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Investigation for Recovery of Polymeric Materials from Spent Li-ion Batteries by Using Supercritical-CO_2

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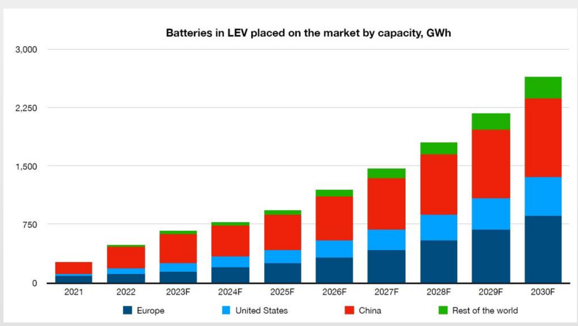
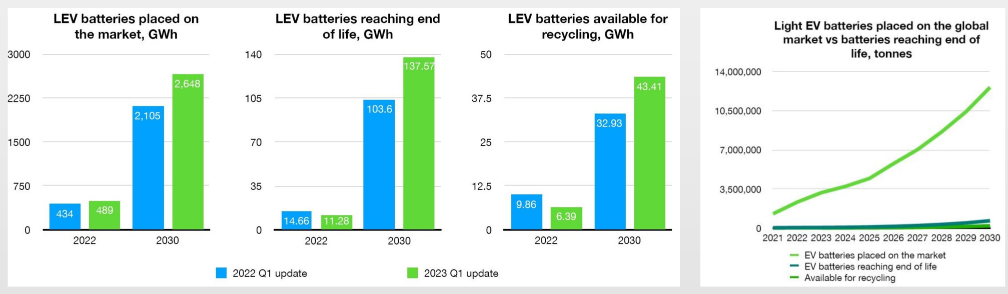
Abstract

Li-ion battery (LiB) production has been increased recently due to its energy storage properties. LiBs has been using for mobile applications such as phone, laptops and electrical vehicles due to its high energy density which gives higher energy storage capability per kg. Sooner or later, they will reach to their end-of-life and then will be considered as a waste. However, waste is what is left when imagination fails. Therefore, recycling should be done. Current recycling methods, hydrometallurgy and pyrometallurgy, are good to recover active materials and casing. However, those process methods sacrifice battery components such as electrolyte, separator and binder. Here novel method of supercritical CO_2 paves the way to recycle organic components of the spent LiB [1]. This study covers separation of PVDF from selected co-solvent mixture at room temperature and preliminary experiments in Sc-CO_2 system.

LiB Production and Future



Batteries in LEV placed on the market by capacity (GWh), estimation till 2030 [2].

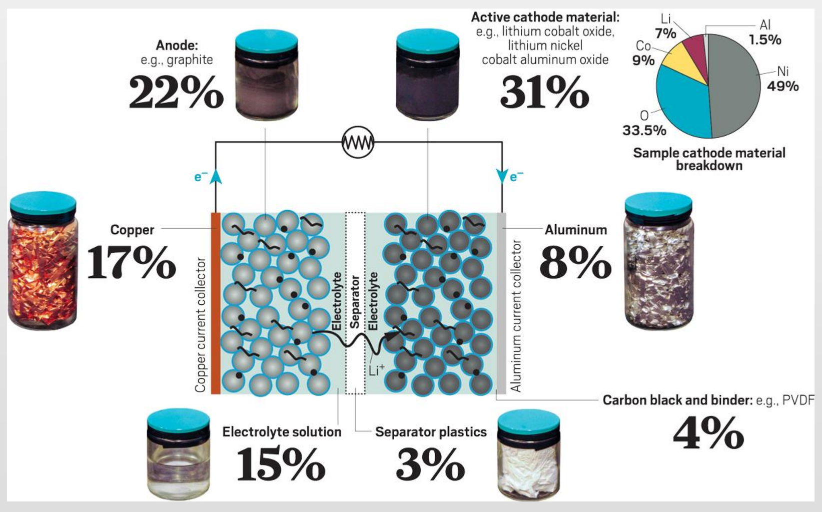


LEV batteries on the market, reaching end of life and available for recycling were showed in capacity (GWh) and in weight (tons) [2].

