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Challenges and Opportunities of Recycling Spent Lithium-ion Batteries

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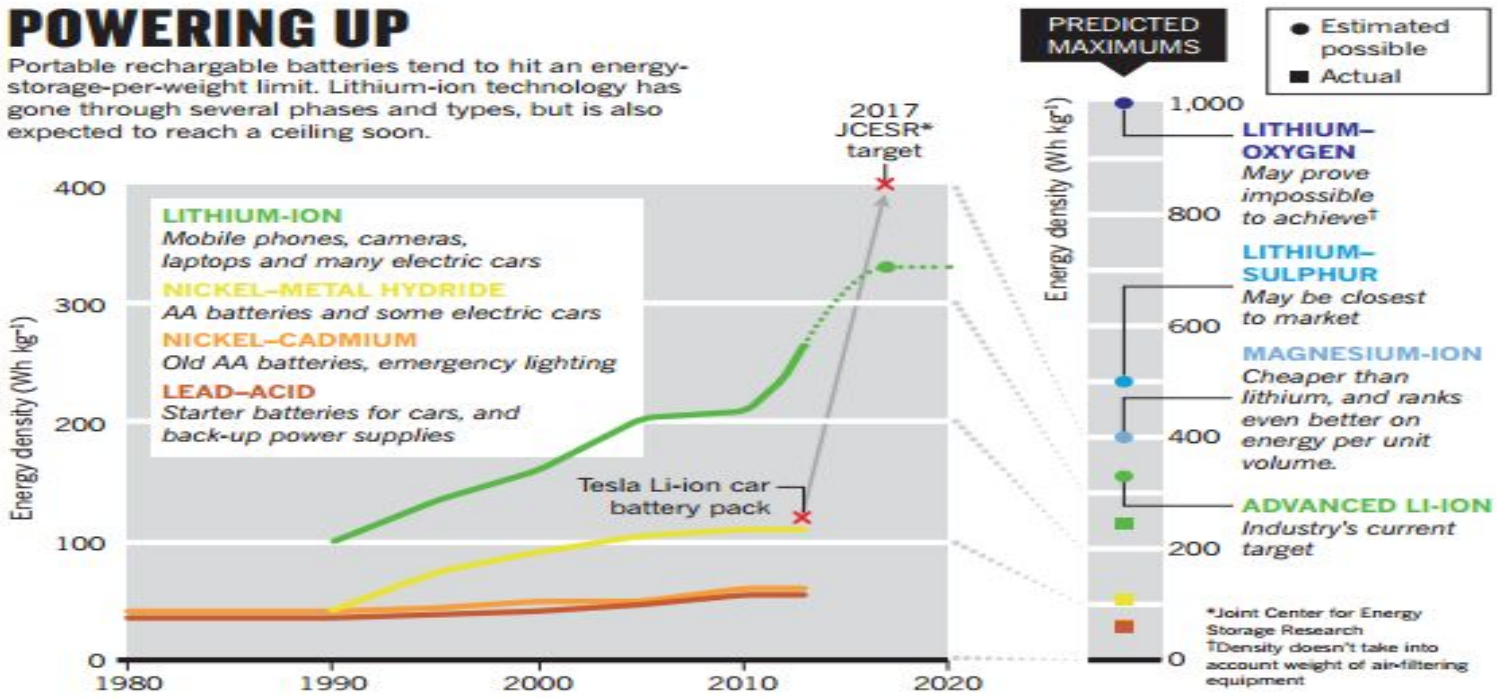
Outline

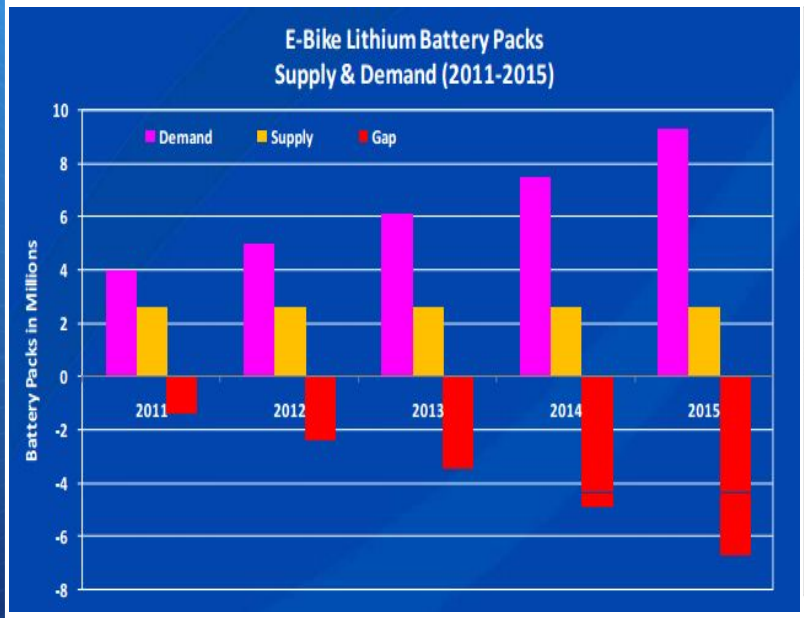
1. Background and recycling status of spent batteries
2. Challenges and Opportunities
3. Recycling technologies for spent LIBs
4. Conclusion

