Effect of Pre-treatment on Leaching of Black Mass from Lithium-Ion Batteries

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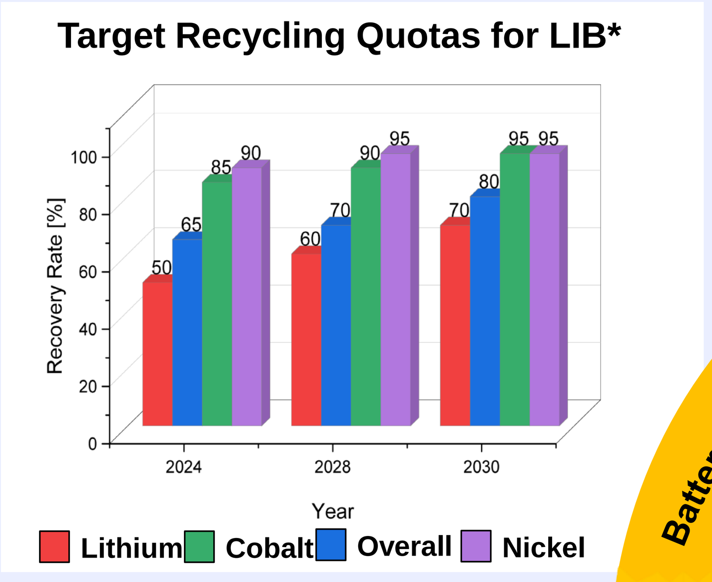
