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Recycling of production residues from primary lithium batteries

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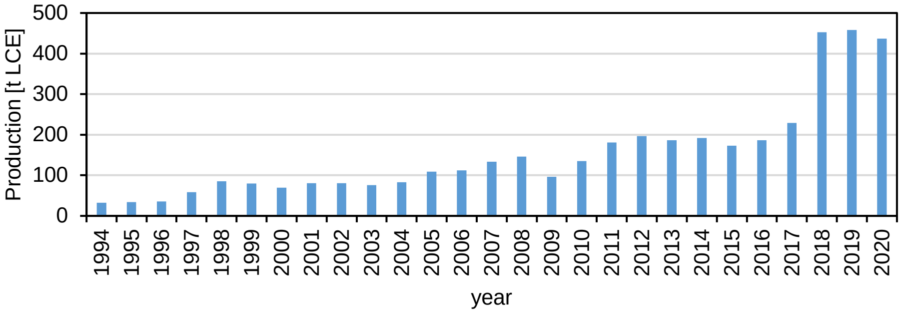
Resource situation

- Lithium is considered one of the **essential metals** for future technologies.
- It is **indispensable** with regard to the **storage of energy**.
    - Electric vehicles, mobile electrical appliances (wireless applications).
- Continuous **increase** in lithium **demand** in the coming years
- LCE **demand** also **increasing**



Forecast to 2027

Reaching **1.000.000 t LCE**

(188.000 t Li)

U.S. Geological Survey, Mineral Commodity Summaries from 1994 to 2020
Roskill, Lithium Outlook to 2030, 17th Edition, available at . https://roskill.com/market-report/lithium/ **2020.**

Resource situation

2020

- Production
    - 82.000 t Li or 436.525 t LCE
    - 55% Australia, 23% Chile, 10% China
- Global reserves
    - 21 Mio. T Li
    - 54% Chile, 18% Australia, 11% Argentina

Classified as **Critical Raw Material**

by European Commission

Lithium recovery from secondary source is mandatory

to reduce supply risk contributing to a circular economy

U.S. Geological Survey, Mineral Commodity Summaries 2020, **2020**.

Lithium recycling

- Current Li recycling rate: < 1%
- Recycling processes mainly focused on spent secondary and primary energy storage systems
- Recycling processes aimed at the recovery of other valuable metals (Ni, Co) from LIB
- Lack of approaches for Li recovery from metallic production residues from battery production

S. Ziemann, D. B. Müller, L. Schebek, M. Weil, *Resources, Conservation and Recycling* **2018**.

Primary batteries production residues

Li recovery

- Production residues are rich in Li (>60%) with high purity (> 99%)
  - Valuable Li source

⚠ Energy release during leaching with H_2O **(~32 MJ/kg Li)** and H_2 generation

$$Li + H_2O \rightarrow LiOH + 0.5\ H_2$$ $\Delta_R H$ = - 222.7 kJ/mol

$$Li_2O + 2\ H_2O \rightarrow 2\ LiOH + H_2O$$ $\Delta_R H$= - 133.3 kJ/mol

M. Kahl, S. Pavón, M. Bertau, *ChemPhysChem*. **2021**

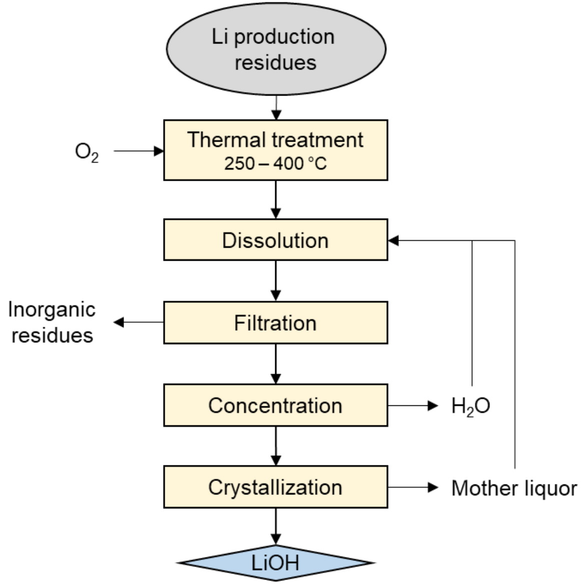
Primary batteries production residues

Li recovery

- Thermal oxidation of Li to Li_2O
  - ✓ Avoiding H_2 generation and heat production
  - ✓ The energy release upon dissolution is reduced by **70 %**

