In Silico Materials Screening for Thermochemical Looping Applications Using Direct and Indirect Property Prediction Methods

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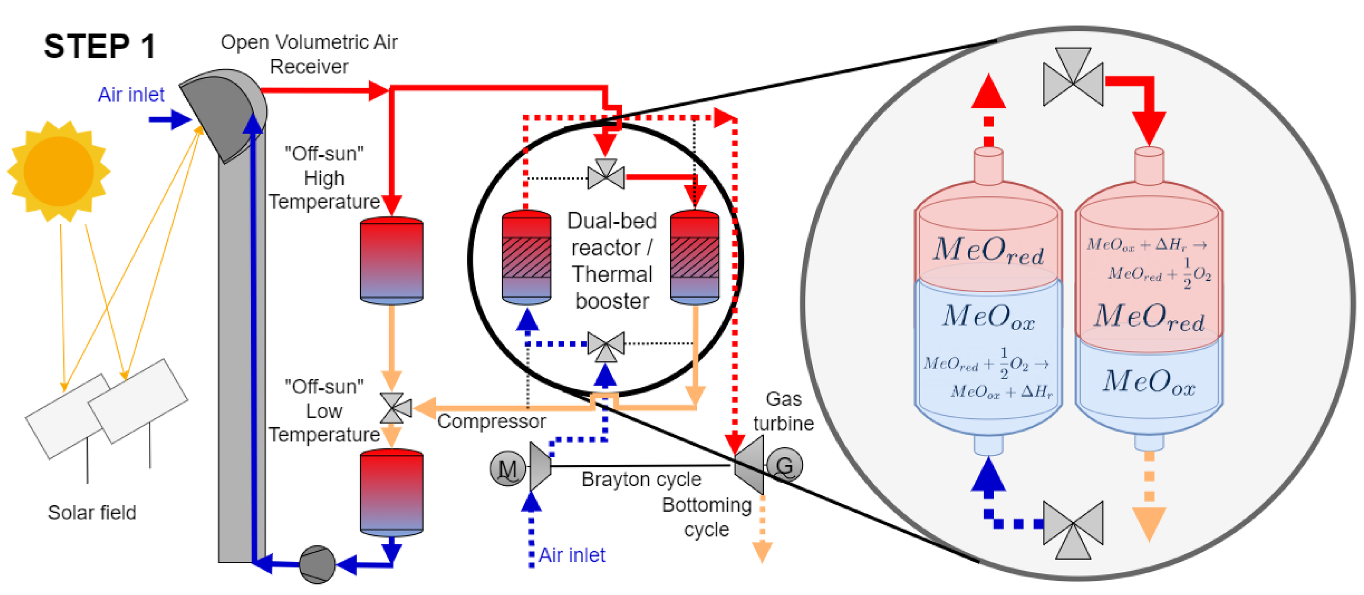
Summary: We use direct and indirect property prediction methods reported in literature to computationally assess the chemical and physical properties of metal oxides relevant for thermochemical looping applications in a high-throughput manner. The results serve as starting points for further computational or experimental validation of the identified compounds.