Background and recycling status of spent batteries



Source: Noorden, Nature 507(2014)

Background and Necessity



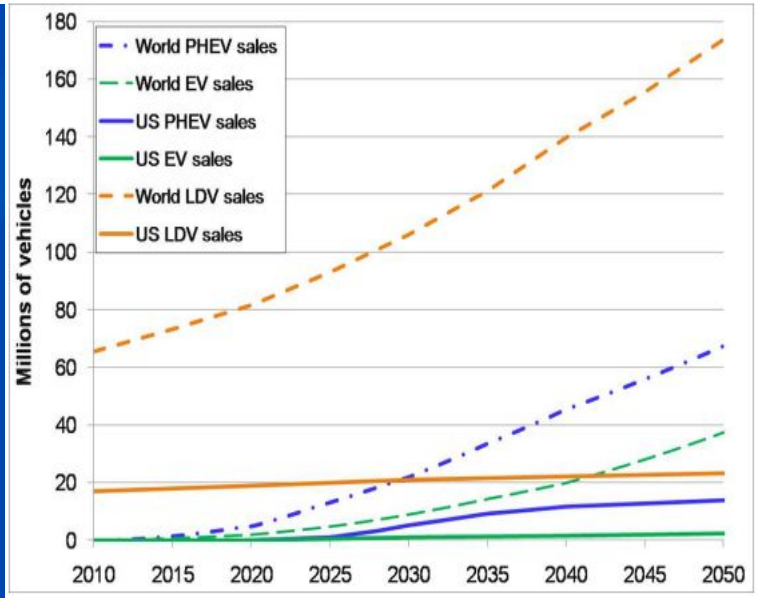


Fig. Light-Duty Vehicle Sales Projection to 2050. Source: Linda Gaines,http://www.transportation.anl.gov/pdfs/B/626.PDF

Source: Galaxy Resources

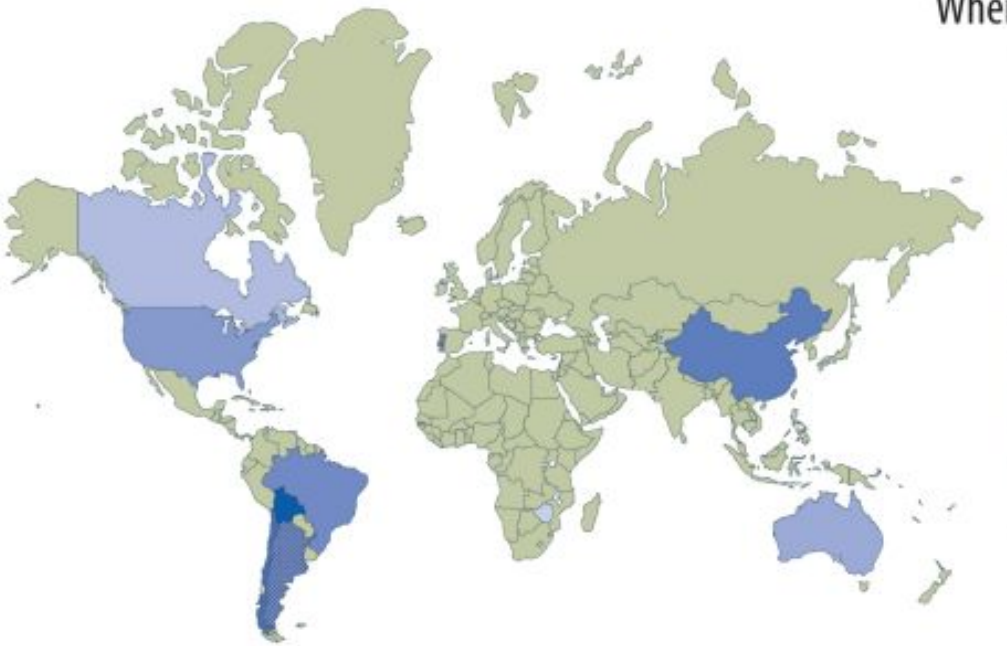
Background and recycling status of spent batteries

- According to a study done by Roland Berger Strategy Consultants, the global automotive LIB market is expected to reach more than 9 billion dollars by 2015 (Russo, 2012). LIBs in most consumer products have a lifespan of less than 3 years and those in hybrid and all-electric vehicles are projected to have a lifespan of roughly 10 years (Lain, 2001; Marano et al., 2009).

- Given these low lifespans as well as increasing production, a rapidly growing battery waste stream is likely. In the US, CA and N Y state legislators have attempted to proactively address this waste challenge by issuing state disposal bans on rechargeable batteries (Rechargeable Battery Recycling Act, 2006; New York Environmental Conservation Law, 2011).

Background and recycling status of spent batteries

- Reserve of valuable metals in Li-ion batteries(Li, Co, Ni);



Where is the Lithium?

