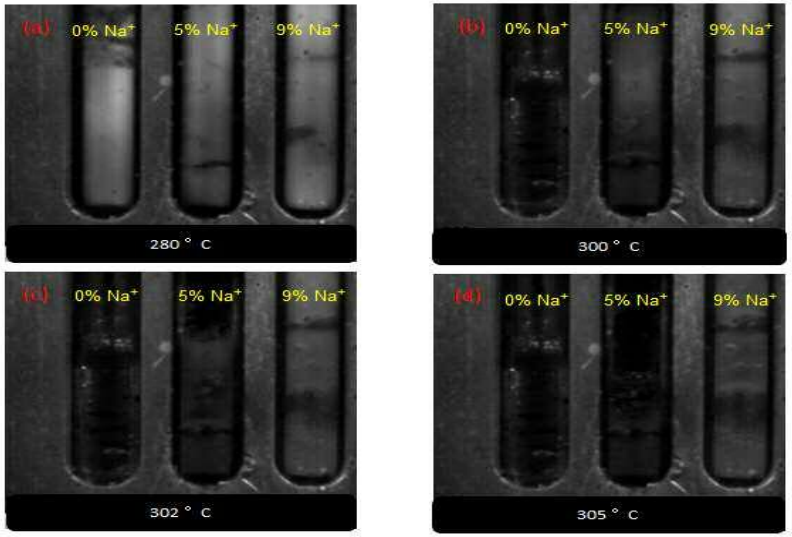
2 Experimental measurements of T_m

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

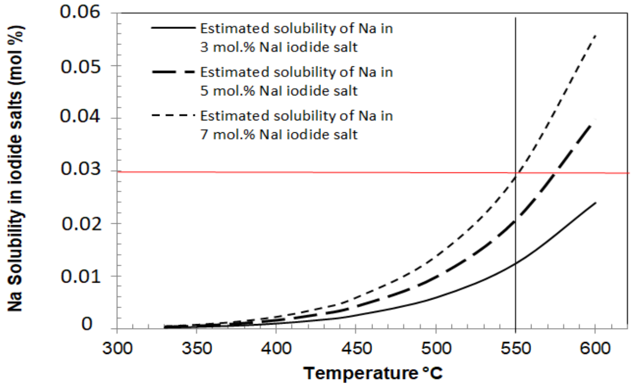


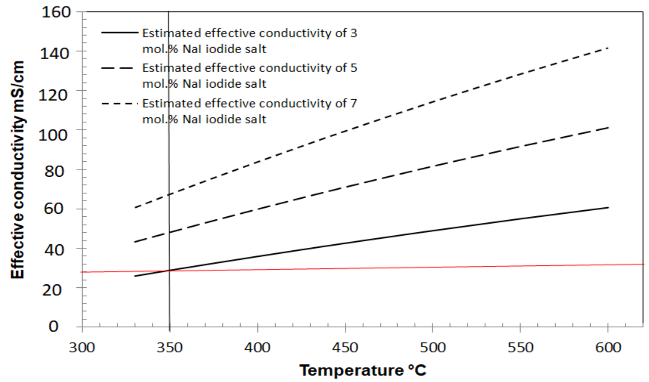


Q. Gong, W. Ding, K. Wang, A. Weisenburger, et al. **Molten iodide salt electrolyte for low-temperature low-cost sodium-based liquid metal battery**, *J. Power Sources*, accepted.

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/cm²)
  - 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)





1) M. Bredig and H. Bronstein, *The Journal of Physical Chemistry*, 64 (1960) 64-67.
2) Molten salts: Volume 1. Electrical conductance, density, and viscosity data, 1968.

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)

Salts	Large-scale prices / USD/kg	Sources
NaI	~3	Current price (CP)*
KI	~4	CP
LiI	~40	CP
NaI-LiI-KI eutectic	~20	Calculated with CPs of single salts
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. **Molten iodide salt electrolyte for low-temperature low-cost sodium-based liquid metal battery**, *J. Power Sources*, accepted.

5 Battery Pre-tests with Selected Molten Salt Electrolytes

- **Test conditions**:
  - ~1 cm thick NaCl(9 mol%)-LiCl-KCl (similar as NaI-LiI-KI) electrolyte,
  - T_w = 450°C, 100 discharge/charge cycles, current up to 1000 mA/cm^2
- **Results**:
  - Higher Coulombic efficiency >95%
  - T_w reduced by >100°C → low costs for structural and isolation materials
  - But unacceptable capacity loss rate → to be improved by battery optimization

LMBs	Electrode	Electrolyte	T_m [°C]	T_w [°C]	Coulombic efficiency [%]	self-discharge rate [mA/cm^2 at full charge]	Capacity loss rate [%/cycle]
Na-LMB (HUST, KIT, DLR)	Anode: Li; Cathode: Bi-based alloy	NaCl-LiCl-KCl	350	450	>95%	To be measured	0.1
Na-LMB (ANL)	Anode: Na Cathode: Bi	NaF-NaCl-NaI (single-cation)	530	580	82	~20	NA

Q. Gong, W. Ding, K. Wang, A. Weisenburger, et al. **Molten iodide salt electrolyte for low-temperature low-cost sodium-based liquid metal battery**, *J. Power Sources*, accepted.