Year/GWh	Placed On Market	Reaching end-of-life	Available for Recycling
2022	489	11.28	6.39
2030 (forecast)	2648	137.57	43.41
Increasing rate	441%	1119%	579%

- Production of LEV batteries will be increased over 400%
- - 2648 GWh equals to 12.6M tons of battery
- Average life span of an EV battery is around 15-20 years
- Collection rate of spent batteries should be considered

Li-ion Battery



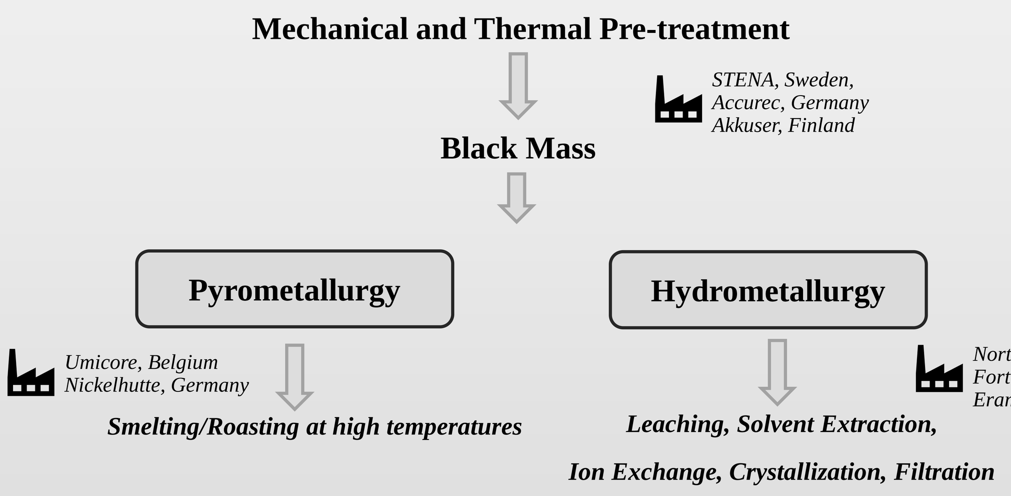
Typical composition of a battery cell. (Argonne National Laboratory)

- In 2030, 12.6M tons of cells will be produced
- Binder is having a portion around 3.85% of the battery pack[3].
- 0.48M tons binder will be needed to recycle

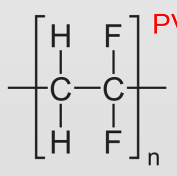
Weight of LEV produce in 2030 ≈ 34 Empire State Building of battery waste (wt.)

Weight of Binder in LEV in 2030 ≈ 3.5 Commerzbank Tower of binder waste (wt.)

Current LiB Recycling Methods



We can recover more than 80% of Electrodes and Casing



PVDF Monomer

- CO_2 Emission
- Fluorinated Compounds: HF

Sacrificed Matters in Spent Batteries

Electrolyte ~15%

Separator PE/PP ~3%

Binder (PVDF) ~3%

Supercritical Carbon Dioxide

Properties

- Non-dipolar solvent
- Weak Lewis acid and base interaction
- Adjustable with change in Pressure and Temperature

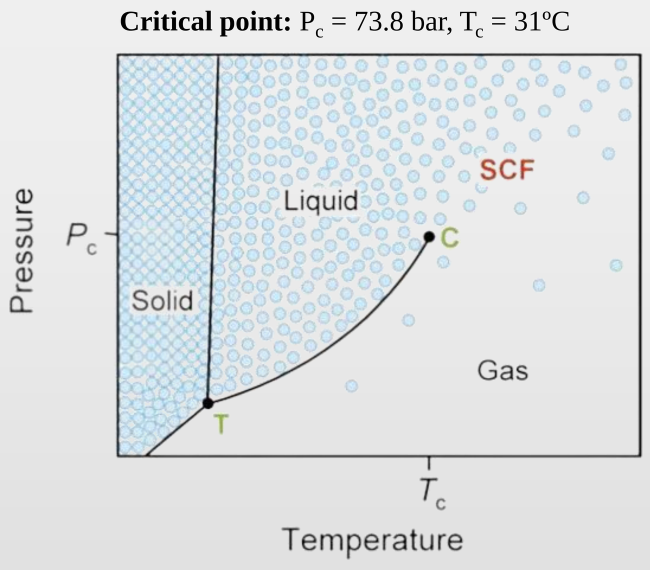
Advantages

- Environmentally friendly
- Non-toxic, non-flammable
- Low cost and reusable
- Readily available industry

