Advancement in Spent LiB Processing

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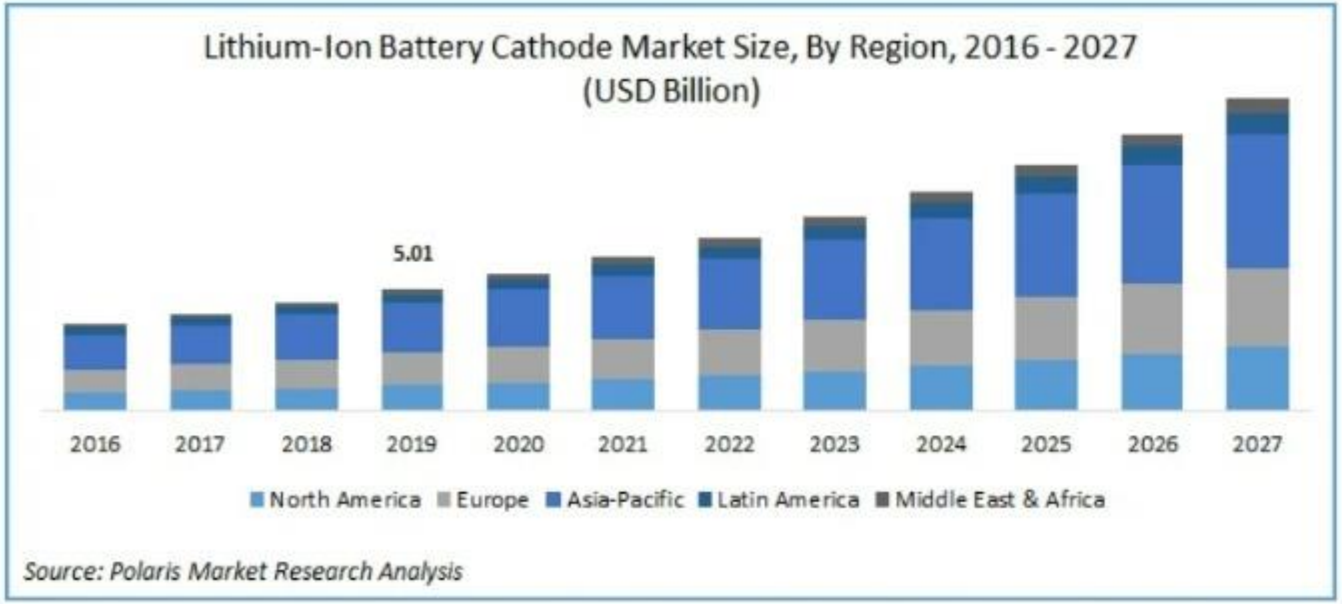
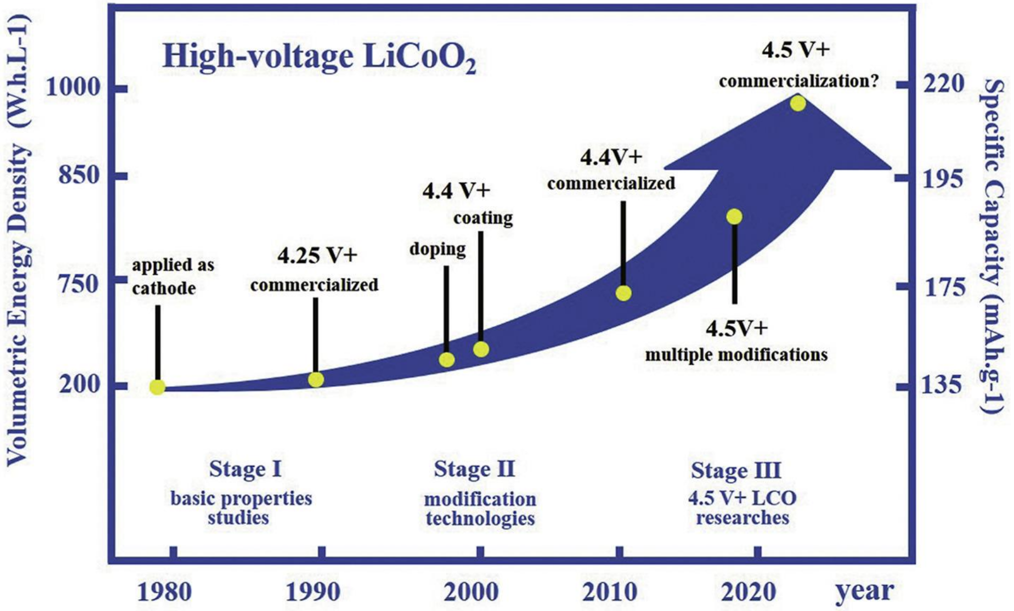
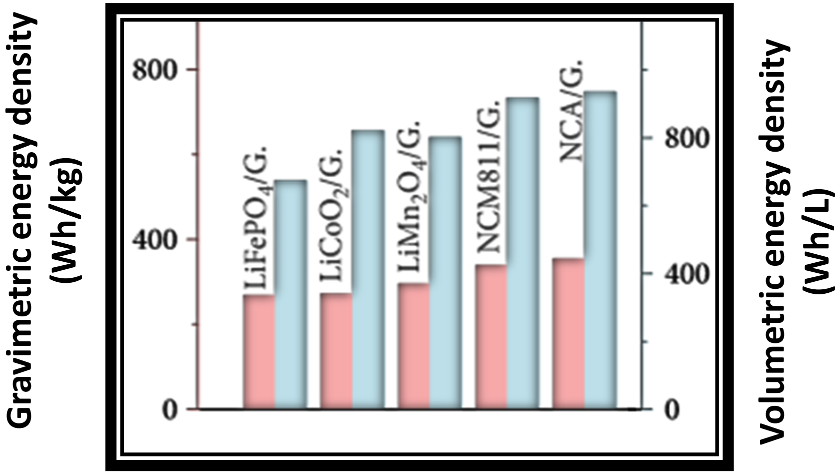
Li-ion Battery Technology Advancement



Estimated market size of LIB cathode material 2016-2027



Development roadmap of cutoff voltage of LCO-graphite full cells (j.jpowsour.2020.228062)



Gravimetric and Volumetric energy densities of common rechargeable LiBs

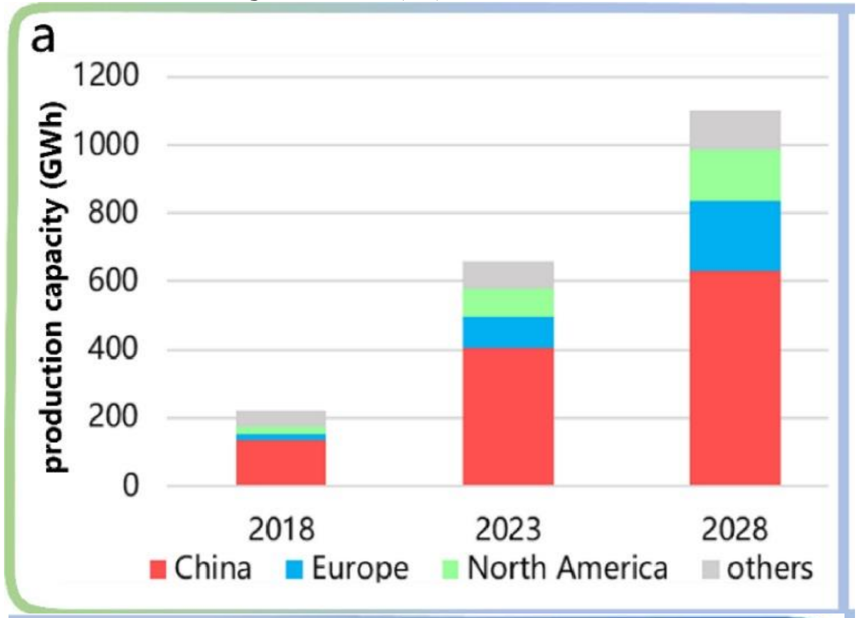
EVs require higher volumetric energy density due to space constraint