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Summary and Outlook

- Next generation TES technology based on molten chloride salts is being developed
  - $MgCl_2$-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

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Thank you for your attention!

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HELMHOLTZ GEMEINSCHAFT

DAAD
Deutscher Akademischer Austauschdienst
German Academic Exchange Service

国家自然科学基金委员会
NSFC

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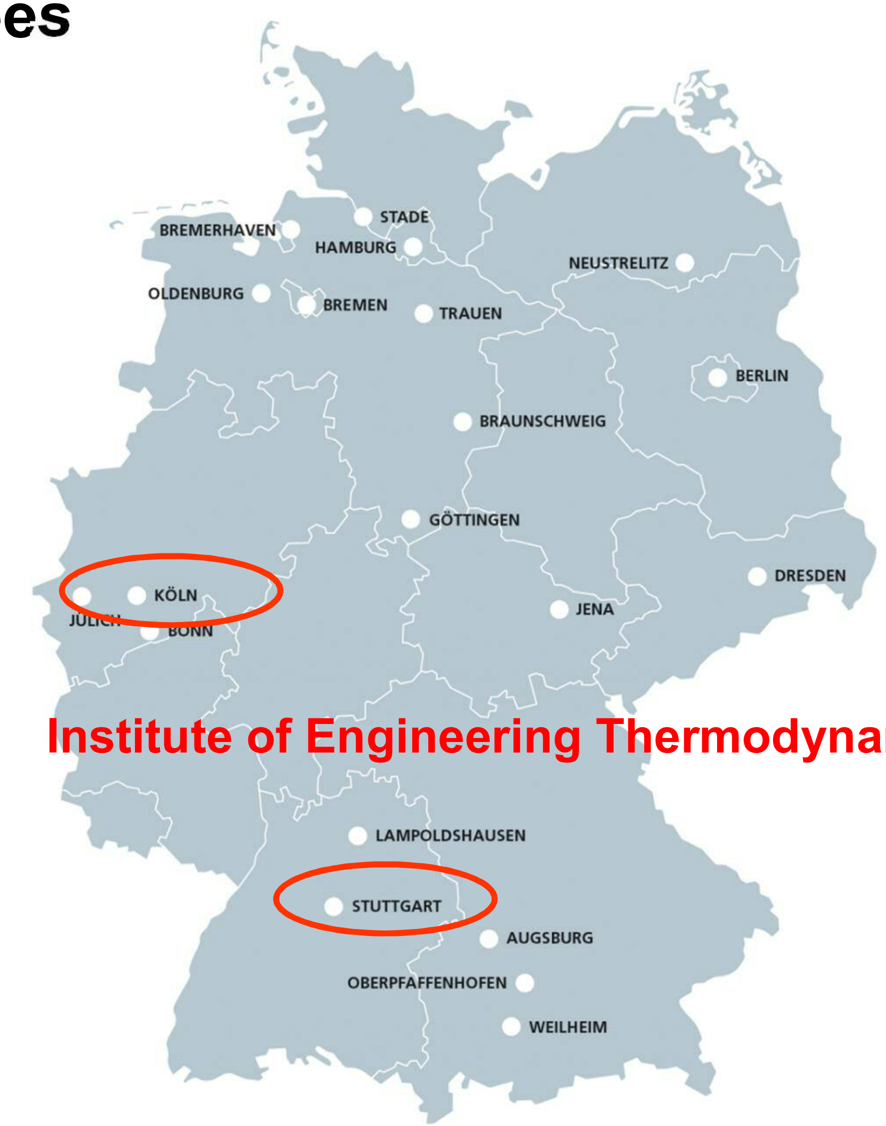
Locations and employees

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

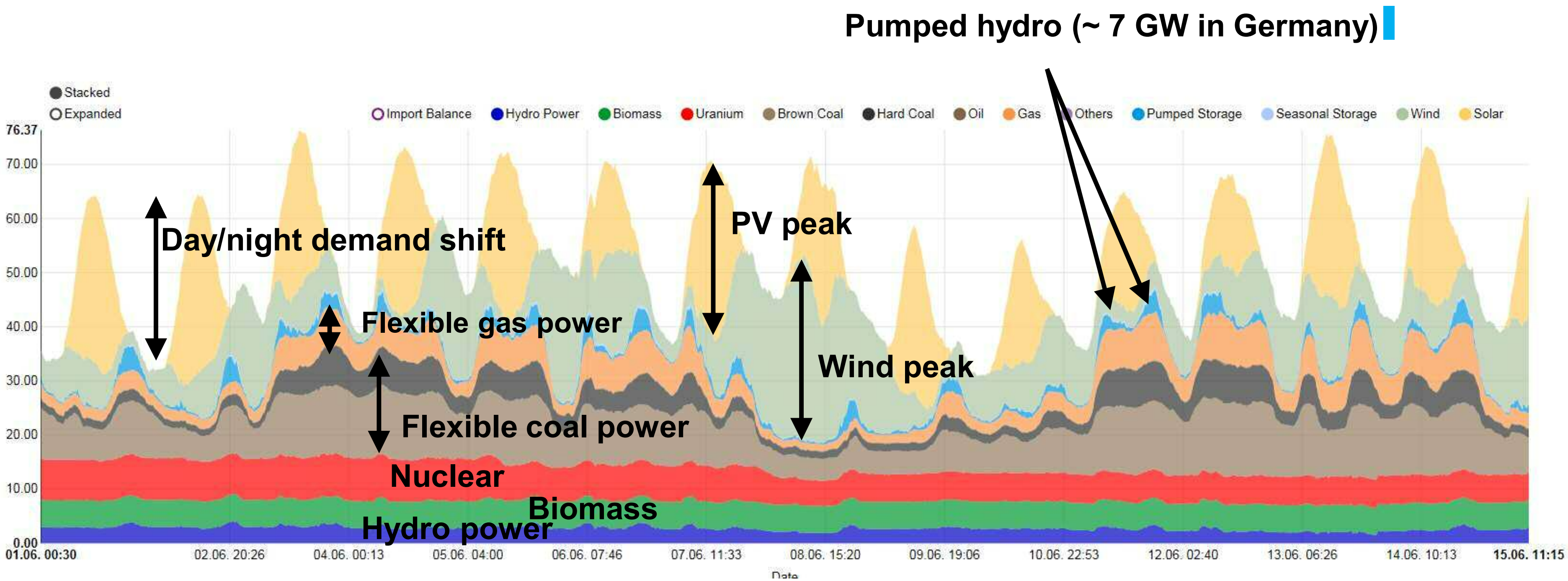
Offices in Brussels, Paris, Tokyo and Washington.

