Developments in Lithium-Ion Battery Recycling Processes

Bryan Tiedemann, Ph.D.

Shiloh Scientific Consulting, LLC

January 24, 2003

About the speaker

- Originally from California
- BS in Chemical Engineering (Caltech, 2002)
  - Research focused on solar energy conversion
- Ph.D. in Chemistry (UC Berkeley, 2007)
  - Focus on synthetic and inorganic chemistry
- Moved to Texas in 2007

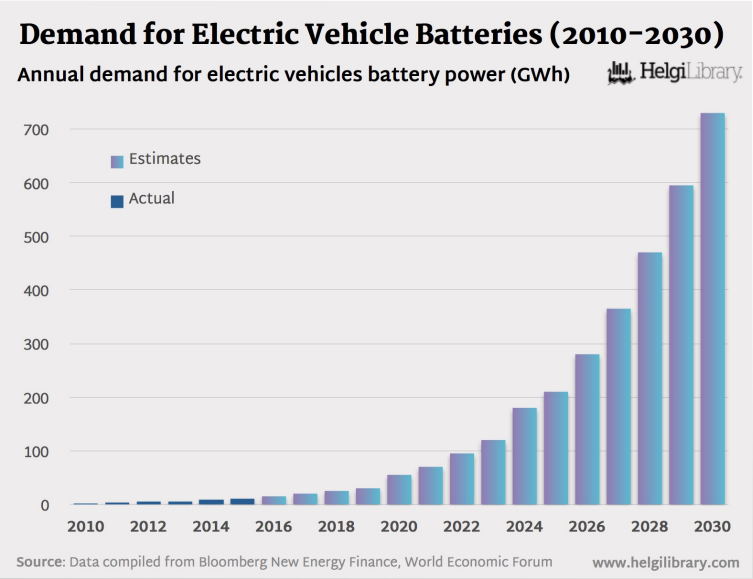
- Work experience since 2007:
  - Matheson Tri-Gas
  - ExxonMobil Chemical Company
  - Shell Chemicals
  - Consultant for Earthineering
  - Momentum Technologies
  - Independent consultant (present)

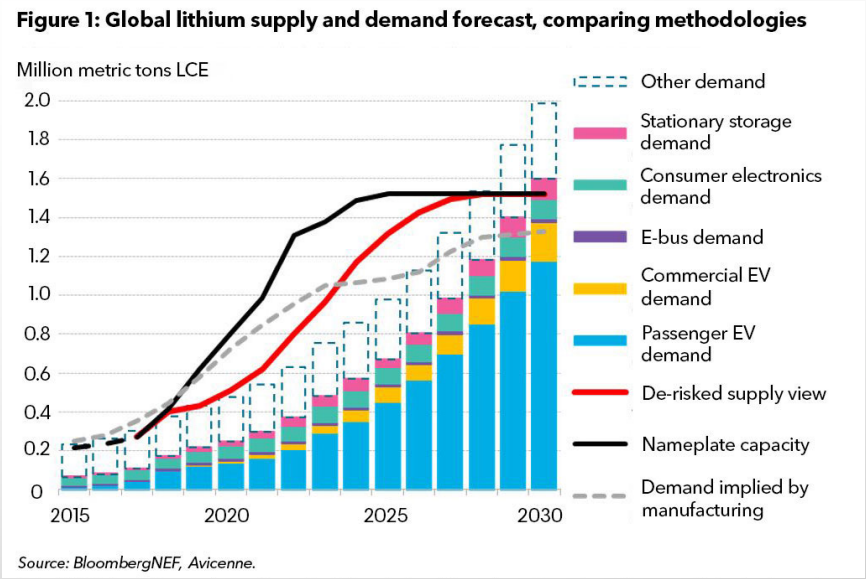
Overview

- EV market conditions and lithium-ion battery demand
- What is a LIB and how are they made
- Mechanical shredding and black mass separation
- Pyrometallurgy
- Hydrometallurgy and solvent extraction
- Membrane-supported solvent extraction
- Summary