Applications

- Caffeine removal
- Textile coloring
- Pharmaceutical applications
- De-binding of a green body (ceramic sintering)

Critical point: P_c = 73.8 bar, T_c = 31°C



Advantages (for spent LiBs)

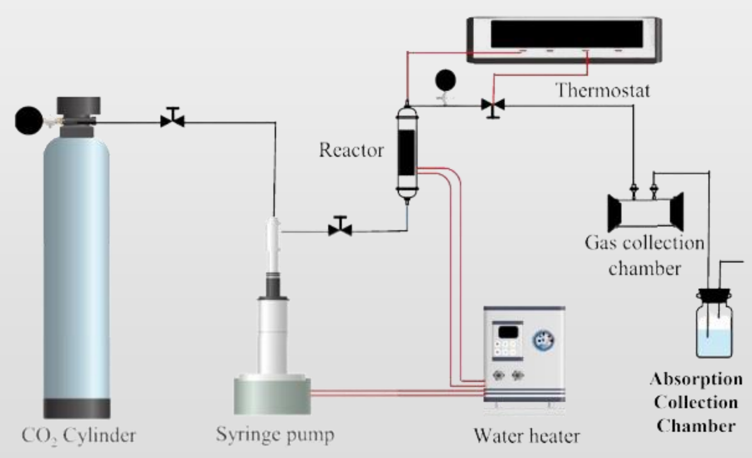
- ✓ Able to recover Polymeric Materials without burning [1]
- ✓ Prevents toxic gas releases

Process Development

Dissolved/Separated PVDF from **Black Mass** should be transferred to the collection chamber

Collected PVDF within the solution should be separated & purified

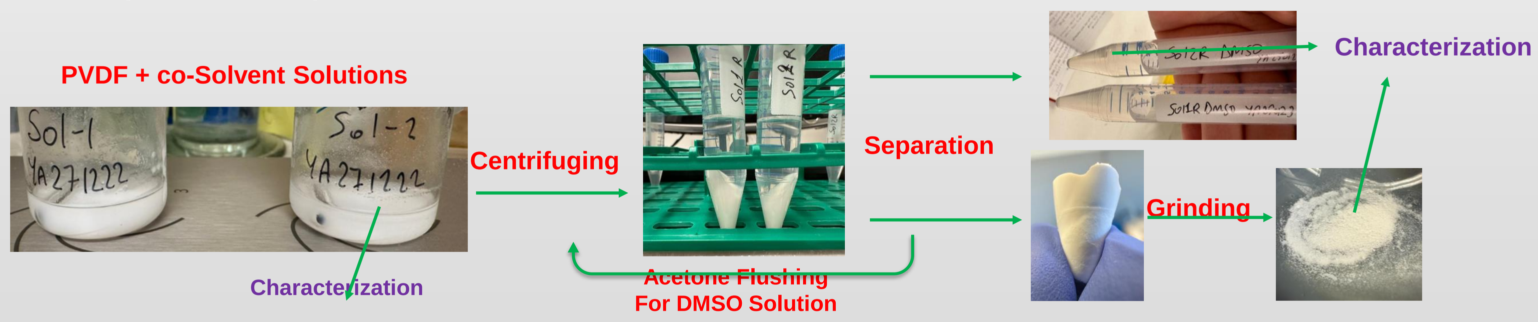
That's why we need a co-solvent as carrying agent