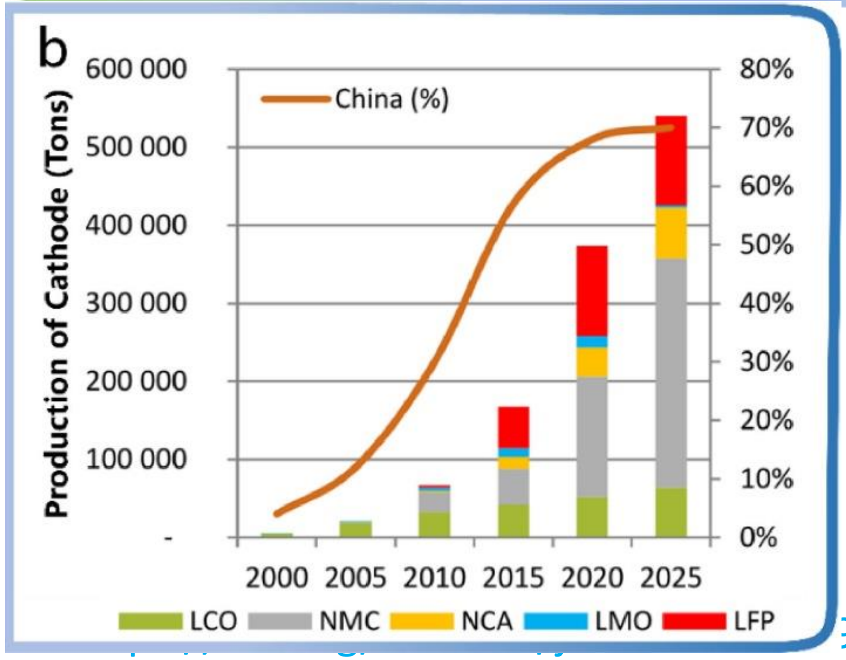
LCO LIBs

- ✓ Easy procession
- ✓ High volumetric energy density
- ✓ High operation potential

Increasing cost-effectiveness and stability with doping, surface coating

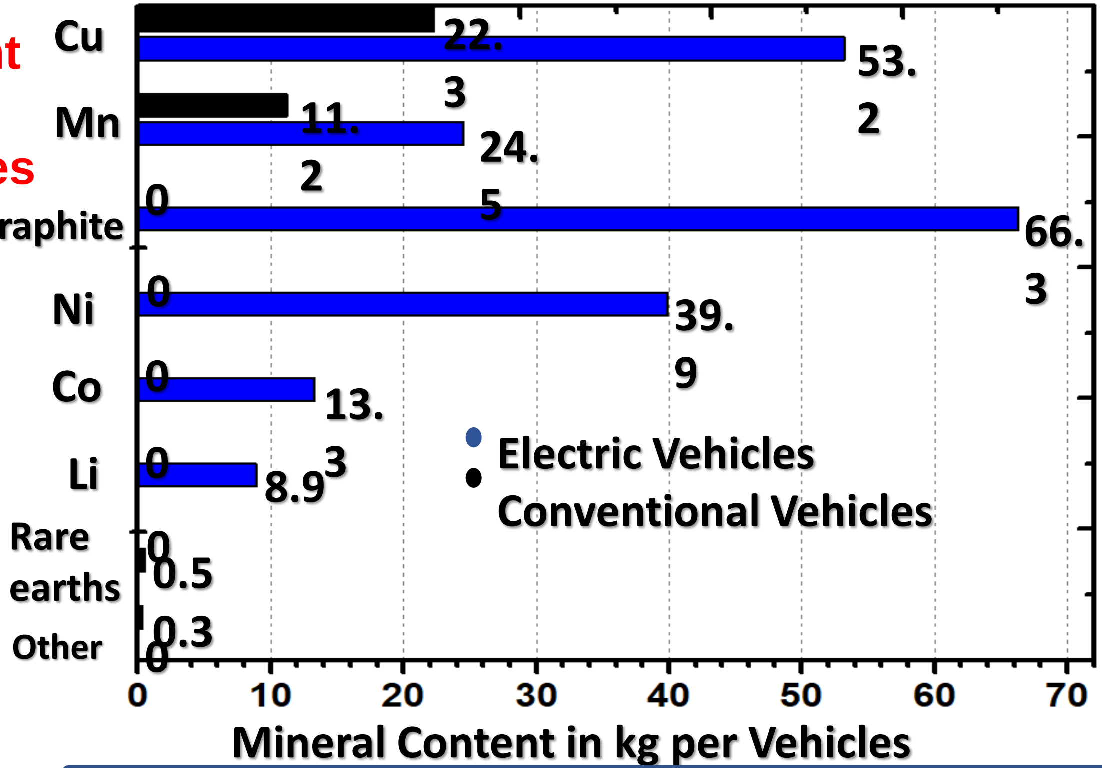
Production capacity growth for (a) Lithium-ion battery and (b) Cathode materials

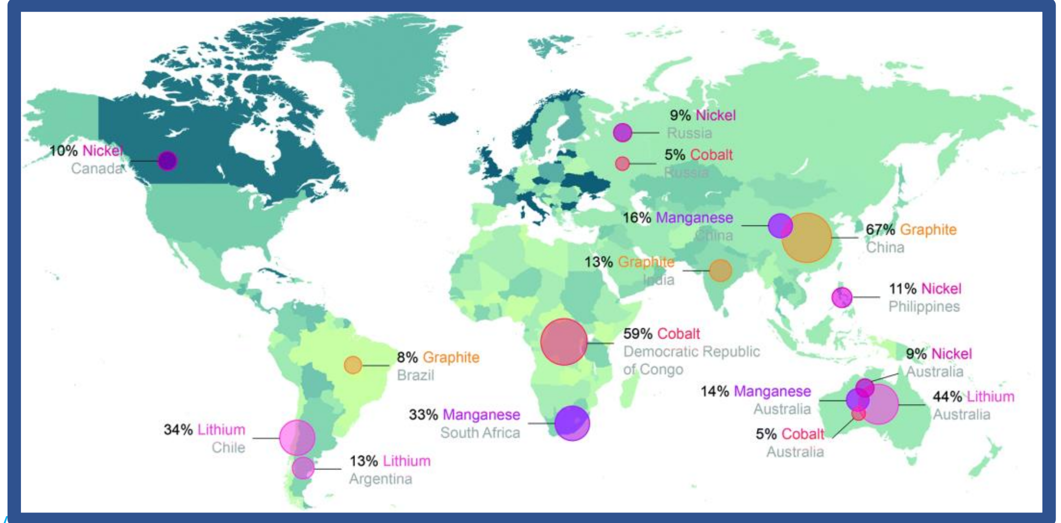




Global production of main LIB materials

Mineral content of battery electric vehicles compared to conventional vehicles as of 2022, by type