Electric vehicles are here

Li-ion battery demand is ramping up





Lithium-ion battery composition

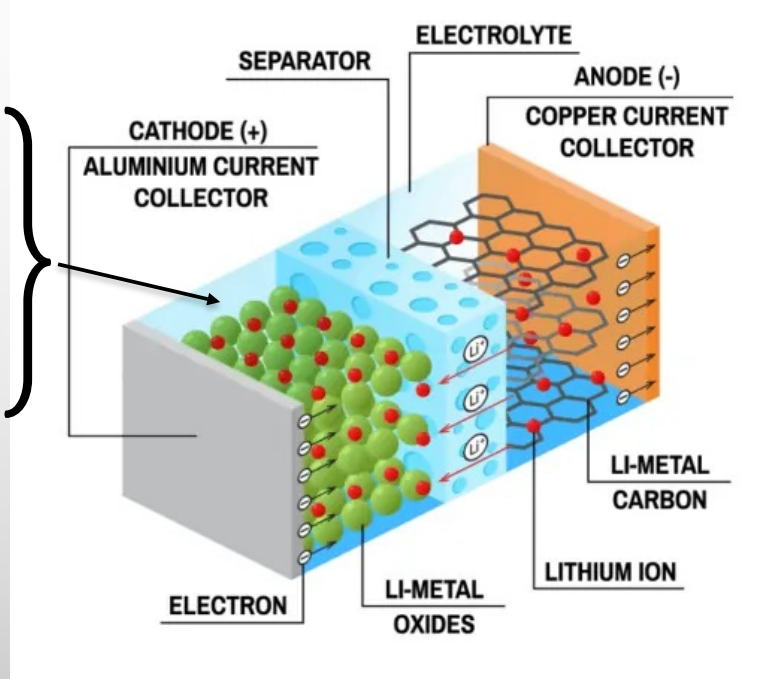
$LiCoO_2$

$LiNi_xMn_yCo_zO_2$

$LiNi_xCo_yAl_zO_2$

$LiMn_2O_4$

$LiFePO_4$



Source: EnergyLink

- Graphite anode
- Various cathode materials
- Organic electrolyte
- Separator
- Copper and aluminum current collectors
- Plastic and steel from casing

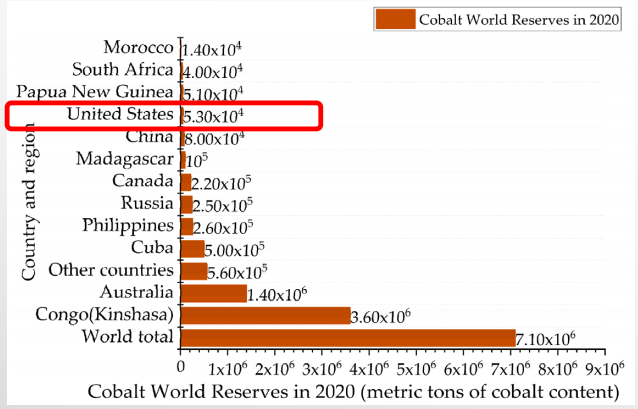
Electrochemical Series – Standard Reduction Potentials