Oxide material selection for thermochemical heat storage



ABraytCSPfuture

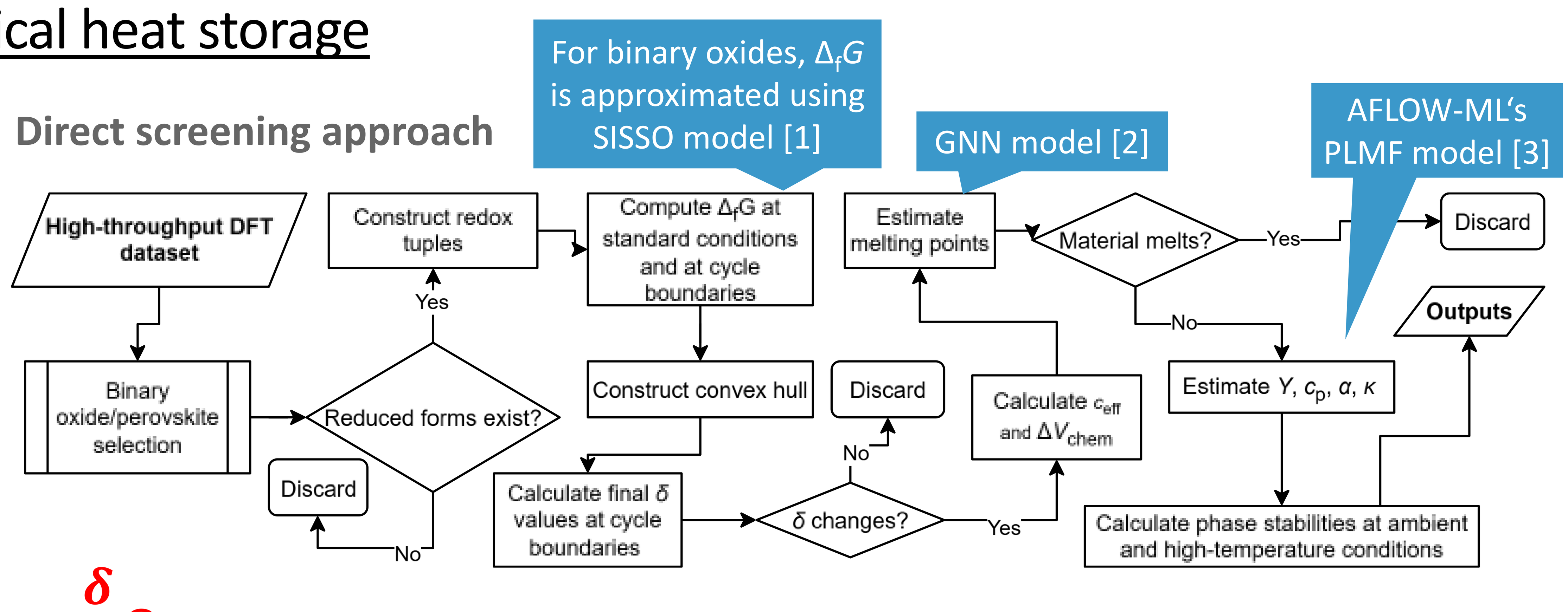
$$MO_x + \Delta H \underset{\text{low } T}{\overset{\text{high } T}{\rightleftarrows}} MO_{x-\delta} + \frac{\delta}{2} O_2$$

Goal: Identify metal oxide materials which can store maximum amount of sensible heat + chemical heat via a reversible redox reaction in an oxygen-containing atmosphere

Boundary conditions:

- Specific stoichiometry/structure, e.g. binary oxides or perovskite oxides
- Stable oxide ceramic bodies during cyclic operation
- Low cyclic expansion/contraction
- High thermal conductivity

Direct screening approach



In silico screening results using Materials Project [4] data for binary oxides heated and cooled between 300°C and 1200°C in air.

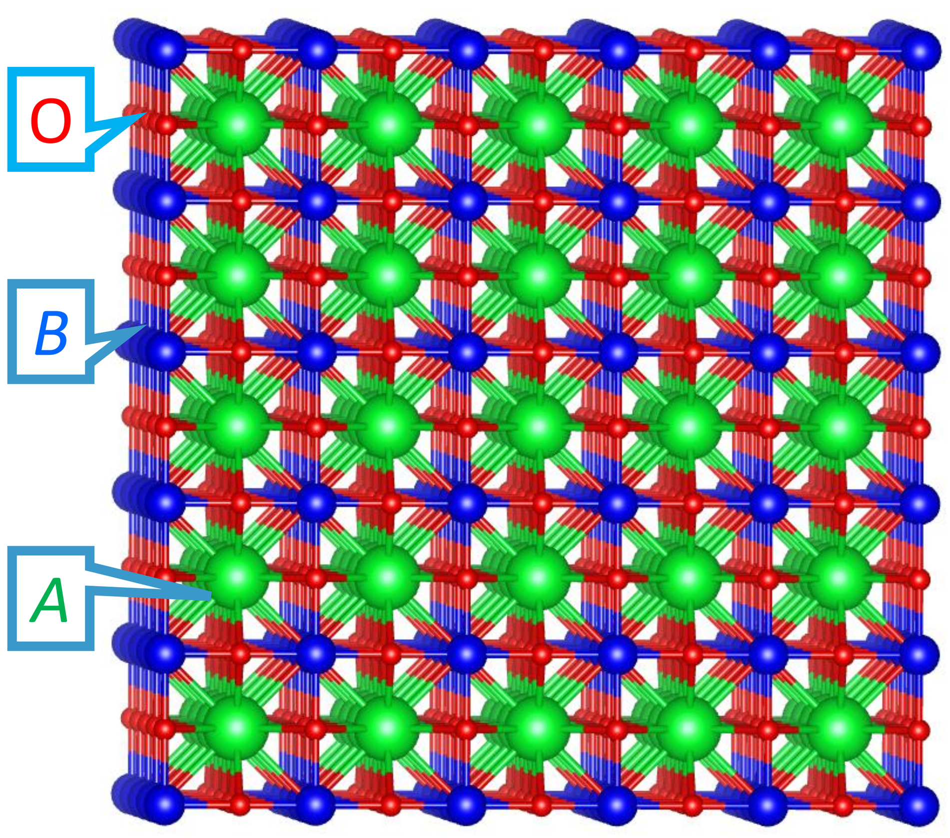
Formula	Heat stored, J/K/g	ΔV, %	Melting Point, °C	Young's modulus, GPa	Thermal conductivity, W/m/k	Stability @ RT, k_BT/atom	Stability @ 1200°C, k_BT/atom
PdO_2	1.17	0	1802	201	2.91	1.54	0.02
MnO_2	1.02	-17	1046	193	2.91	0.00	0.00
CoO_2	0.97	-10	2024	109	3.28	0.00	0.37
BaO_2	0.89	2	1639	293	2.98	0.00	0.00
PtO_2	0.78	19	1612	190	2.55	0.00	0.07
Sb_2O_5	0.72	-4	1337	239	2.92	0.00	0.00