- Oxidation product dissolved in water

- $LiOH \cdot H_2O$ is obtained after crystallization



Development of a holistic process, which is suitable for maximizing the Li oxidation regardless the type of production residues from primary batteries

M. Kahl, S. Pavón, M. Bertau, *ChemPhysChem*. **2021**

Primary batteries production residues

Li recovery - Materials

- Residue (1)

Rolled lithium sheets with 0.1-1 mm thickness

99.89% Li

0.11% Na impurity

represents ≥ 90% of production residues

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- Residue (2)

Anode material in stainless steel wire

63.65% Li

21.03% Fe

15.32% Plastics

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Primary batteries production residues

Li recovery - Optimization

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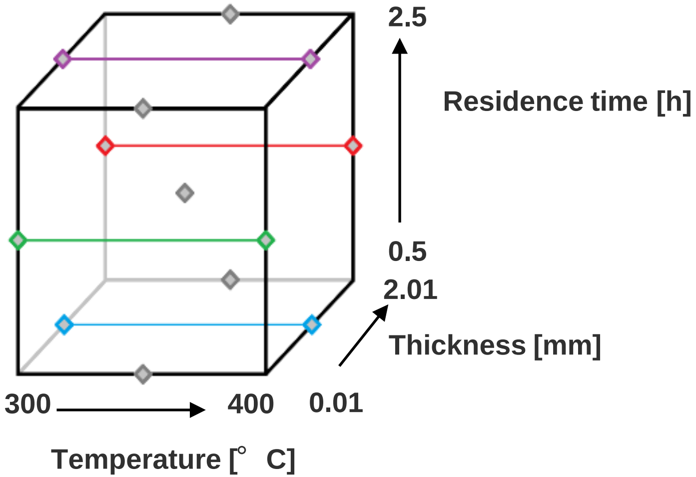
Material (1)

- Li oxidation optimized by using a Design of Experiments (DOE)
  - ✓ Optimum => global (instead of local)
  - ✓ Interaction evaluation
  - ✓ Model equation

- 3^3 Box Behnken design

Factors		Factor levels		
		-1	0	+1
A	Temperature [°C]	300	350	400
B	Thickness [mm]	0.01	1.01	2.01
C	Residence time [h]	0.5	1.5	2.5



M. Kahl, S. Pavón, M. Bertau, *ChemPhysChem*. **2021**

Primary batteries production residues

Li recovery - Optimization

Material (1)

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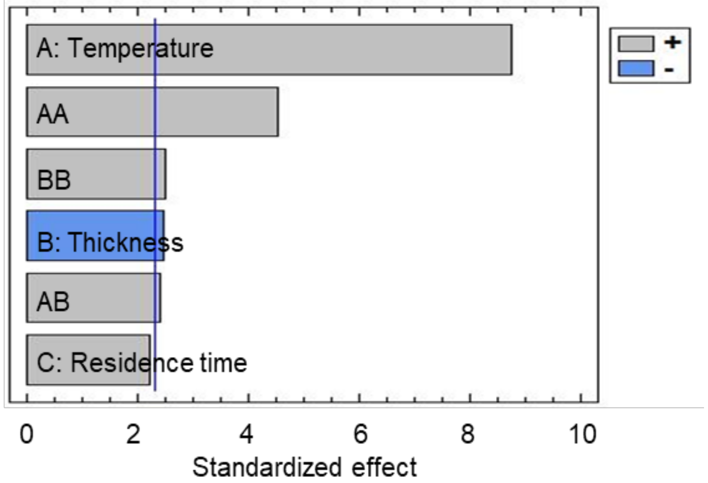
Pareto Diagram



- Temperature
  - ✓ Complete oxidation at T = 400 ° C
  - ⚠ Increasing temperature might interfere with the oxidation process by sintering of Li metal fragments
- Thickness