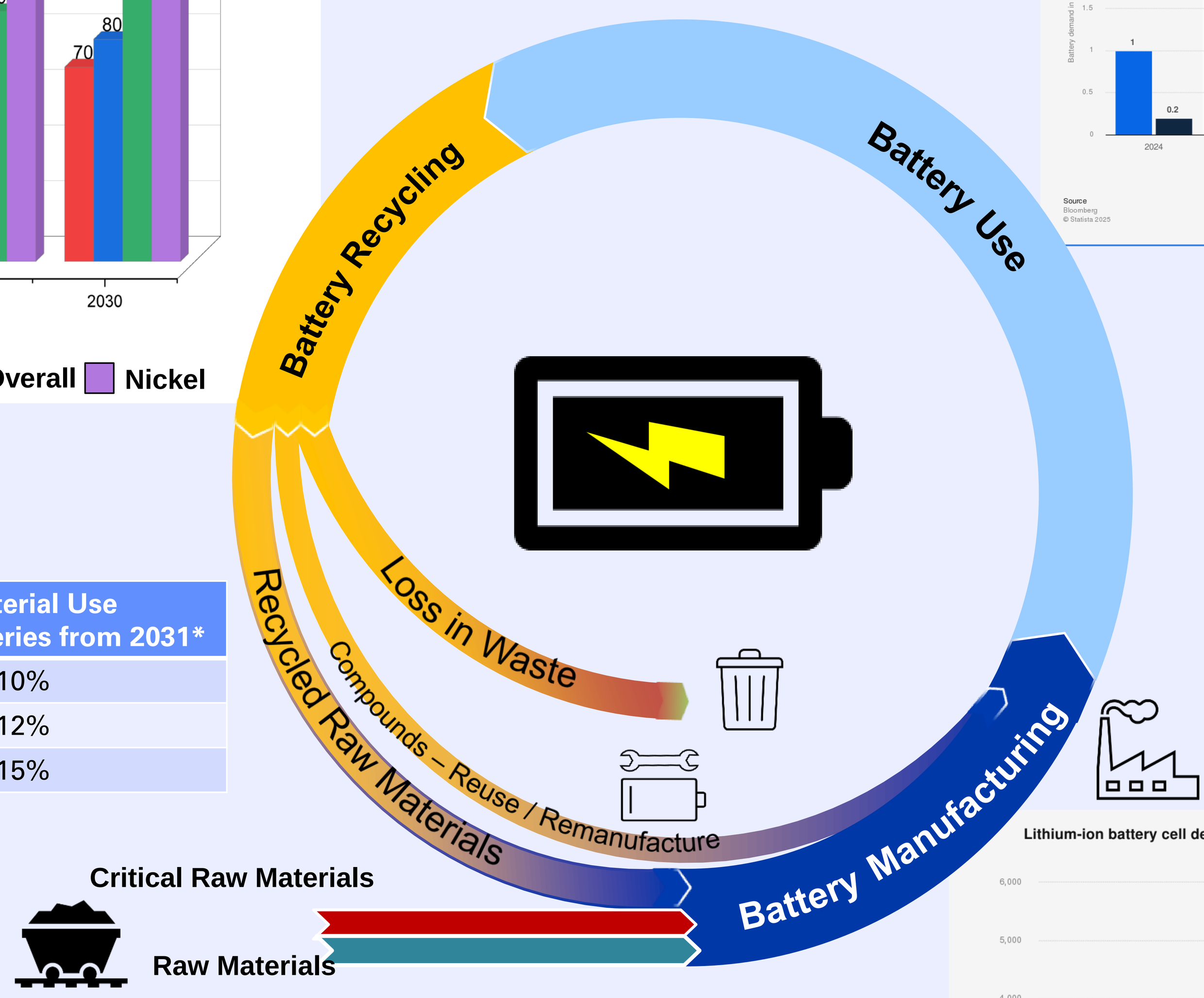
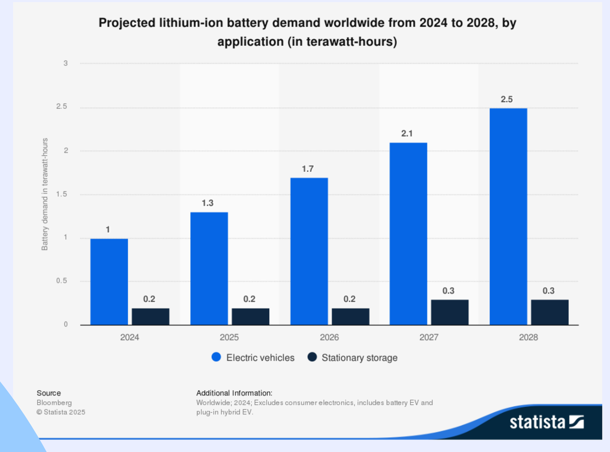
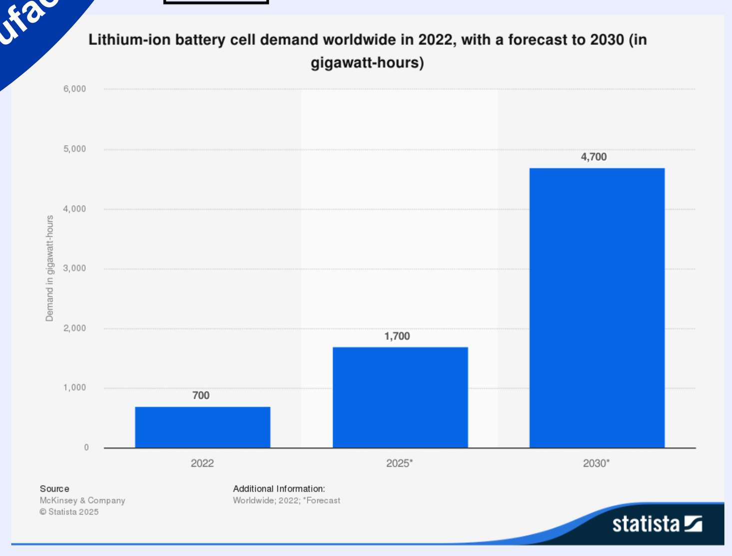
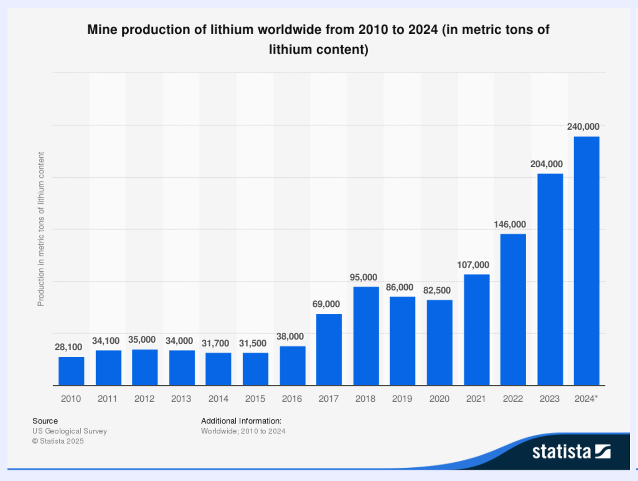
Background of Lithium-Ion Battery