And a research site of concentrated solar power (CSP) in Almeria/Spain



Institute of Engineering Thermodynamics

Electricity generation in Germany (Example)



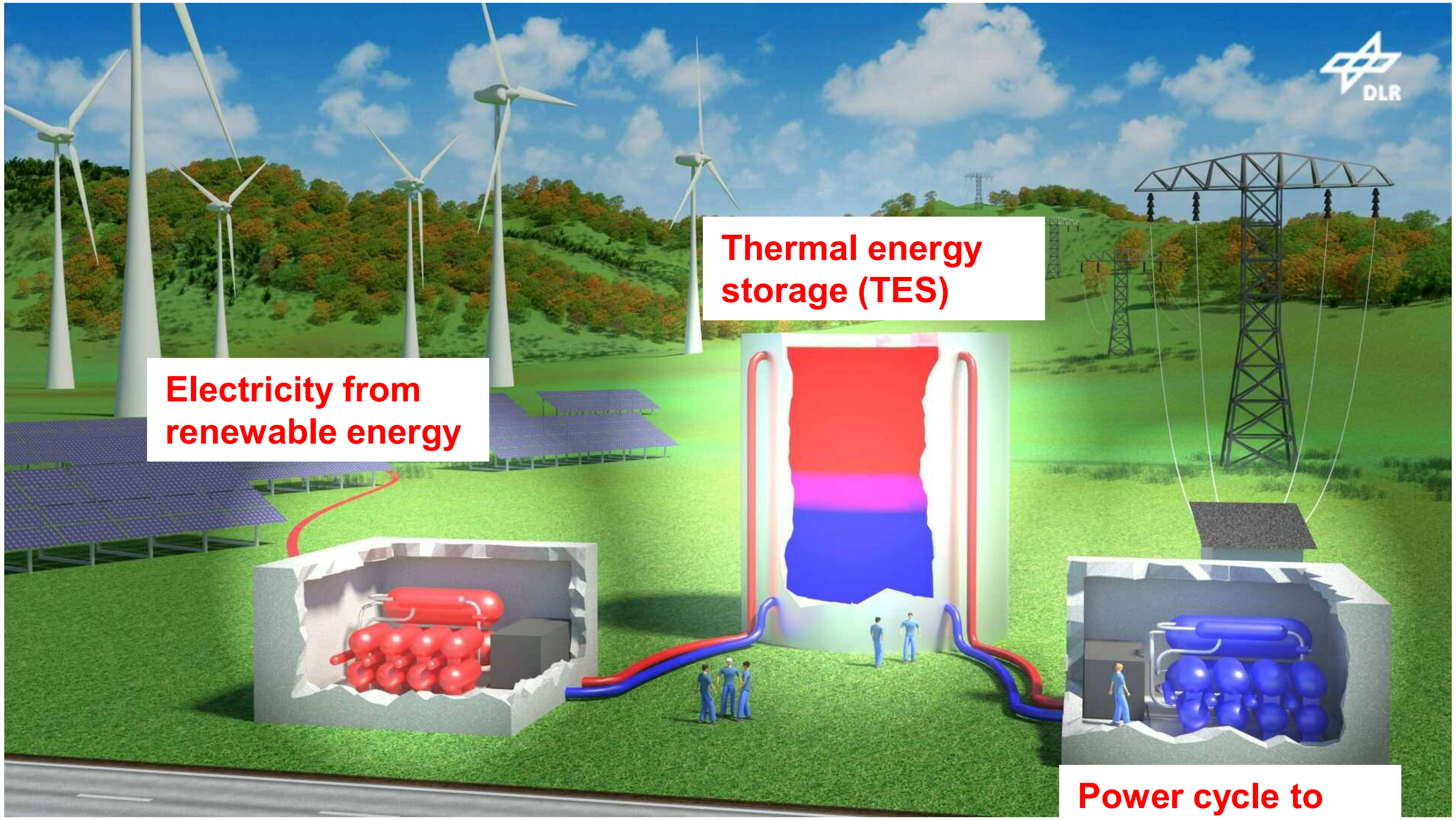
Source: https://www.energy-charts.de/

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

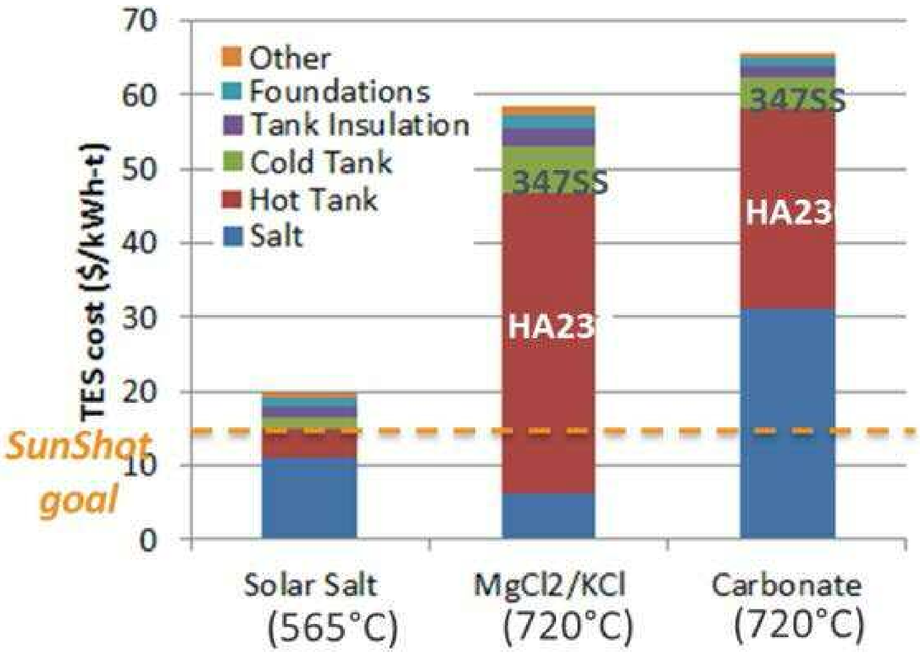
→ **Flexibility requirement**: Large-scale energy storage, power-to-X, demand side management, hybrid operation,…