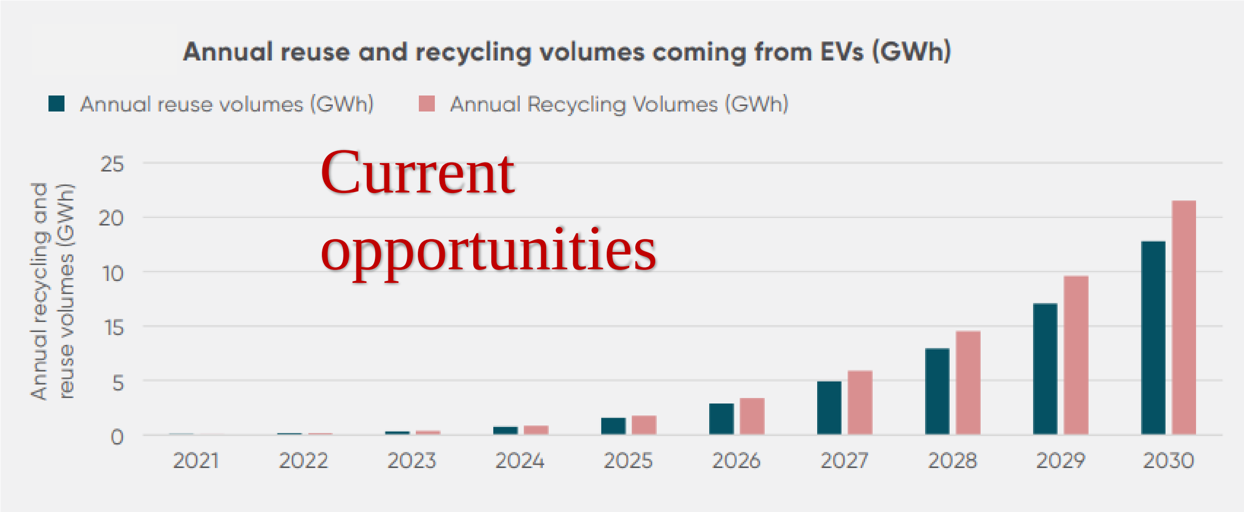


9.029

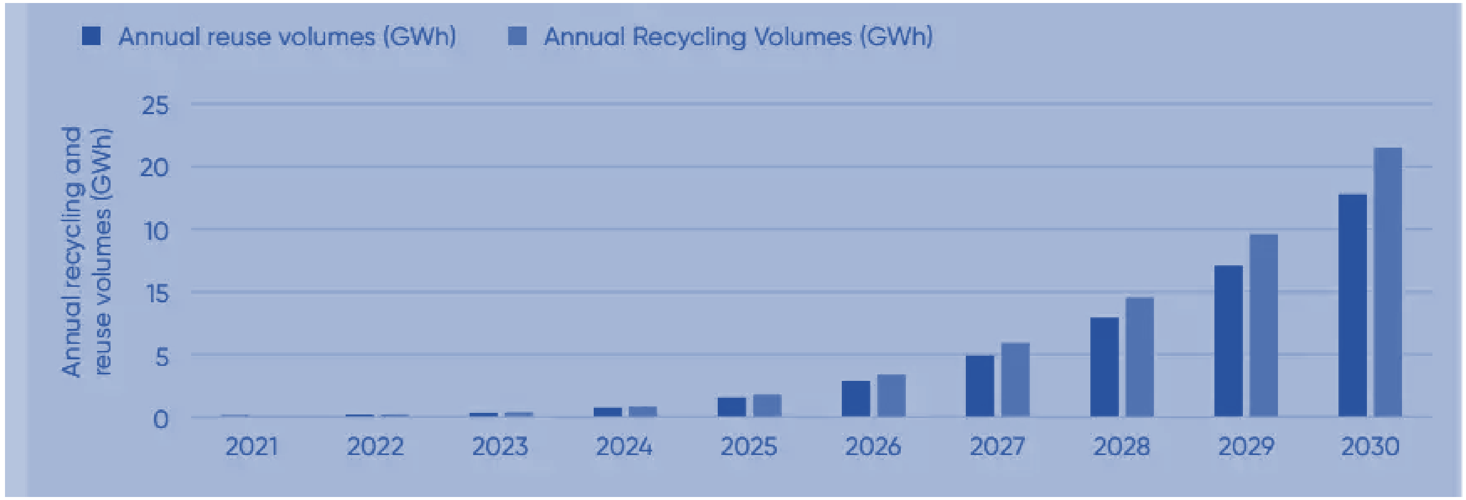
https://www.statista.com/statistics/1315835/mineral-content-of-ev-versus-conventional-vehicles-by-mineral-type/

Why Recycling?

- 0.5 million ton of spent LIB repository in 2020 is expected to reach 3.5 million tons by 2030
- Scenario of Li and Co reserves: In India, Co - 44.91 M tonnes of cobalt ore and Li – 30k tonnes of lithium ore (16 M tonnes worldwide)
- Spent LIB can explode or catch fire in landfill if they are damaged or become over-heated



Annual reuse and recycling volume come from EV: Indian Scenario



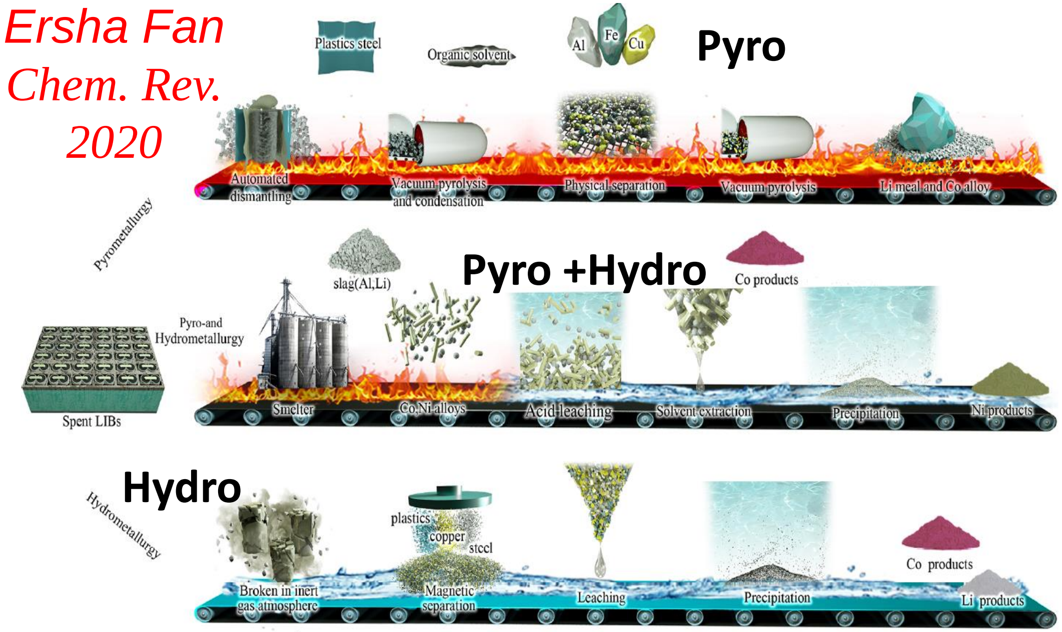
600GWh across all the segments of battery energy storage. Around 63% of this investment portfolio would be covered by the electric mobility segment, followed by grid applications (22%), BTM applications (07%) and CEAs (08%).