Country	Reserve Base (tonnes)
Bolivia	5,400,000
Chile	3,000,000
China	1,100,000
Brazil	910,000
Argentina	not available
United States	410,000
Canada	360,000
Australia	220,000
Portugal	not available
Zimbabwe	27,000
World total (rounded)	11,000,000

Source: Linda Gaines, http://www.transportation.anl.gov/pdfs/B/626.PDF

- Reserve of valuable metals in Li-ion batteries(Li, Co, Ni);

Safe disposal may become a serious problem

Heavy metals

Hazards

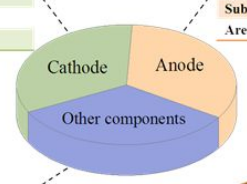
Organic solvents

Air pollution

Challenges and Opportunities

Active material	$LiCoO_2$
Binder	PVDF
Loading (total)	11.57 g
Current collector	Al foil (25μm)
Leads	Al
Thickness (total)	0.018 cm
Cathode length	49.5 cm
Substrate length	52.0 cm
Substrate width	5.4 cm
Area (both sides)	535 cm

Active material	Nongraphitized carbon
Binder	PVDF
Loading (total)	4.92 g
Current collector	Cu foil (25μm)
Thickness (total)	0.020 cm
Anode length	51.1 cm
Substrate length	53.7 cm
Substrate width	5.4 cm
Area (both sides)	552 cm



Electrolyte	PC/DEC, $LiPF_6$
Separator	Celgard (25μm)
Insulator	PP disk
Leads	Aluminum
Case	Nickel-plated steel
Header	Aluminum safety vent
Closure	Crimp

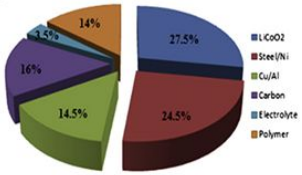


Fig. 3 Typical design parameters and chemical structure of a C/$LiCoO_2$ 18650 cylindrical cell

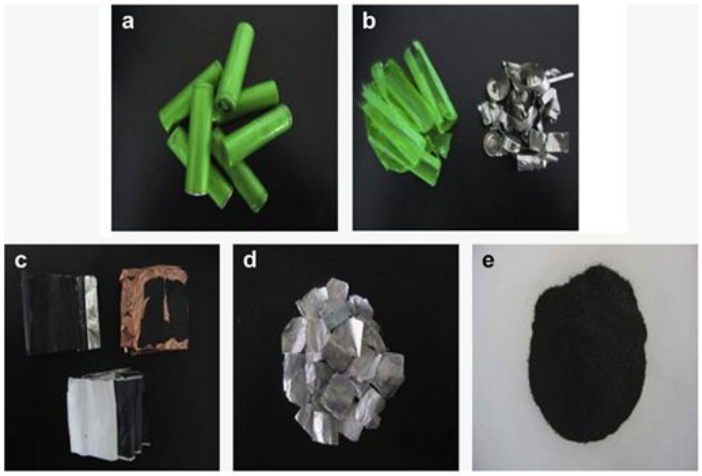


Fig. 5 Illustrations of different parts dismantled from spent Li-ion batteries: (a) spent Li-ion batteries, (b) plastic and metallic shells, (c) cathode, anode and separator, (d) Al foils after immersion in NMP, and (e) the active materials after filtration and

Challenges and Opportunities

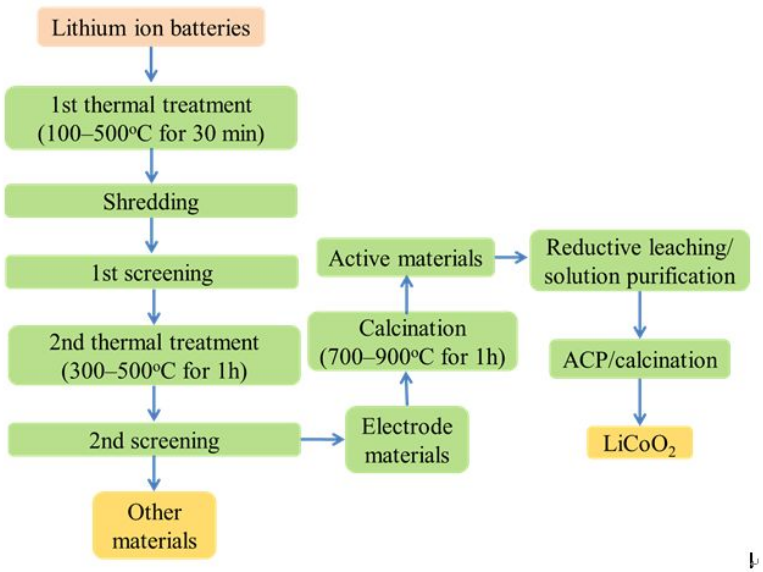


Fig.7 Flowchart of the thermal treatment recovery process
Source : C.K. Lee, J. Power Sources, 2002, (109), 17–21.