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



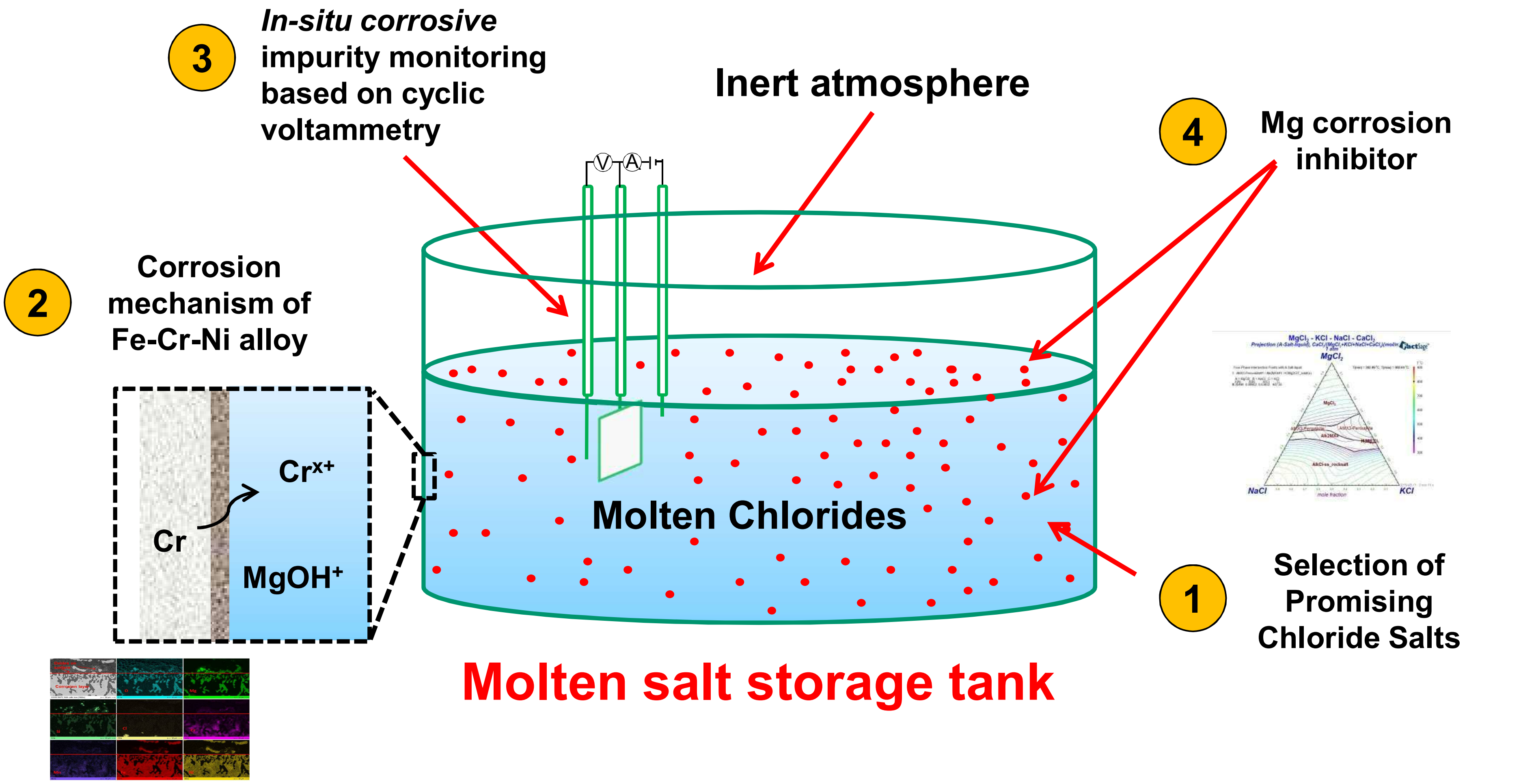
Estimated costs of various TES systems*

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.

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

Reducing corrosiveness of chlorides
→ Reducing tank (TES) costs by using cheaper alloys

R&D of Molten Chlorides for Thermal Energy Storage



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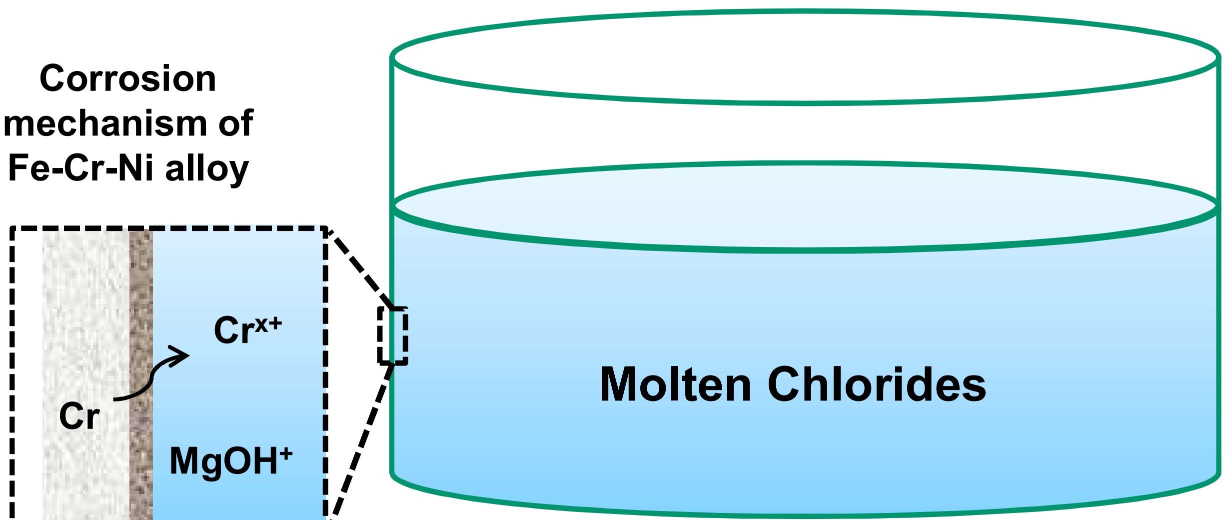
*W. Ding, et al., ***Frontiers of Chemical Science and Engineering***, 2018, 12(3): 564–576.