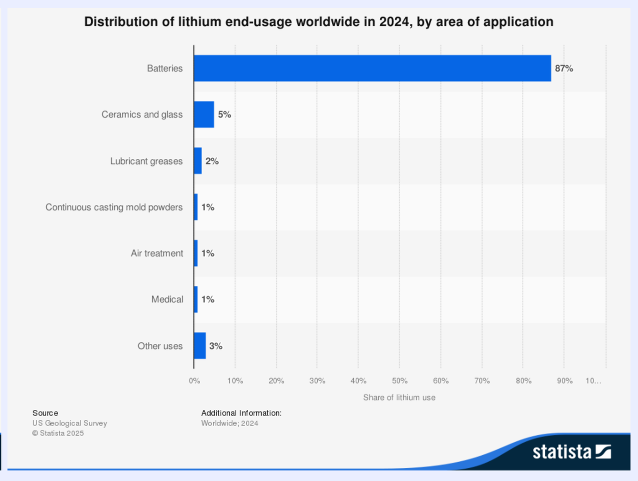












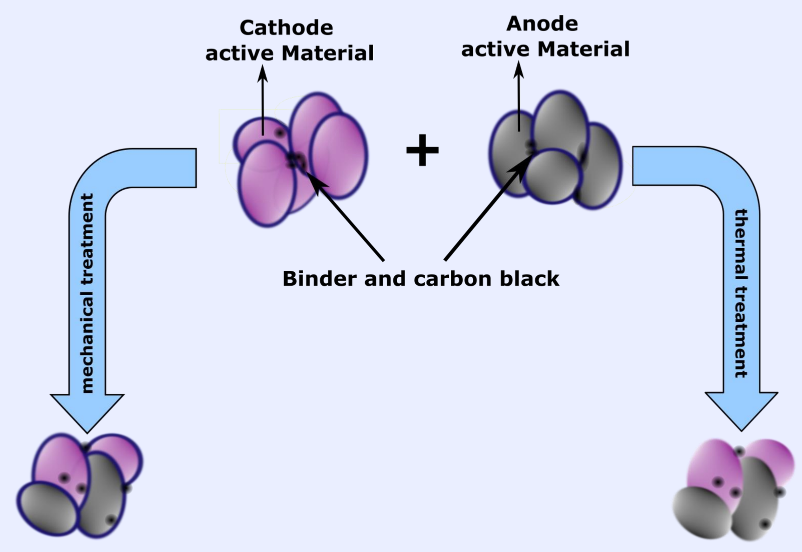
Element	Recycled Material Use for new batteries from 2031*
Lithium	Minimum of 10%
Cobalt	Minimum of 12%
Nickel	Minimum of 15%

Background of Pre-treatment

Pre-treatment is necessary to produce from end of life (EoL) batteries so called Black Mass (BM). Therefore several process steps are investigated. Not all of them are always used and the order is valuable.

- Dismantling
- Discharging
- Pyrolysis
- Shredding
- Sorting
- Sieving

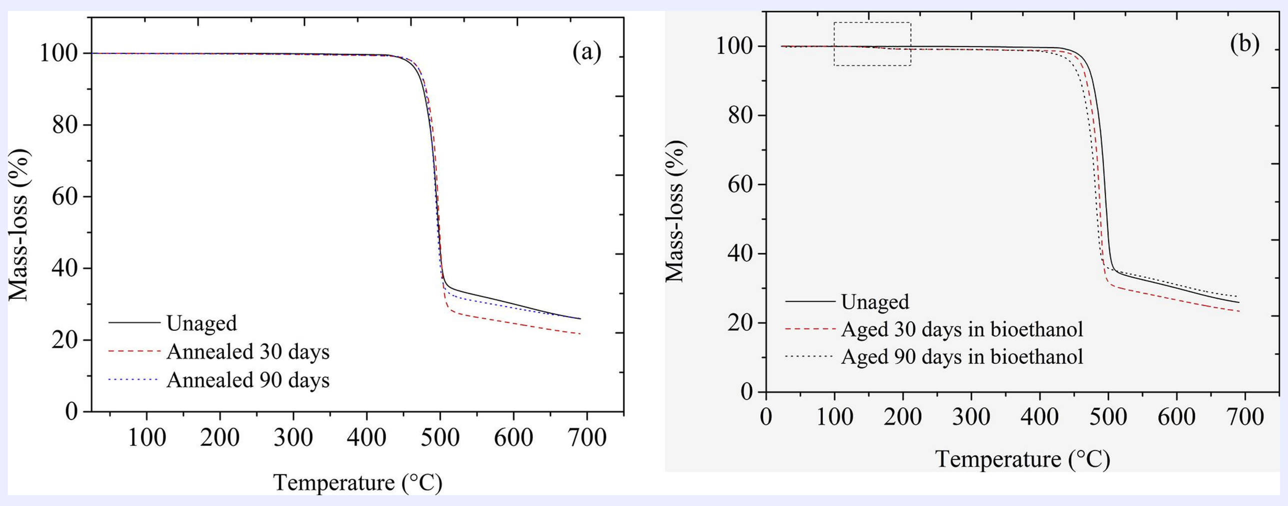
In the Pre-Treatment pyrolysis is the only process step, which influence significant the Binder of the Battery and additionally the chemistry structure of most cell chemistries like LCO or NMC batteries. A common binder is Polyvinylidene fluoride (PVDF).



Consequently to pyrolyze or not pyrolyze batteries has a huge impact for the following hydrometallurgy processes.