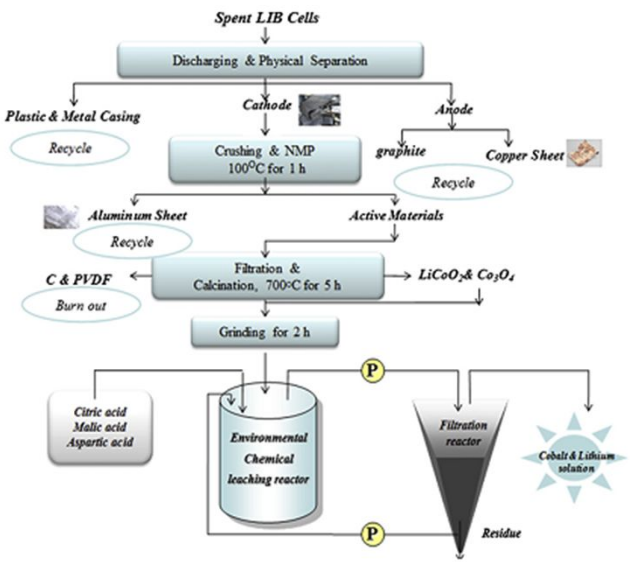


Fig. Flowchart of the hydrometallurgical recycling process of spent LIBs Source: Li.Li, et al. J. Power Sources. 2013, 233, 180-189.

Recycling process in practical cases

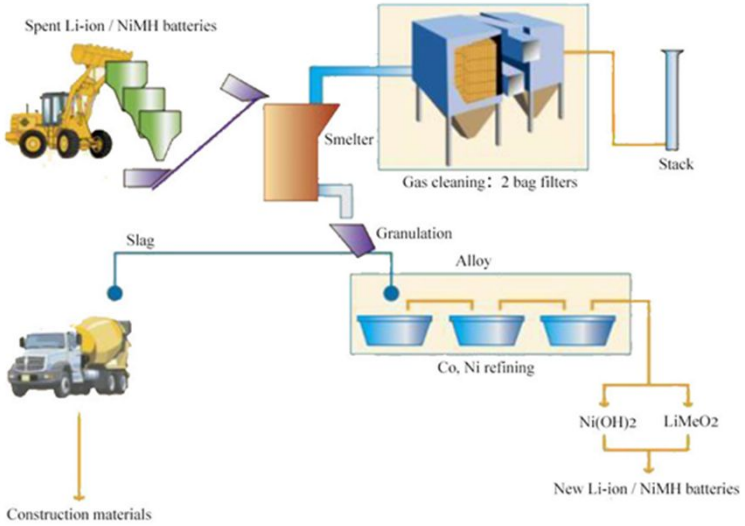


Fig. Flowchart of Umicore recycling process of spent LIBs (in Belgium)

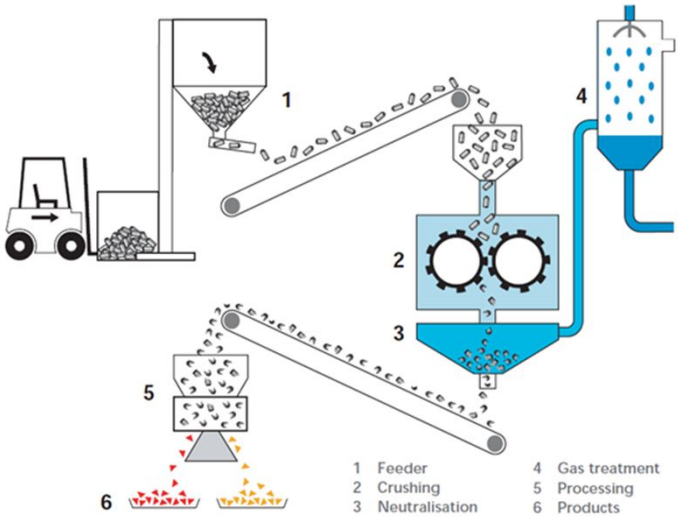


Fig. Flowchart of Batrec Industrie AG recycling process of spent LIBs (in Switzerland)