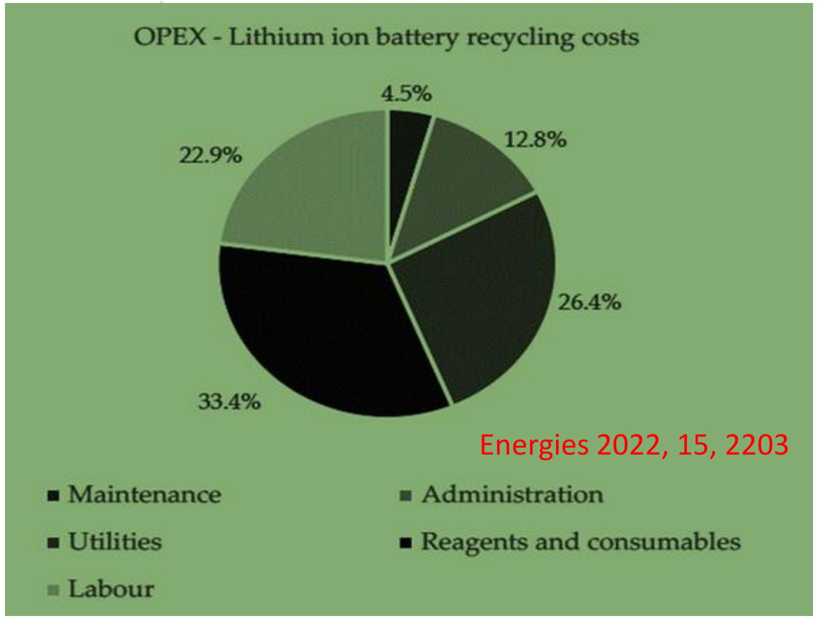
https://www.aftermarketnews.com/why-oems-are-investing-in-lithium-ion-battery-recycling/