  Thinner sheets are easier to oxidize
    - ✓ Beneficial greater surface volume ratio
    - ✓ Lower charge density
- Residence time
  - ✓ After half an hour oxidation is finished. It enables high throughput, which is favorable for an industrial application

M. Kahl, S. Pavón, M. Bertau, *ChemPhysChem*. **2021**

Primary batteries production residues

Li recovery - Optimization

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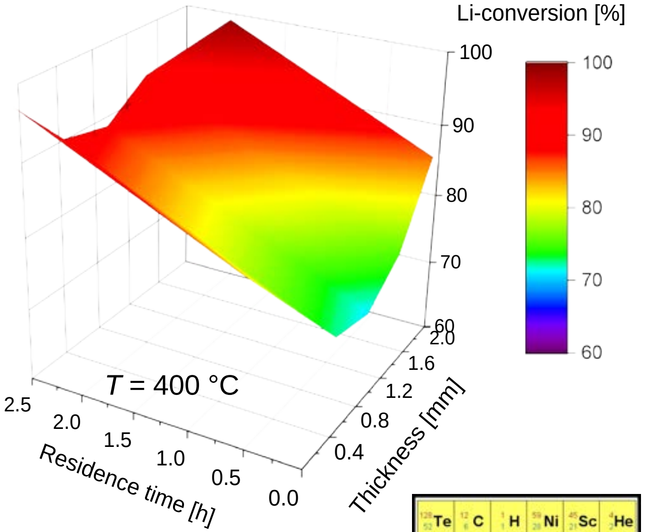
Material (1)

- Model equation

$$Li - conversion\ [\%] = 932.894 - 5.417 \cdot A - 104.905 \cdot B + 6.869 \cdot C + 0.008 \cdot A^2 + 0.211 \cdot A \cdot B + 11.546 \cdot\ B^2$$

where:

A: Temperature [°C]
B: Thickness [mm]
C: Residence time [h]



- Optimum

<u>Model:</u> 99.99% Li-conversion using 400 °C I 2 mm I 2.50 h

<u>Experimental:</u> 96.9 ± 2.6% Li-conversion

M. Kahl, S. Pavón, M. Bertau, *ChemPhysChem*. **2021**

Primary batteries production residues

Li recovery - Optimization

Material (2)

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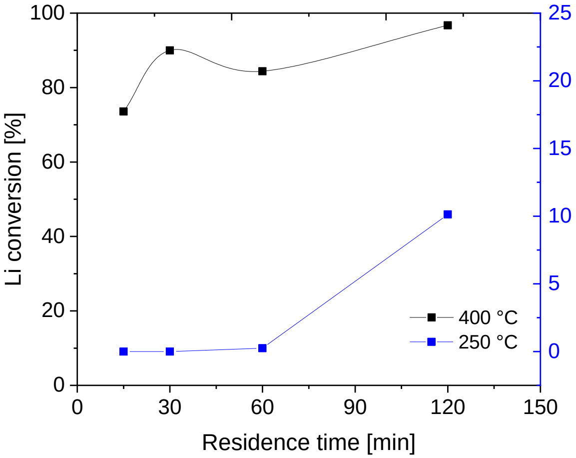
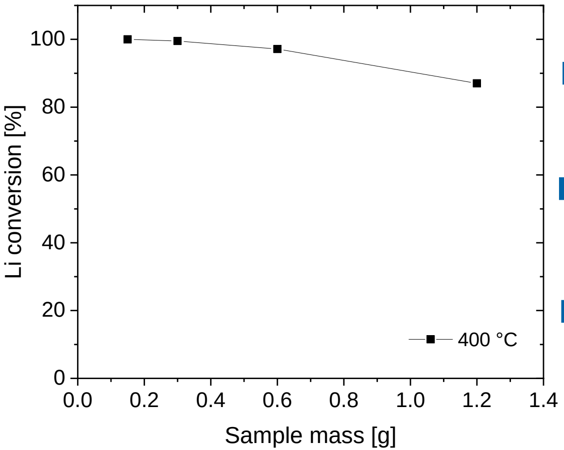
- Preliminary experiments



Effect of temperature/time on Li-content using 0.3 g



Effect of the sample mass on Li-content at 400 °C

3^3 Box Behnken design

	Factors	Factor levels		
		-1	0	+1
A	Temperature [°C]	250	325	400
B	Residence time [h]	0.25	0.50	0.75
C	Sample mass [g]	0.30	0.75	1.20