Recycling process in practical cases

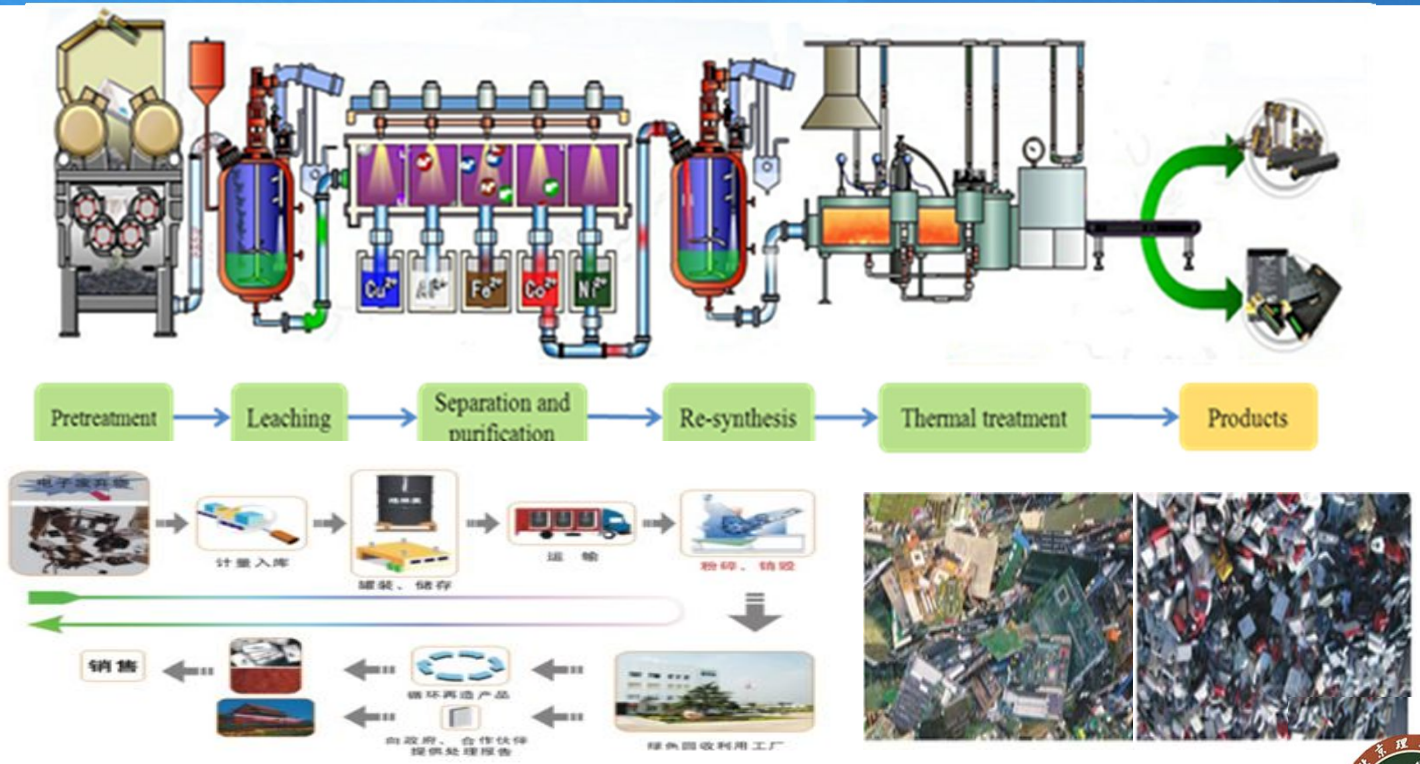
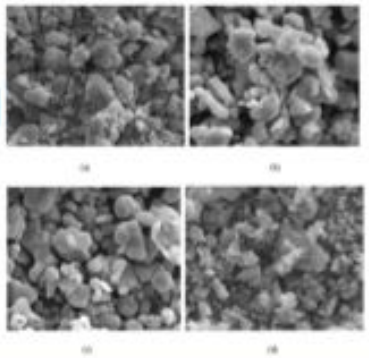
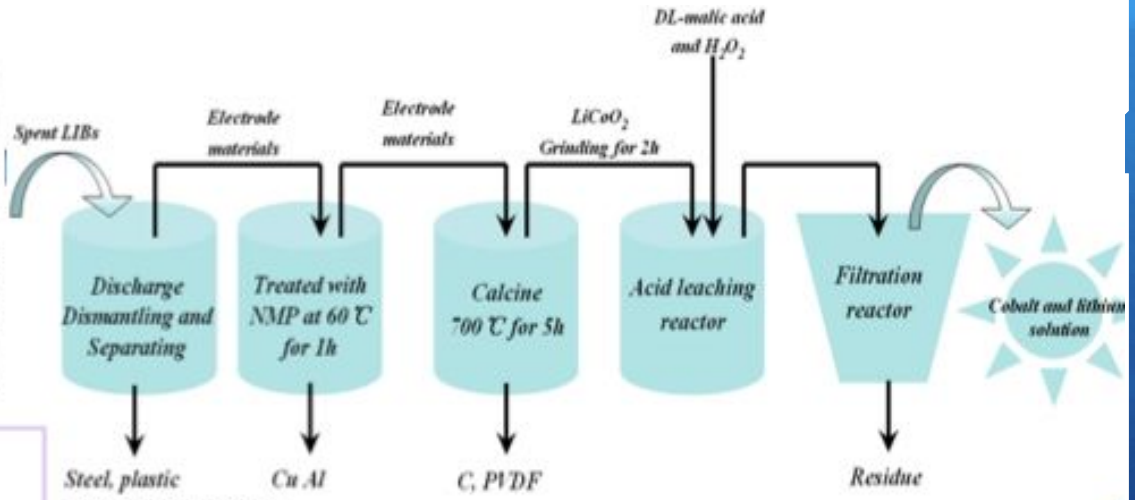


Fig. Flowchart of GEM recycling process of spent LIBs (in China)

Recovery of metals from spent LIBs with organic acids as leaching reagents





- Environmental friendly method:
  - ✓ Process controlling: using organic acids instead of strong inorganic acids to reduce toxic gases and waste liquids