Methods of Recycling and Economics

Flow chart of industrial LIB recycling process

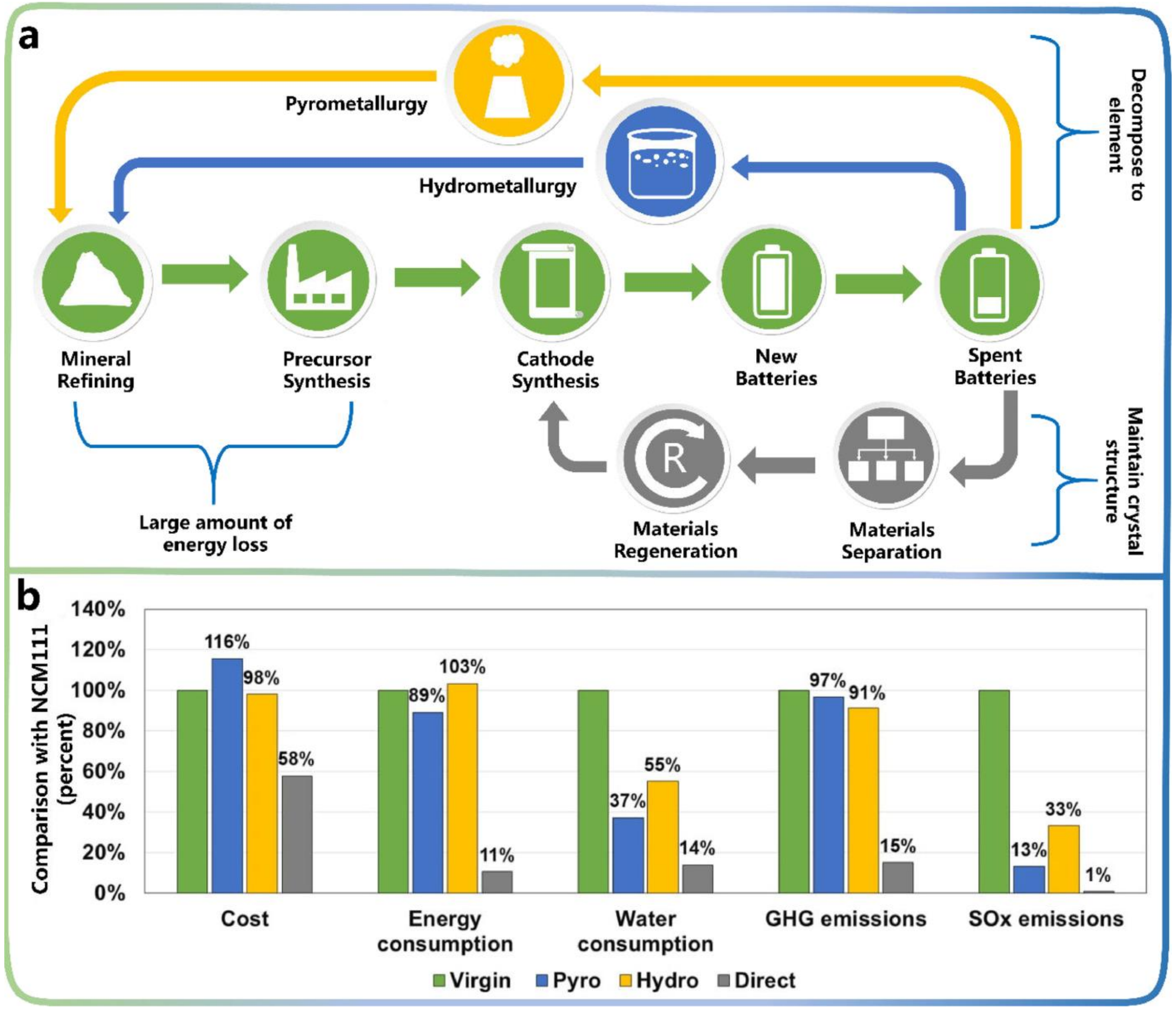
Ersha Fan
Chem. Rev. 2020





Energies 2022, 15, 2203

https://doi.org/10.1016/j.ensm.2022.09.029

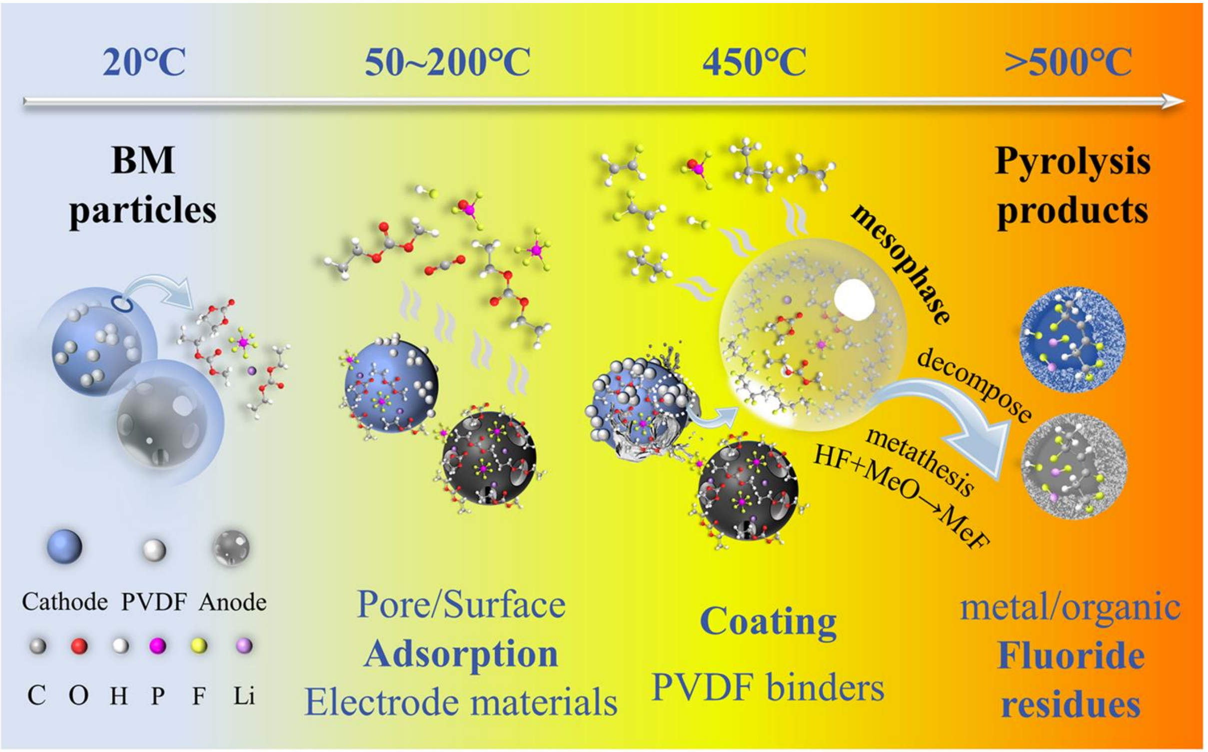


Resynthesized cathode materials

Re-synthesized cathode material	Method	Energy density (Wh kg^{-1})	Ref
$LiNi_{0.5}Co_{0.5}O_2$	ammonia leaching, co-precipitation	539.46	Li et al. (2020)
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	co-extraction, co-precipitation	555.00	Yang et al. (2017)
Al-doped $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	D, L-malic acid and H_2O_2 leaching, sol-gel	602.73	Zhang et al. (2020)
$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$	homogeneous thermochemical process	592.00	Deng et al. (2020)
$LiCoO_2$	molten-salt-electrolysis, sintering	646.00	Zhang et al. (2019)
$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$	supplementing metal ions, granulation, ion doping and heat treatment	703.26	Fan et al. (2021)
$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$	ammonia leaching, sol-gel	924.38	Li et al (2022)

Strategy provides inspiration for effective recovery of complex spent lithium-ion batteries, which can selectively separate the multiple metal with high-efficient reutilization

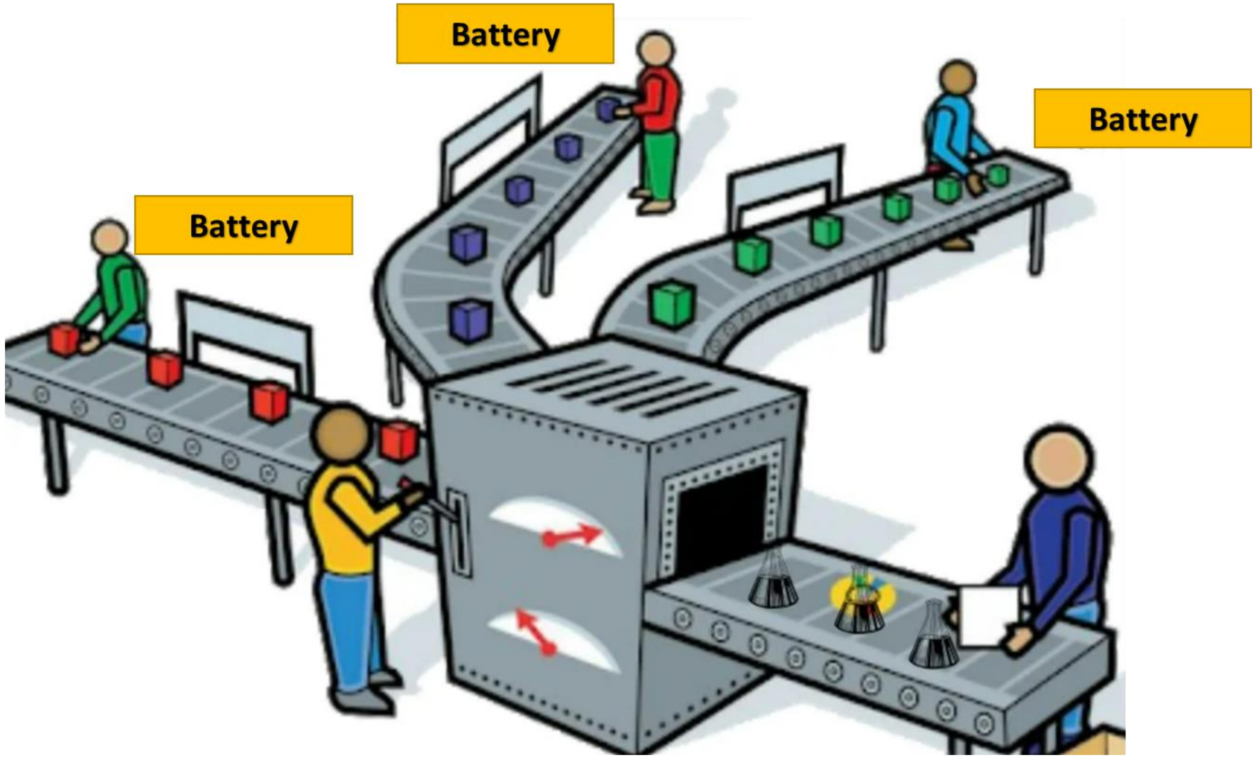
Fluoride containing residue in Cathode materials



Journal of Hazardous Materials 435 (2022) 128974

The migration of fluorine element during the pyrolysis of black mass from spent LIBs. The adsorption and the wrapping effect result in the residue of fluorine-containing pollutants

Industrial approach of recycling LIB



https://www.slideshare.net/ApekshaPatil23/lithium-ion-battery-recycling-market

Key Players

- Umicore
- GEM
- Brunp Recycling
- SangEel HiTech
- Taisen Recycling
- Batrec
- 4R Energy Corp

Recycling industries in INDIA

- ACE Green Recycling Inc
- Lohum Cleantech
- Gravita India Ltd
- Ziptrax Cleantech
- Attero Recycling

Global LIB recycling market segmentation

By Product type
$LiCoO_2$ Battery
NMC Battery
$LiFePO_4$ Battery

End Application
Automative
Marine
Industrial

IMMT Recycling Segmentation

By Product type
$LiCoO_2$
Li3AlF6
$LiFePO_4$
NMC
Ni-Co-O
Ni-Co-OX

End Application
Ceramics
Electrocatalytic application
Energy storage (Sup cap, Battery)

Recovery of material from spent LIB

Objective: To regenerate cathode material

Achieved- TRL 3-4

- ❑ Battery material development from spent cathode
- ❑ Activated cathode: NCM, NCA type cathode materials successfully produced