Selection of Co-solvent

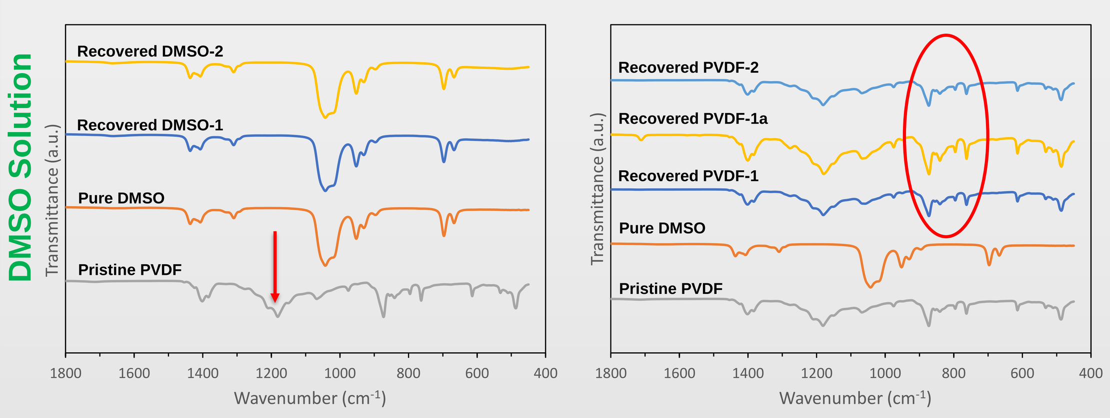
- NMP is dissolving PVDF but not environmentally friendly
- Alternatively, DMSO, ethyl acetate and acetone were selected as a co-solvent