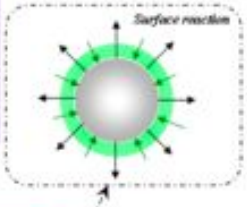
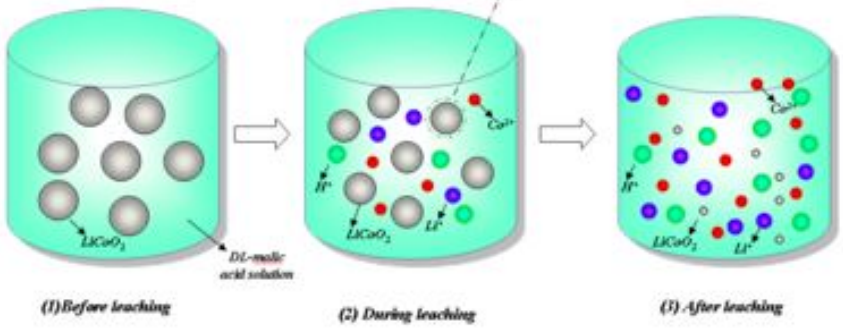
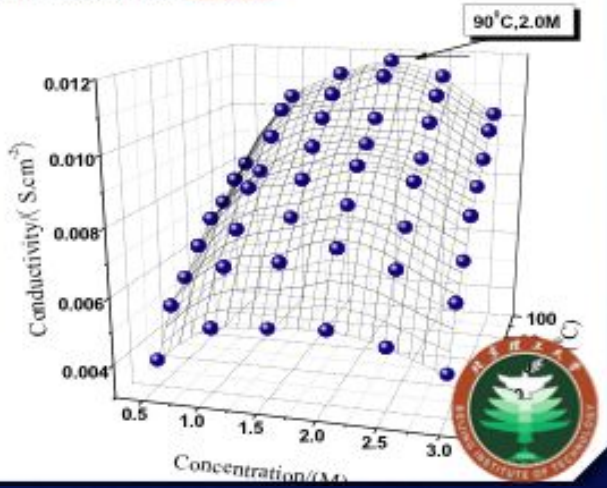


Fig. 2. Flow sheet for the recovery of Co and Li from spent Li-ion batteries using DL-malic acid as a leachant





Recycling technologies for spent LIBs

- Economically, recycling has also traditionally offered an opportunity to recover valuable materials used in battery production, namely cobalt, which is widely used in LIBs due to its high energy density.
- However, cobalt is a costly metal, and manufacturers are moving toward low-cost cathode materials to reduce the cost of battery manufacturing.
- Cathode materials such as lithium iron phosphate and lithium manganese-spinel are projected to be the next generation of LIB technology (Ritchie and Howard, 2006). The transition from expensive cathode materials to less expensive options reduces the economic incentives to recycle those batteries at their end of life.

Low-cost cathode materials

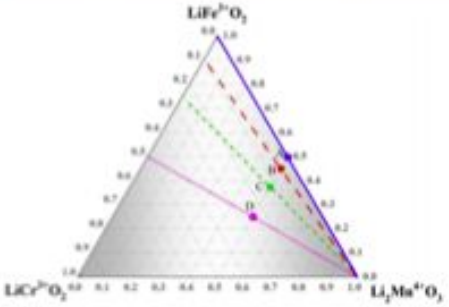


Fig. 1. Compositional phase diagram of lithium-excess Mn-based layered oxide: $LiFe^{3+}O_2$–$LiCr^{3+}O_2$–$Li_2Mn^{4+}O_3$ [$LiFe_{1-x}Cr_xO_2$·Li_2MnO_3]. Points A, B, C and D in the triangular phase diagram represent $LiFeO_2$·Li_2MnO_3 (x = 0), $LiFe_{0.9}Cr_{0.1}O_2$·Li_2MnO_3 (x = 0.1), $LiFe_{0.75}Cr_{0.25}O_2$·Li_2MnO_3 (x = 0.25) and $LiFe_{0.5}Cr_{0.5}O_2$·Li_2MnO_3 (x = 0.5), respectively.

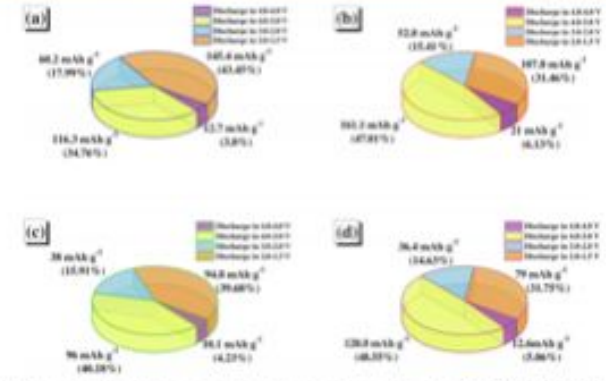


Fig. 6. 3D pie charts of initial discharge capacities and proportions in different voltage ranges of as-prepared samples $LiFe_{1-x}Cr_xO_2$·Li_2MnO_3 (a) x = 0, (b) x = 0.1, (c) x = 0.25, (d) x = 0.5.

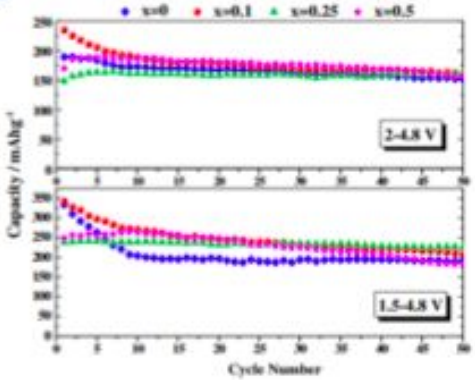


Fig. 9. Discharge capacities of the $Li/LiFe_{1-x}Cr_xO_2$·Li_2MnO_3 half-cells (x = 0, 0.1, 0.25, 0.5) with different discharge cut-off voltages.