Primary batteries production residues

Li recovery - Optimization

Material (2)

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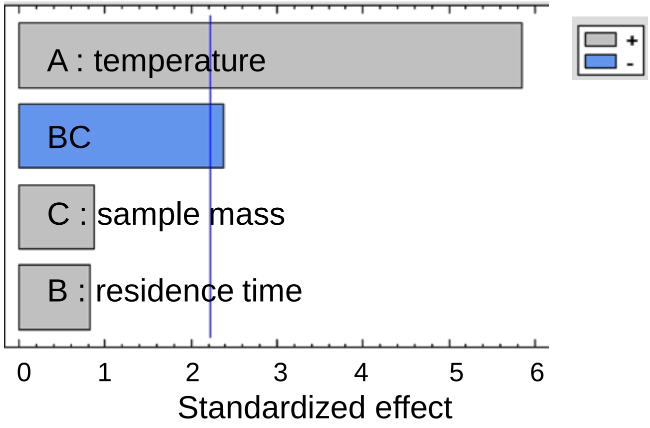
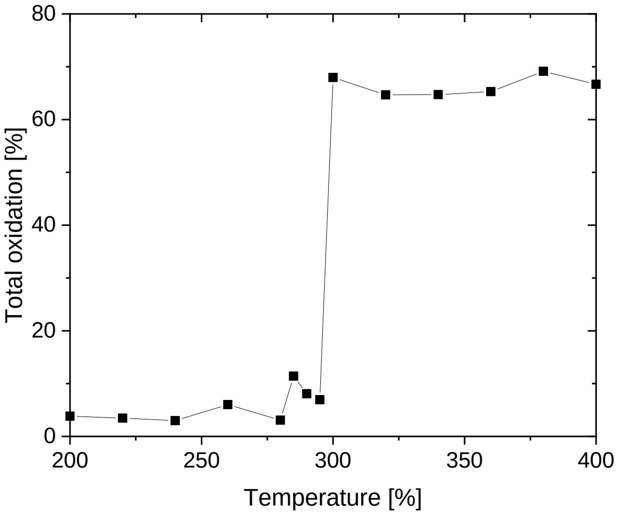
- ⚠ Temperature is the single factor that shows significant effect on the target value





Primary batteries production residues

Li recovery - Optimization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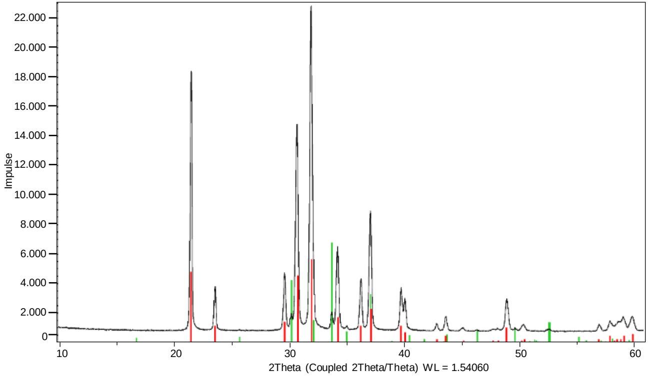
Material (2)

- Optimized oxidation conditions obtained by Material (1) applied on Material (2)
  - Optimal conditions 400 °C I 2.0 mm I 2.5 h
- Total oxidation: **93.08 ± 0.43%**

Isolation of Li_2CO_3



- **85.5 ± 3.0%** Li after a single precipitation step with CO_2
- Product characterization **96.72 ± 0.23% Li_2CO_3**
  3.0 ± 0.23% $LiOH \cdot H_2O$
  < 0.1% Na_2CO_3

Primary batteries production residues

Conclusions

- Conditions of Material (1) suitable for primary batteries production residues

Holistic approach!

- Optimal conditions for oxidation primary batteries production residues

400 °C I 2.0 mm I 2.5 h

- Recovery of **85.5% Li** by single precipitation step
  - **Li_2CO_3** as a product with high purity **(≥ 96%)**

Thank you for your attention !

Vielen Dank für Ihre Aufmerksamkeit!

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