Direct and indirect property prediction methods

Material property predictions using machine learning models can be performed <u>directly</u> by inferring them from simple properties like structure, composition etc. or <u>indirectly</u> by explicitly calculating them using machine-learned interatomic force fields (MLIFFs).

Perovskite oxides for chemical looping air separation (CLAS)

SolaGrAm project:



$$ABO_{3-\delta_1} \underset{\text{low } T}{\overset{\text{high } T}{\rightleftarrows}} ABO_{3-\delta_2} + \frac{\delta_2 - \delta_1}{2} O_2$$

Goal: Identify materials which can remove maximum amount of oxygen from gas phase per mass

Boundary conditions:

- Perovskite oxide structures ABO_3
- Partial reduction mechanism via oxygen vacancies
- Reduced materials have to be reactive at low O_2 partial pressures p_{O2}

Indirect screening approach

- Select stable perovskite oxide candidate structures containing only non-critical elements from structure database
- Create simulation cells with at least **500 atoms**, i.e. $\Delta_{min}\delta \leq 0.01$
- For each perovskite, remove O atoms up to δ = 0.5, i.e. **at least 50 $ABO_{3-\delta}$ structures**
- Calculate **Gibbs energy changes** for reduction reactions using ***Orb* MLIFF** [5] energy differences and experimental entropy and enthalpy terms for O_2
- Calculate **equilibrium δ values** for different temperatures and p_{O2}

High-throughput MLIFF calculation results for CLAS perovskite materials cycled between (1) $p_{O2} = 10^{-5}$ bar and T = 350°C, (2) p_{O2} = 0.21 bar and T = 700°C with Materials Project [4] starting structures.

$$OSC = \frac{n_{O_2}}{m_{ABO_3}}$$

Composition	δ_1	δ_2	$\Delta\delta$	OSC, 10^{-5} mol/g
$Sr_{0.75}Mg_{0.25}MnO_3$	0.023	0.297	0.273	156
$SrFeO_3$	0.230	0.430	0.200	104
$Sr_{0.75}Ca_{0.25}Mn_{0.125}Fe_{0.875}O_3$	0.229	0.410	0.181	101
$SrCe_{0.5}Fe_{0.5}O_3$	0.008	0.242	0.234	100
$Ba_{0.5}Sr_{0.5}FeO_3$	0.203	0.414	0.211	98
$Ba_{0.125}Sr_{0.875}Mn_{0.125}Fe_{0.875}O_3$	0.167	0.354	0.188	95
$CaFeO_3$	0.250	0.370	0.120	84
$Sr_{0.75}Ca_{0.25}Mn_{0.375}Fe_{0.625}O_3$	0.174	0.319	0.146	81
$La_{0.5}Mg_{0.5}Fe_{0.5}Cu_{0.5}O_3$	0.241	0.389	0.148	78
$Ca_{0.5}La_{0.5}Fe_{0.5}Cu_{0.5}O_3$	0.148	0.287	0.139	70
…				

References

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[5] M. Neumann et al. arXiv:2410.22570 [cond-mat.mtrl-sci]

Funded by the European Union

This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No. **101084569**.

Kofinanziert von der Europäischen Union

Ministerium für Wirtschaft, Industrie, Klimaschutz und Energie des Landes Nordrhein-Westfalen

This project has received funding from the European Regional Development Fund and the Just Transition Fund under grant agreement no. **EFRE-20800374**.

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The authors gratefully acknowledge the computational and data resources provided through the joint high-performance data analytics (HPDA) project "terrabyte" of the German Aerospace Center (DLR) and the Leibniz Supercomputing Center (LRZ).