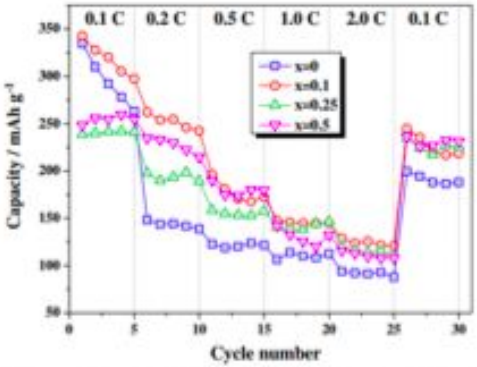


Fig. 11. Rate capabilities of the $Li/LiFe_{1-x}Cr_xO_2$·Li_2MnO_3 half-cells (x = 0, 0.1, 0.25, 0.5) at various C rates.

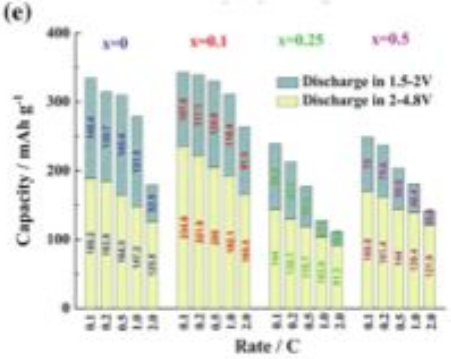
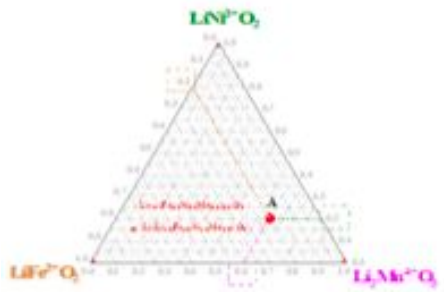
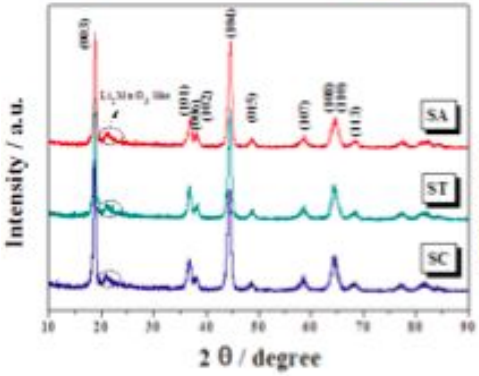
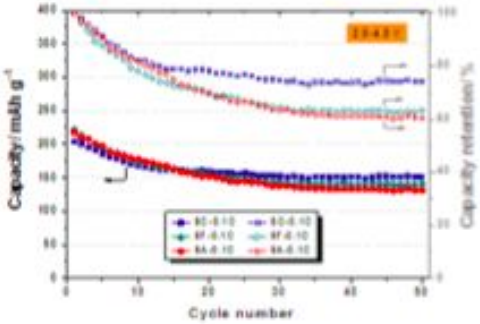


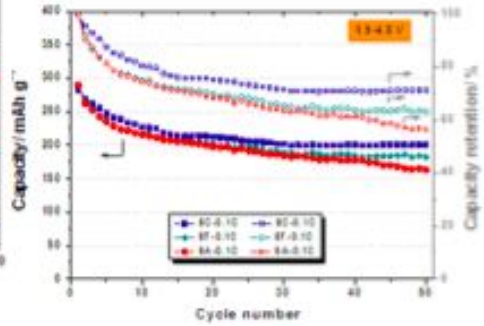
Fig. 10. Initial rate capabilities of the $Li/LiFe_{1-x}Cr_xO_2$·Li_2MnO_3 half-cells at various rates. (a) x = 0, (b) x = 0.1, (c) x = 0.25, (d) x = 0.5, (e) detailed data of initial discharge capacities.

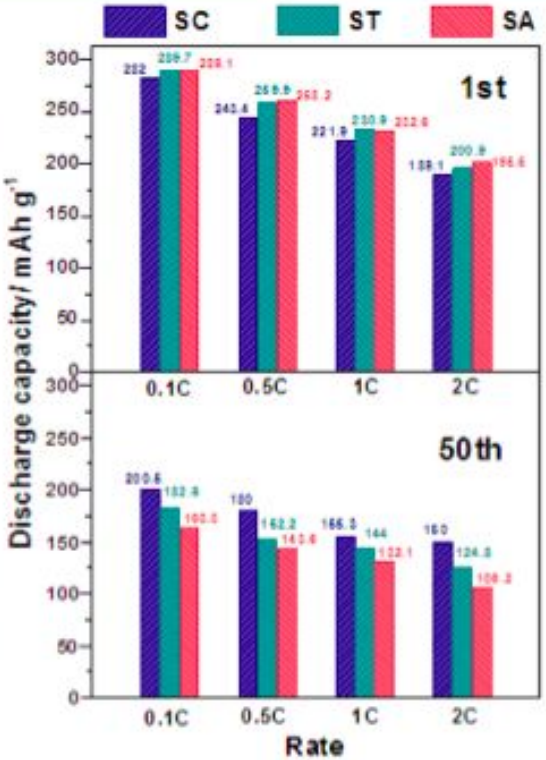
Low-cost cathode materials











Comparison of recycled versus virgin materials.