2 Corrosion Mechanism of Commercial Fe-Cr-Ni Alloys

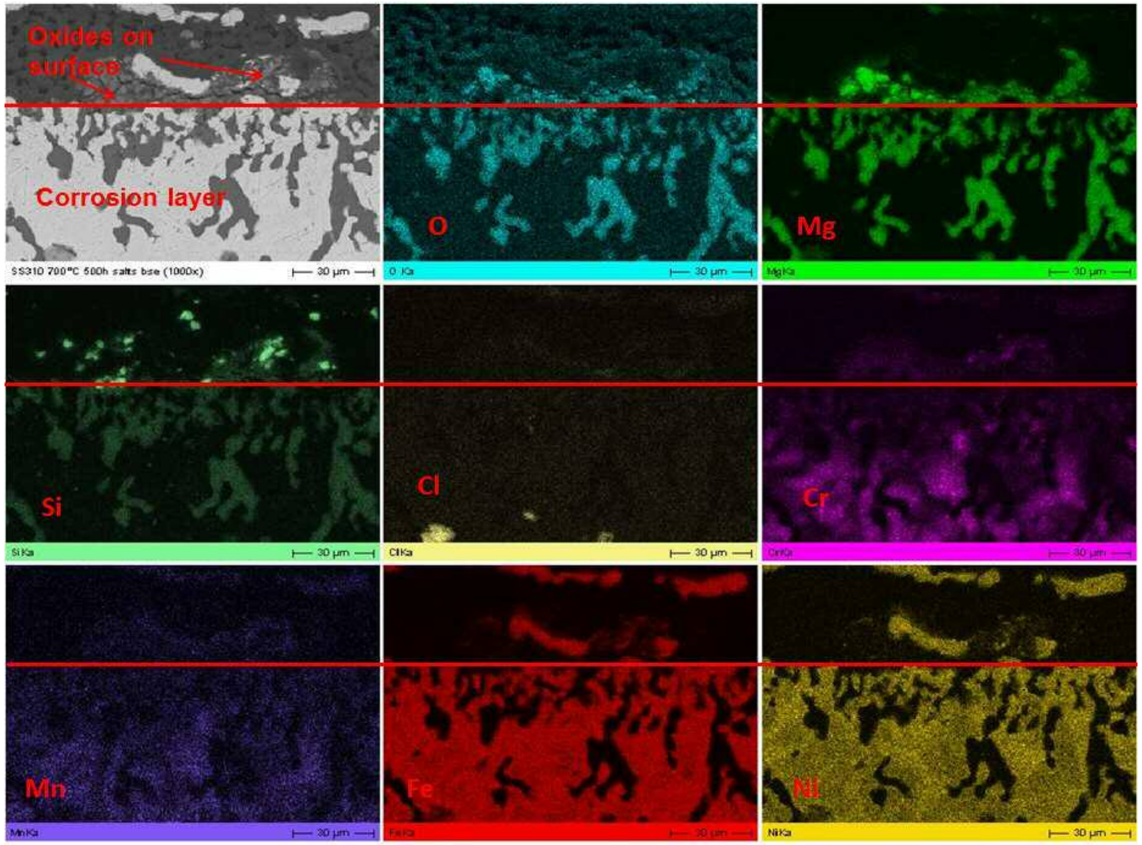
2 Corrosion mechanism of Fe-Cr-Ni alloy



Molten salt storage tank

*W. Ding, et al., ***Solar Energy Materials & Solar Cells***, 2018, 184: 22–30.

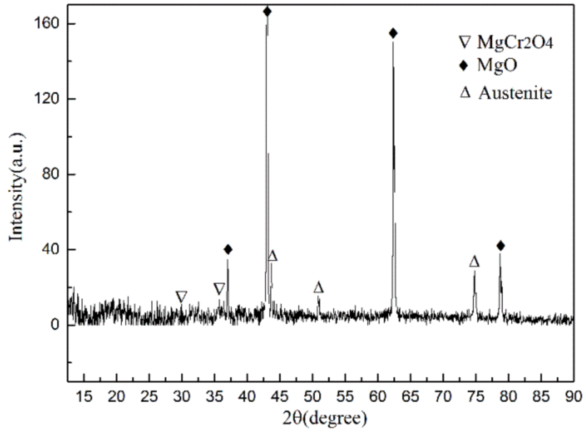
2 Proposed Corrosion Mechanisms



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

*W. Ding, et al., ***Solar Energy Materials & Solar Cells***, 2018, 184: 22–30.

XRD for oxides on surface



- Large amount of Mg and O detected in holes in corrosion layer
- $MgCr_2O_4$ and MgO detected in oxides on surface

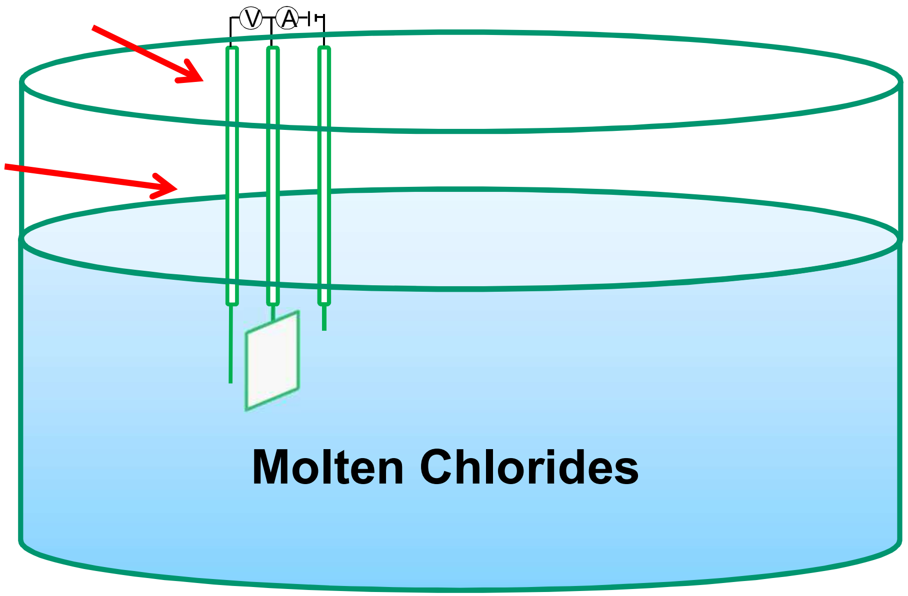
Corrosion mechanisms:

- Cr dissolved preferentially
- Corrosion is driven by impurities like MgOHCl

3 In-situ Monitoring of Corrosive Impurities

3 *In-situ* corrosive impurity monitoring based on cyclic voltammetry

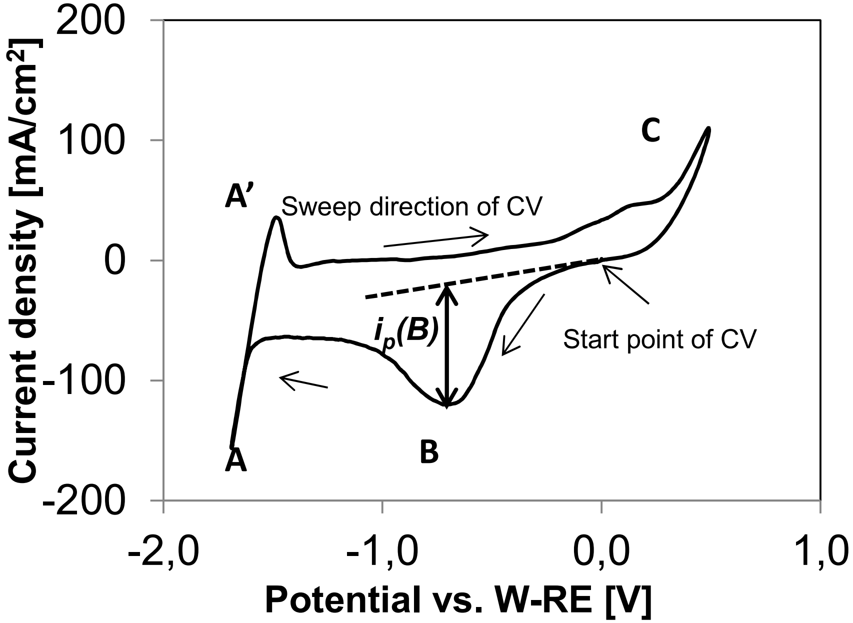
Inert atmosphere



Molten salt storage tank

W. Ding, et al., ***J. Energy Storage***, 2018, 15: 408–414.

3 Cyclic Voltammetry (循环伏安法)



MgCl$_2$/KCl/NaCl (60/20/20 mole%) at 500 °C,
Tungsten as working, counter and reference electrode

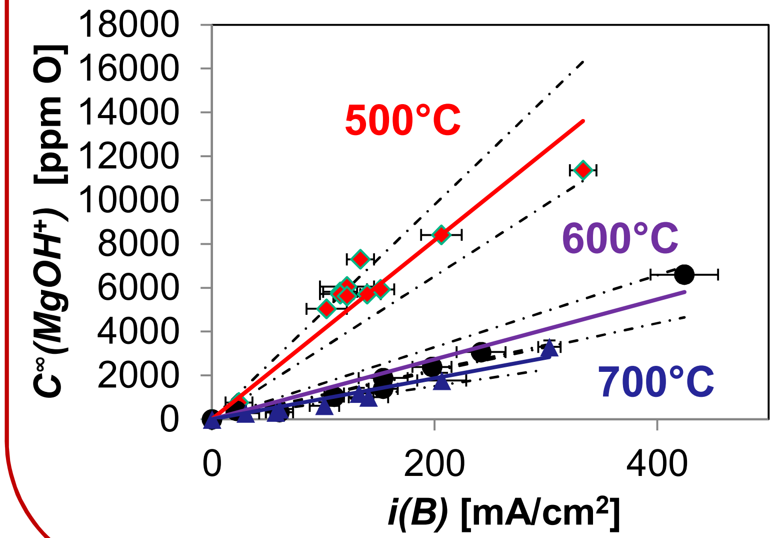
Most stable corrosive impurity **$MgOH^+$**

Reaction B: $MgOH^+ + e^- = MgO + ½ H_2$

W. Ding, et al., ***J. Energy Storage***, **2018**, 15: 408–414.

Peak current density of the peak B ($i_p(B)$) **proportional** to bulk concentration of $MgOH^+$ in molten chloride, i.e.,