Objective: Recovery of lithium compound from spent LiB

Achieved- TRL 4-5

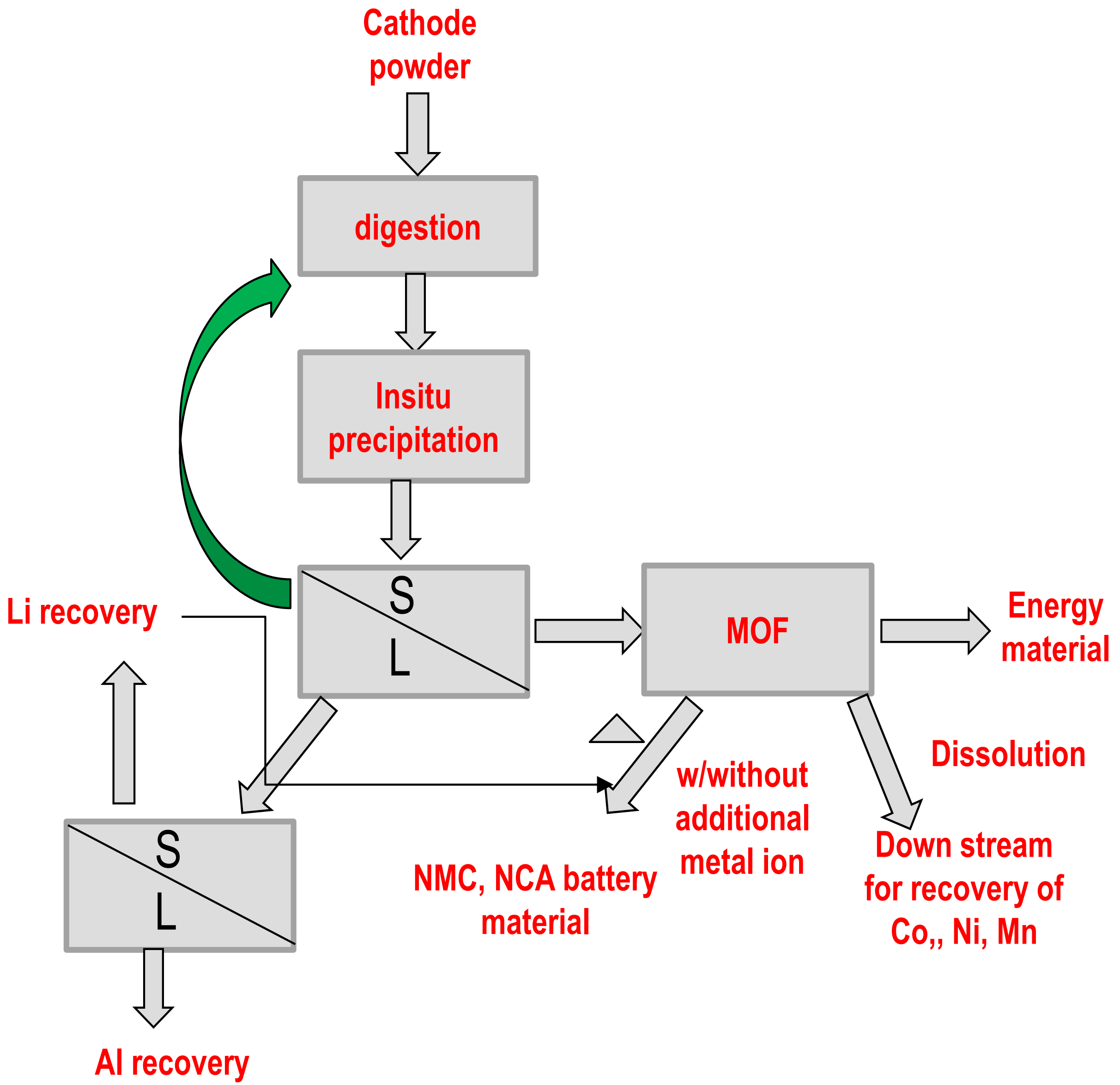
- ❖ Bench scale completed for processing of 1 kg of spent material having ~ 5% Li
- ❖ Li & Al- enriched solution is generated
- ❖ Li separated from solution as Li_2CO_3

Objective: Recovery of graphite from spent LiB anode

Achieved- TRL 4-5

- ➢ Bench scale completed for processing of 1 kg of spent material having ~ 0.99% Li
- ➢ Regenerated graphite tested for half cell showing discharge capacity of 320 mA h g^{-1}

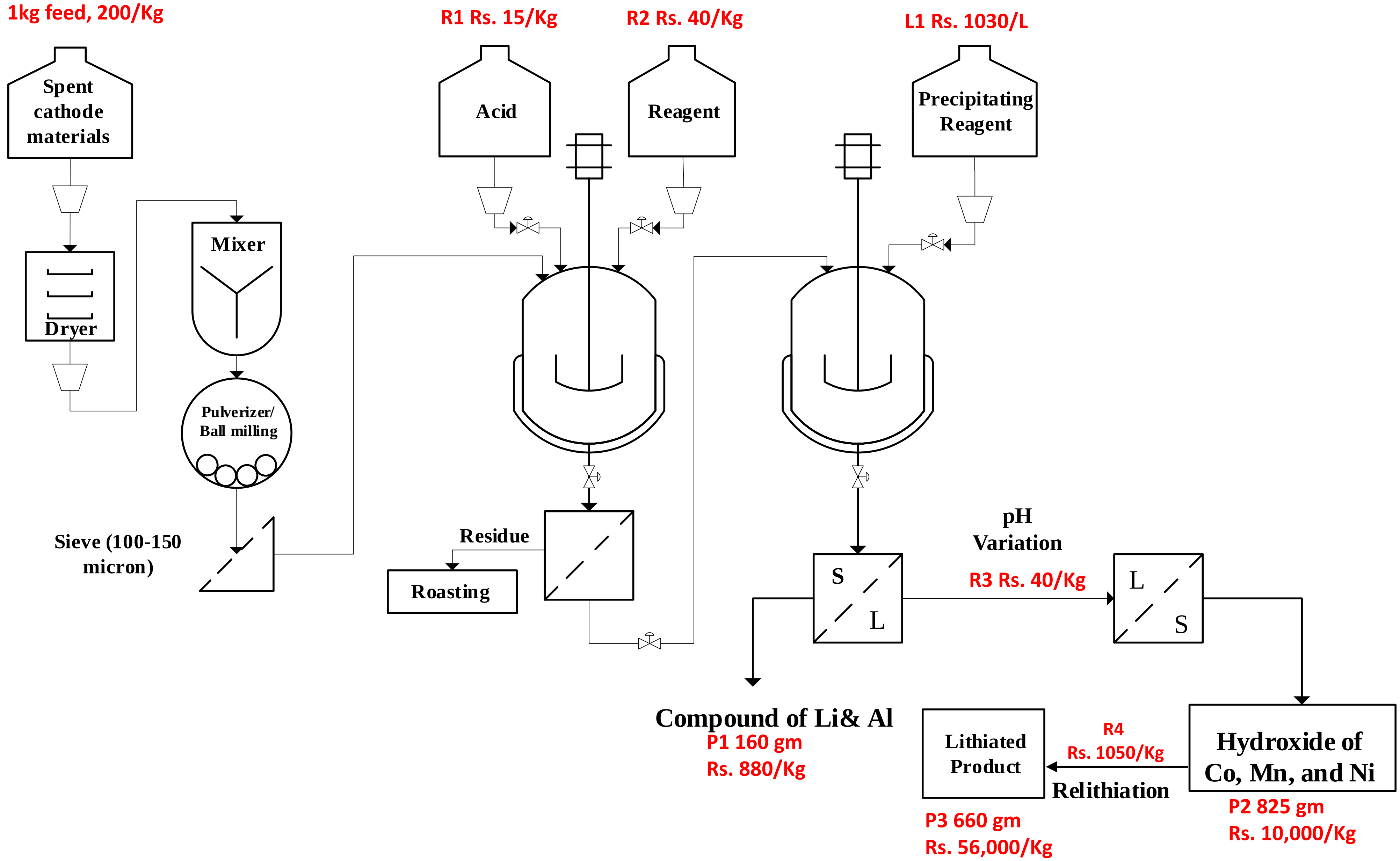
Integrated approach for fast dissolution, in-situ precipitation and selective separation (FADIPSS) Flowsheet 1