Stability of the Binder

Temperature stability of PVDF



TGA thermograms of annealed PVDF (a), and PVDF aged in bioethanol during experimental times of 30 and 90 days (b), at 20 °C min^{-1} heating rate, compared to unaged material.**

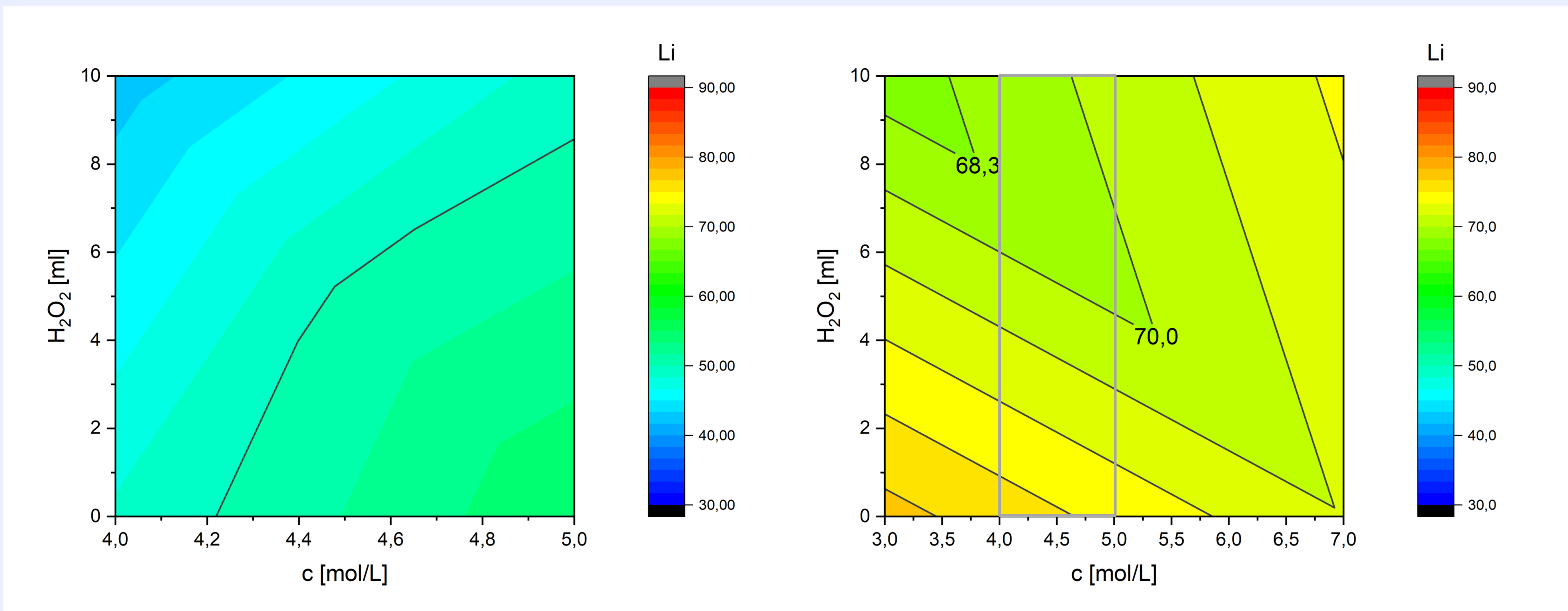
Chemical stability of PVDF

Chemical Compound	PVDF resistance
Citric Acid Aq.	Excellent
Hydrochloric Acid Aq.	Excellent
Hydrobromic Acid Aq.	Excellent
Hydrofluoric Acid Aq.	Excellent
Hydrogen Peroxide Aq.	Good
Sulphuric Acid Aq.	Good
Nitric Acid Aq.	Excellent
Anilin	Bad

Excellent | Good | Bad | Not Recommended ***

PVDF is created as a quite stable Polymer. Especially against inorganic chemicals like mineral acids. Additional aging effects not influence the stability significant. The combustion temperature is around 500 °C.

Acid Leaching Results



On the x axis is the acid concentration of formic acid, On the y axis the adding in ml of H_2O_2 in a total batch of 50 ml Volume. In The z axis as color code the leaching Efficiency of Lithium.

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Firstly the Design of Experiment study for the 811 NMC BM without thermal pre-treatment was performed. As a learning in the second study the acid concentration range was extended from 4-5 mol/L to 3-7 mol/L.
The highest leaching yield of Lithium without thermal pre-Treatment was achieved at 5 mol/L and no using of hydrogen peroxide was around 55 %.
The highest leaching yield of Lithium with thermal pre-Treatment was achieved at 3 mol/L and no using of hydrogen peroxide was around 77 %.

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The authors are responsible for the contents of this publication.

Federal Ministry for Economic Affairs and Climate Action
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