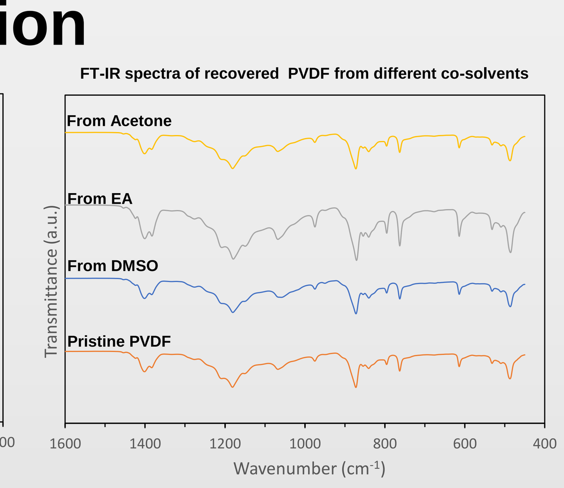
Process Flow Chart

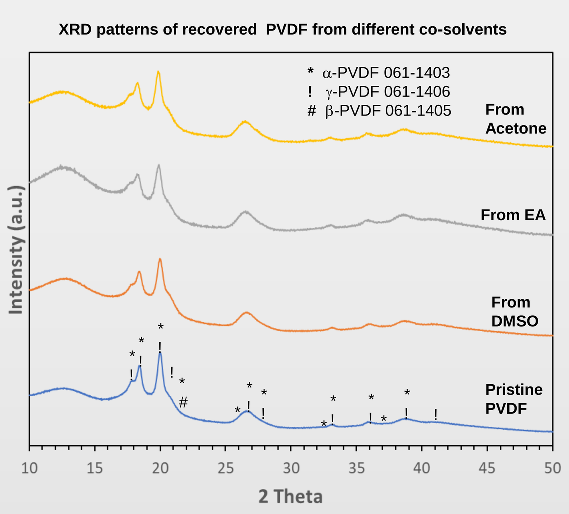


Room Temperature PVDF Separation

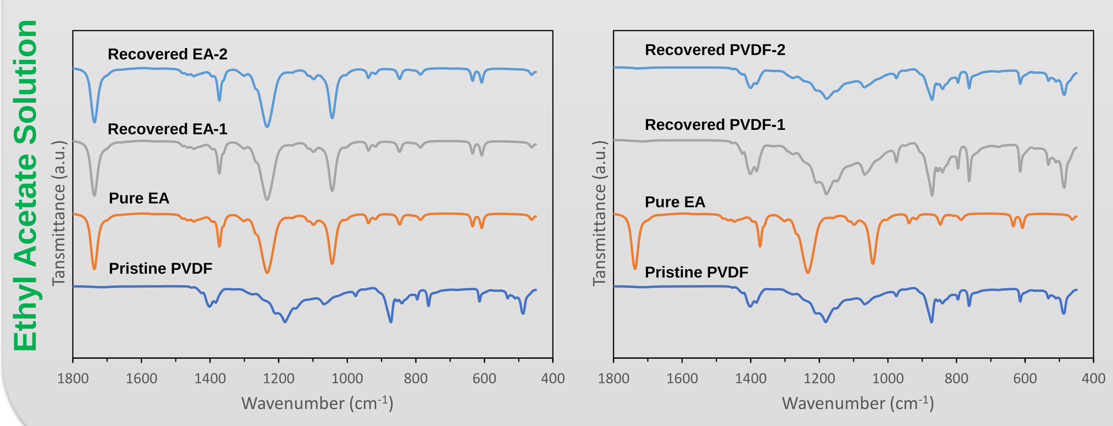
DMSO Solution







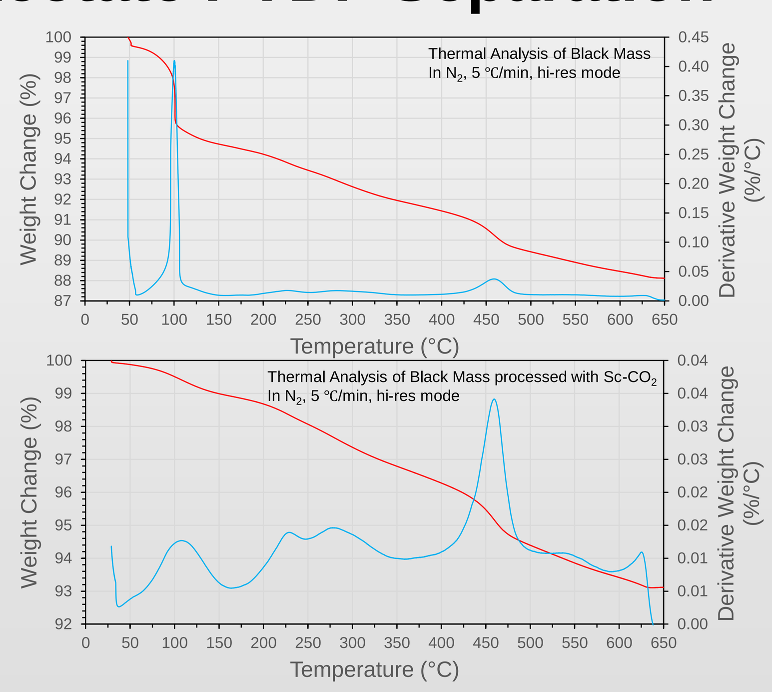
Ethyl Acetate Solution



- PVDF is partially dissolving in DMSO, EA and Acetone at R.T.
- Co-solvent and PVDF were successfully separated at R.T. by using centrifuge
- Over 91% of the initial DMSO and 94% of initial PVDF were recollected
- Around 35-45% of the initial EA and over 80% of initial PVDF were recollected
- Recollected PVDFs are still in same crystal structure (α and γ)
- Black mass processed with Sc-CO_2 and co-solvent (ethyl acetate) still has PVDF
- However, 80% of the electrolyte can be removed
- DMSO will be studied for further PVDF recovery

Sc-CO_2 and Ethyl Acetate PVDF Separation

	Temp. Range (°C)	Black Mass (wt. %)	BM processed with Sc-CO_2 and Ethyl Acetate (wt. %)	Removal Yield (%)
Electrolyte and Water	RT-150	5.73	1.006	82
Salts, Separator, CMC	150-375	3.18	2.449	23
PVDF	375-510	2.36	2.259	4
Total	RT-700	14.71	9.257	37



References

[1] Y., Fu et al. *Resources, Conservation and Recycling*, **2021**, *172*, 105666.

[2] Hans Eric Melin, **2023**, Update on end-of-life battery volumes from light electric vehicles with forecast to 2030, Circular Energy Storage, Research and Consulting

[3] L. Gaines et al., **2011**. Life-cycle Analysis of Production and Recycling of Lithium-Ion Batteries, Transportation Research Record, 2252(1), 57–65.

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