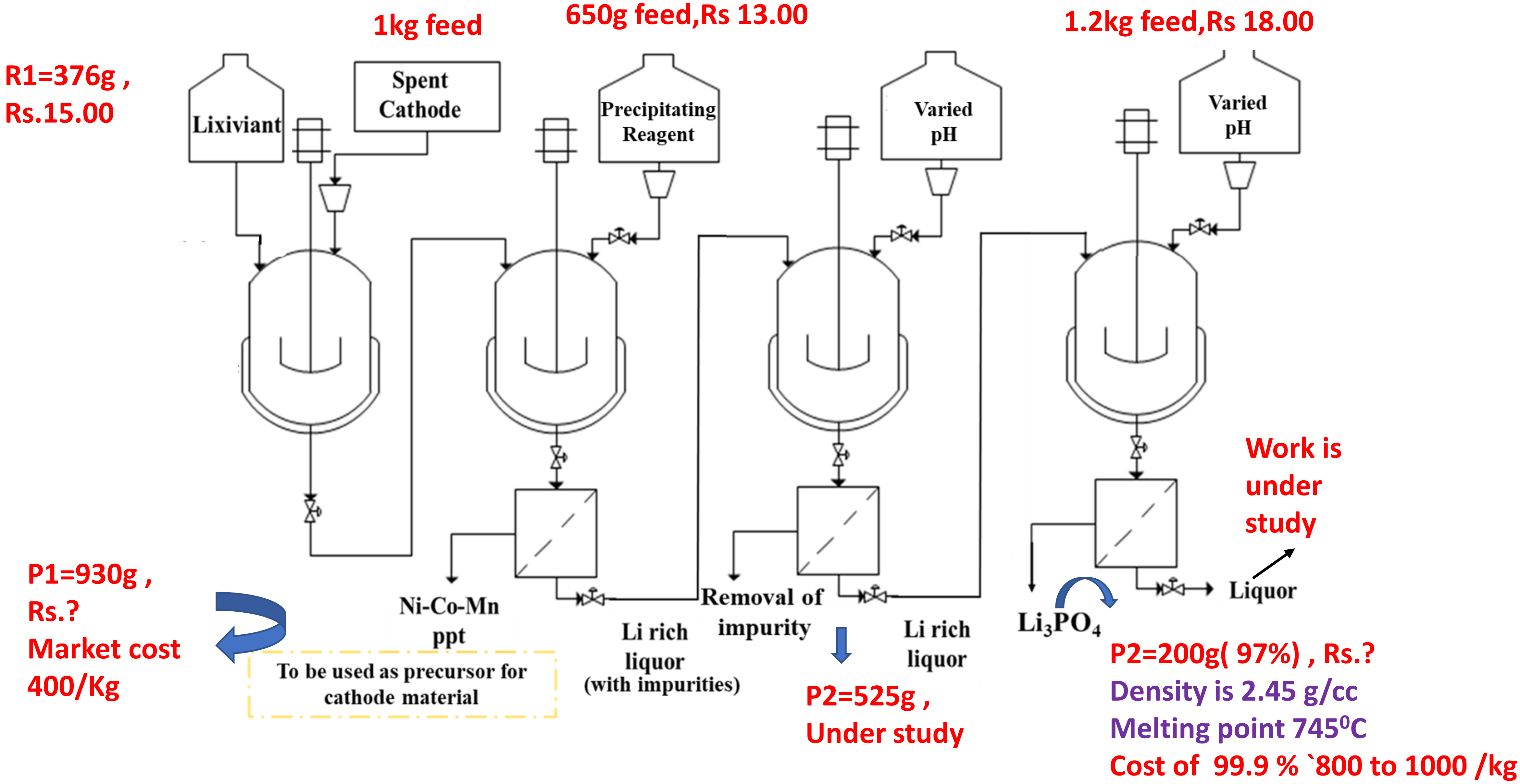
Advantages of the process

- Green route
- Pulp density 100g/L (tested upto 500 g scale)
- One step separation of Li and Al from Transition metals
- Recovery of reagent
- Zero effluent

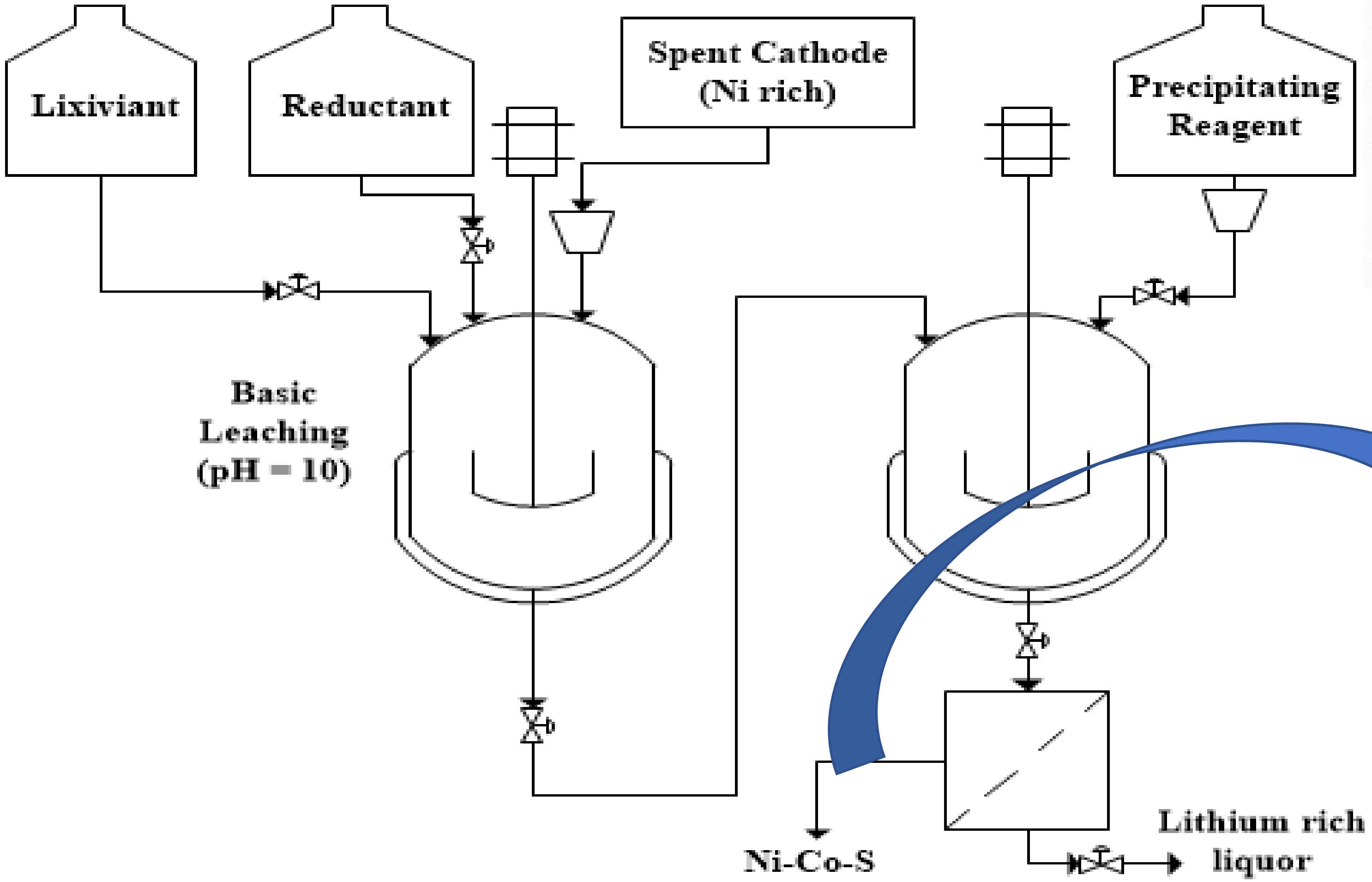
Process flow Sheet 2: Mixed Acid route - Fluoride, Li, Co, Ni recovery