Table 6 Price and cost to recycle one-ton cathode materials from spent Li-ion batteries[42]

Substance	Price ($/ton)	Cost ($)
$MnSO_4 \cdot H_2O$	600	265
$NiSO_4 \cdot 6H_2O$	6000	4831
$CoSO_4 \cdot 7H_2O$	7500	0
H_2O_2, 30%	500	62
Na_2CO_3	300	222
NaOH	350	400
Li_2CO_3	8000	2621
H_2SO_4	150	210
Total		8611

Table 7 Prices and cost of virgin materials used to produce $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ by co-precipitation

	Price ($/ton)	Cost ($)
$MnSO_4 \cdot H_2O$	600	487
$NiSO_4 \cdot 6H_2O$	6000	7575
$CoSO_4 \cdot 7H_2O$	8000	10 801
Li_2CO_3	8000	4259
Total		23 121

- The cost of synthesizing NMC is $16635 $/ton using virgin materials. While using recycled materials, the cost is only $6195/ton. The cost differential is $10 440/ton, which is significant.
- It is believed that synthesizing NMC using recycled materials can save $10440/ton in chemicals not including energy savings. There are additional economic benefits from recycling in that the Cu current collector, the electrolyte, and carbon may be recovered.
- The analysis results clearly show that recycling can not only save the cost of production, but also save energy and reduce resource consumption.

Haiyang Zou, Eric Gratz, Diran Apelian et al. Green Chem., 2013, 15, 1

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Environmental assessment of recycling process

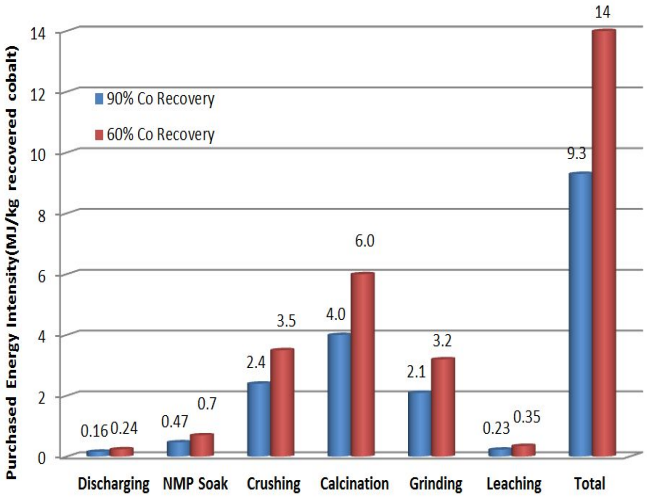

Figure 14. Purchased energy intensity (MJ/kg recovered Co) of the recycling process.

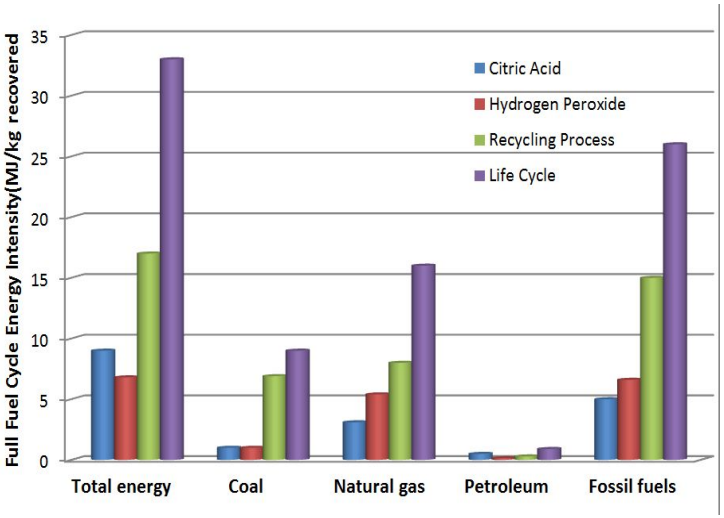

Figure 15. FFC energy intensity for organic acid, H_2O_2 and the recycling process for 90% recovery of Co

Li.Li, J.B.Dunn , L.Gaines, Feng Wu , K. Amine. Journal of Power Sources. 2013, 233:

Conclusion

- The rapidly growing volume of spent LIBs requires a well- functioning collection and recycling infrastructure to minimize associated environmental impacts.
- One of the most daunting challenges we face is sustainable development. With population increasing and energy demand increasing, the need for recycling is pivotal. The Li-ion battery market is posed to grow, and we must establish closed loop systems to ensure sustainable development.
- Developing a real cost-effective, environmental friendly recycling process with high recycling efficiency remains as a challenge. Low-cost cathode materials, organic acid leaching and LCA are better solutions for the future development of recycling spent Li-ion batteries.

Thank You !

- The work was supported by National 973 Program in China.
- Thank Dr. Khalil Amine, Dr. Michael Wang, Dr. Linda Gaines , Dr. Jun Lu and Dr. Jennifer B. Dunn at Argonne National Lab.