$$C^\infty(MgOH^+) = k(T, v)(B) * i_p(B)$$



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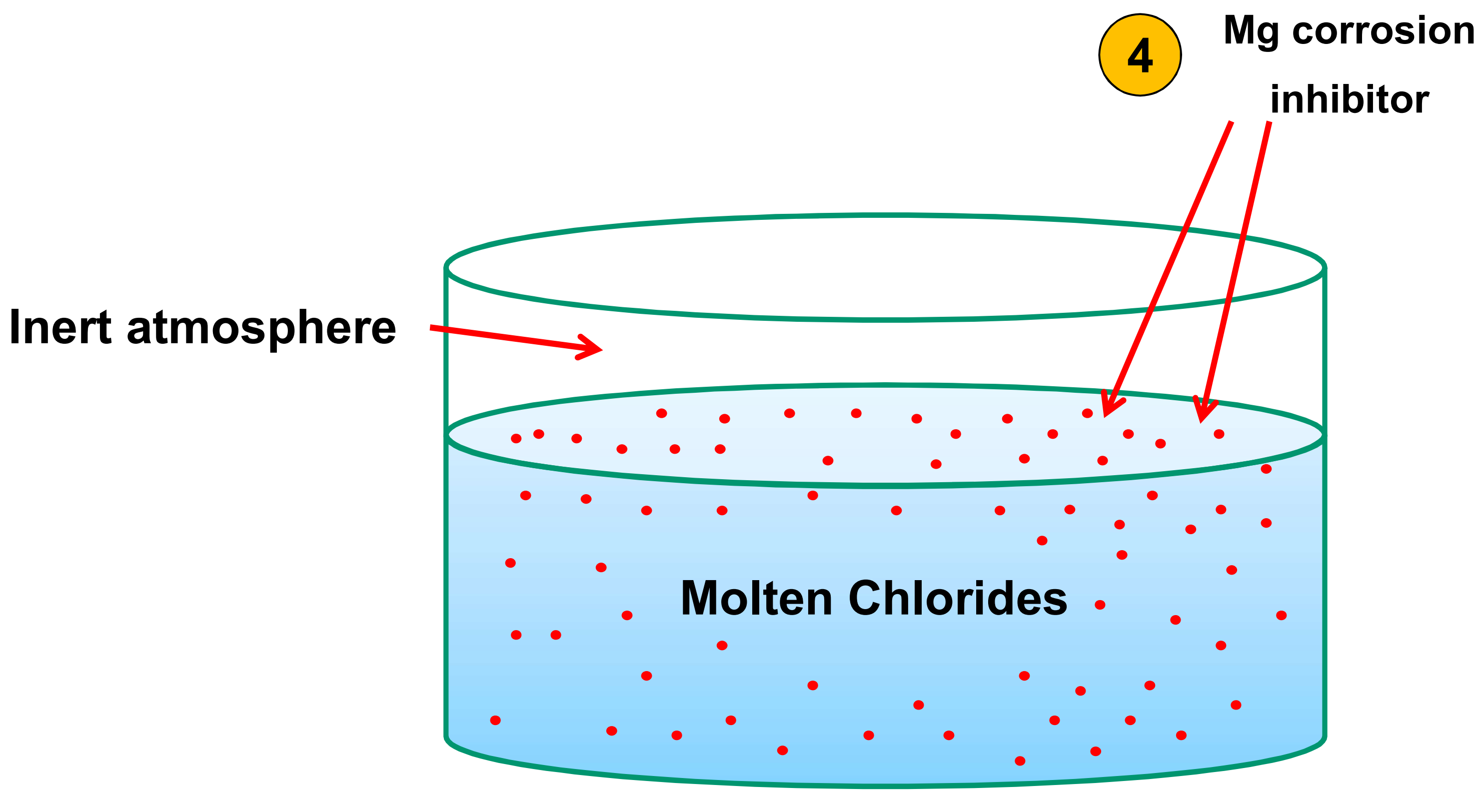
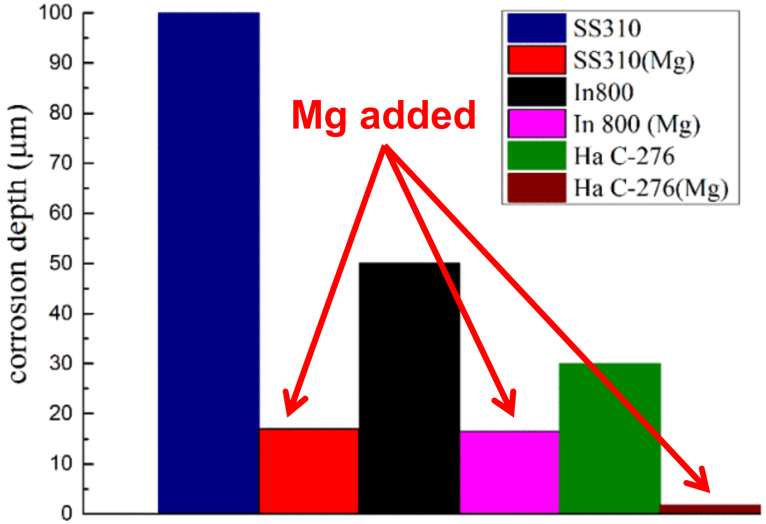
4 Mg Corrosion Inhibitor （腐蚀抑制剂）



Molten salt storage tank

*W. Ding, et al, ***Solar Energy Materials & Solar Cells***, 2019, 193:298-313.

4 Reduced Corrosion Rates by Mg



Measured corrosion depth of alloys after exposure to molten $MgCl_2$-KCl-NaCl at 700 °C for 500 h without and with Mg addition

*W. Ding, et al, ***Solar Energy Materials & Solar Cells***, 2019, 193:298-313.

Calculated redox potential of $MgCl_2$-KCl-NaCl (60–20–20 mol%) with Mg addition at 800 °C, and calculated equilibrium molar fractions of $CrCl_2$, $FeCl_2$ and $NiCl_2$ in the melt.

		Redox potential ΔG_{Cl_2}	Mg^{2+}	$MgOH^+Cl^-$	Cr^{2+}	Fe^{2+}	Ni^{2+}
EMF at 800 °C (V)			2.46	1.46	1.35	1.12	0.875
ΔG_f^0 at 800 °C (kJ/mol)			− 475	− 141	− 261	− 216	− 170
C_{eq} (mol%)	without Mg	− 360 kJ/mol (0.1 bar H_2)		4×10^{-3}	1.5×10^{-5}	9.8×10^{-8}	5.6×10^{-10}
		− 298 kJ/mol (0.1 mbar H_2)		4×10^{-3}	1.5×10^{-2}	9.7×10^{-5}	5.6×10^{-7}
	with Mg	− 500 kJ/mol	0.6	4×10^{-9} (0.1 mbar H_2)	2.3×10^{-12}	1.5×10^{-14}	8.5×10^{-17}

- 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.

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