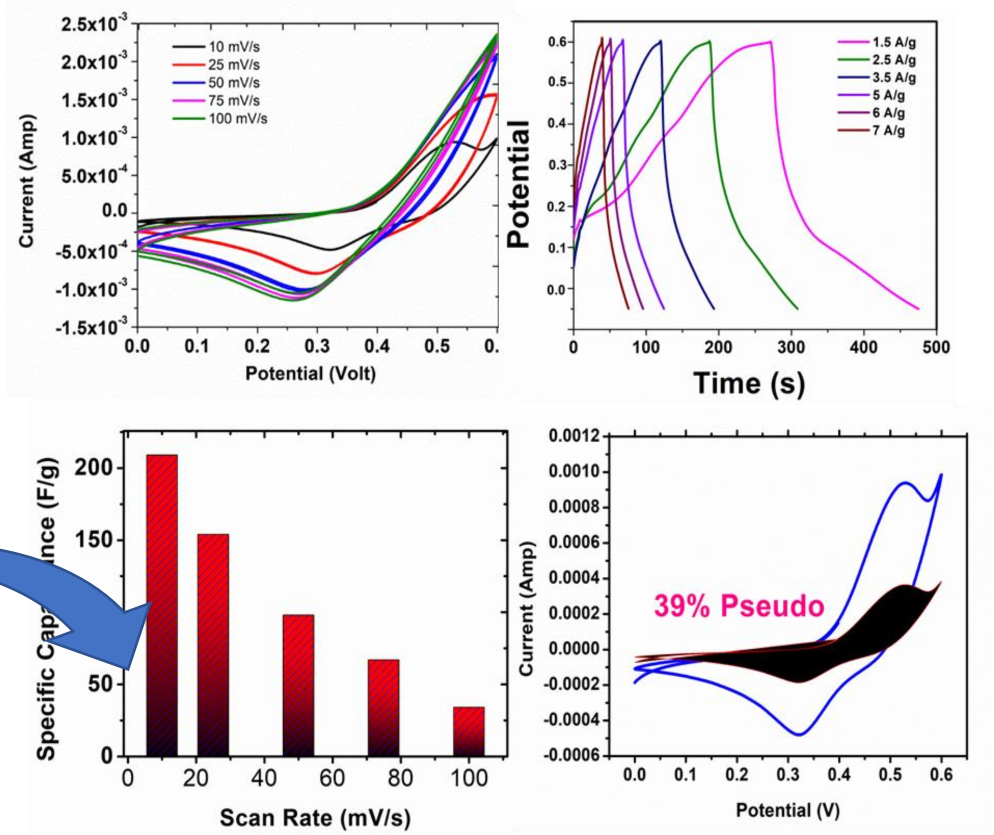


Process flow Sheet 3: Recovery of phosphate and oxide based material



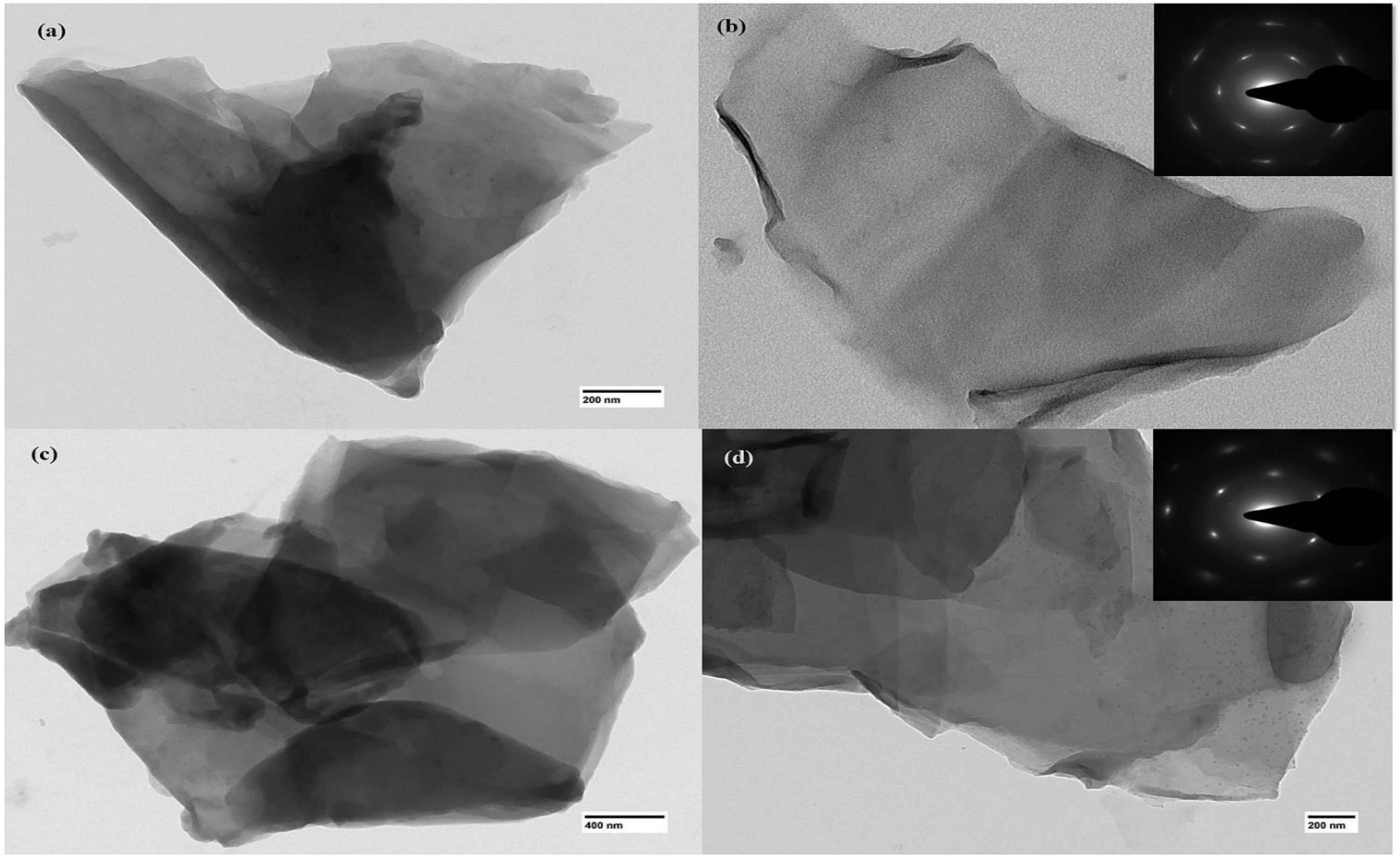
Process Flowsheet 4: through alkali route, recovery of sulphide material





- ❖ Base leaching
- ❖ Selective separation of transition metals
- ✓ Good electrical conductivity
- ✓ High specific capacity
- ✓ High redox reaction
- ✓ Exposed active sites

Anode recycling



- ❑ Existence of disordered carbon from lattice pattern as well as less sharp and less intense six single diffraction spots. Thus, confirms the carbon atoms are arranged in hexagonal pattern and typical arrangement for graphene material.
- ❑ Noteworthy, thinner layered graphene sheet texture is obviously seen in the form of higher transparency with excellent smooth and homogenous nature.

1. **P. Perumal,** et al **Journal of Environmental Chemical Engineering**, 9 (2021) 106455
2. **P. Perumal,** et al **Journal of Energy Storage,** 52 (2022) 104989
3. **P. Perumal,** et al **Journal of Physics: Energy,** 4, (2022) 45003

Conclusions

- Spent LIB Processing
- Re-use of Co, Li, Cu, Al, Ni, Mn in new LIB
- Several alternate routes depending on economics and environmental friendly

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Thank You!!!

In a quest of greener solution..