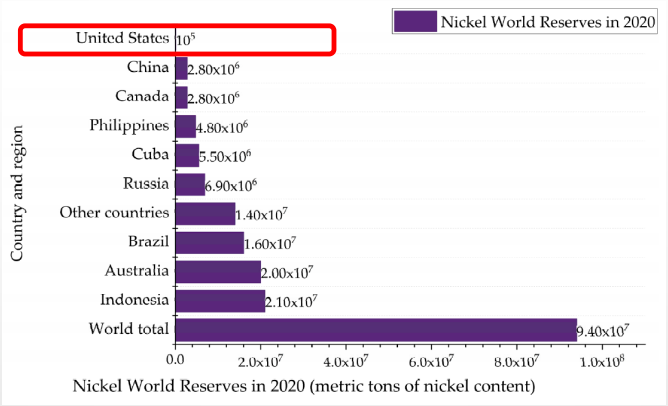
$$\Delta G^\circ = -nFE^\circ$$

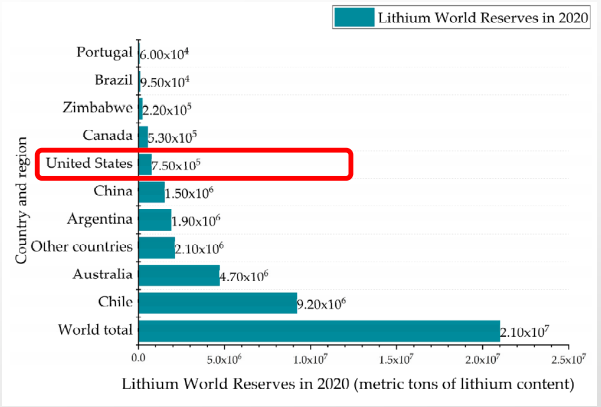
	E° (V vs. SCE)		E° (V vs. SCE)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87	$2H^+ + 2e^- \longrightarrow H_2$	0
→ $Co^{3+} + e^- \longrightarrow Co^{2+}$	1.81	$Pb^{2+} + 2e^- \longrightarrow Pb$	-0.13
$Au^+ + e^- \longrightarrow Au$	1.69	$Sn^{2+} + 2e^- \longrightarrow Sn$	-0.14
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	1.61	$In^{3+} + 3e^- \longrightarrow In$	-0.34
$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09	$Fe^{2+} + 2e^- \longrightarrow Fe$	-0.44
$Ag^+ + e^- \longrightarrow Ag$	0.80	$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34	$V^{2+} + 2e^- \longrightarrow V$	-1.19
$AgCl + e^- \longrightarrow Ag + Cl^-$	0.22	$Cs^+ + e^- \longrightarrow Cs$	-2.92
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.15	→ $Li^+ + e^- \longrightarrow Li$	-3.05

Uneven global distribution of resources

US vulnerable to supply chain disruptions for LIB critical elements







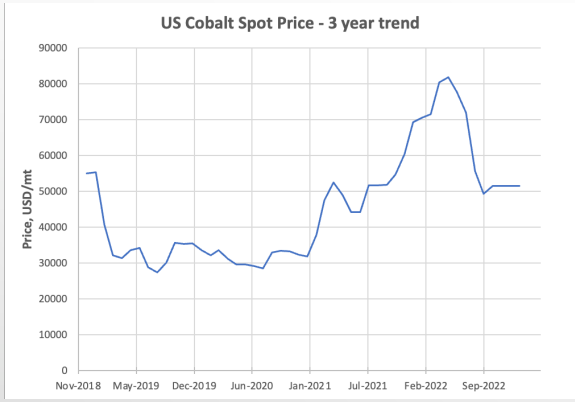
Projected cumulative world battery material demand to 2025 (1000 tons).

Element	Projected Demand		USGS Reserves
	If all NMC is low-Co (811)	If all NMC is high-Co (111)	
Lithium	230	230	16,000
Cobalt	790	910	7,100
Nickel	580	340	74,000

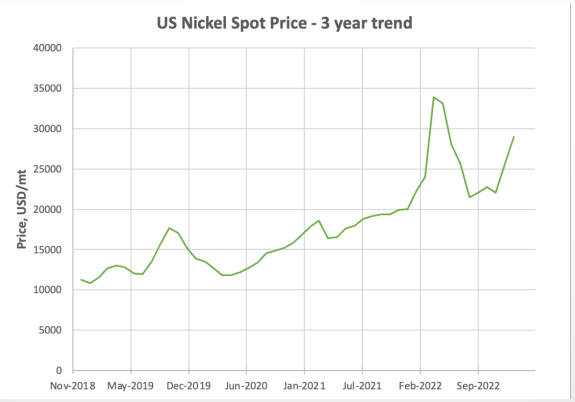
Graphs: Duan, X.; Zhu, W.; Zhongkui, R.; Xie, M.; Chen, J.; Ren, X.; *Energies*, **2022**, *15*, 1611
Table: Gaines, Linda; *Sustainable Materials and Technologies*, **2018**, *17*, e00068

EV battery demand driving up prices for LIB materials

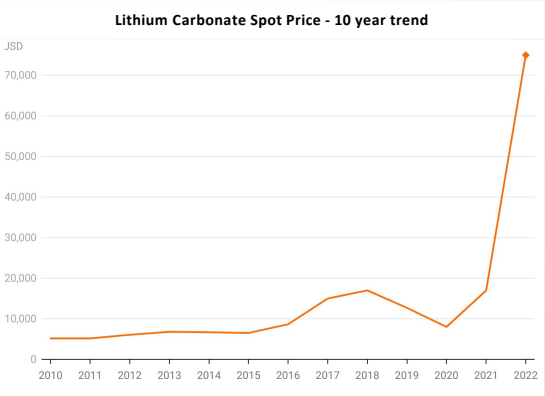
LIB recycling can be profitable



Source: Ycharts.com

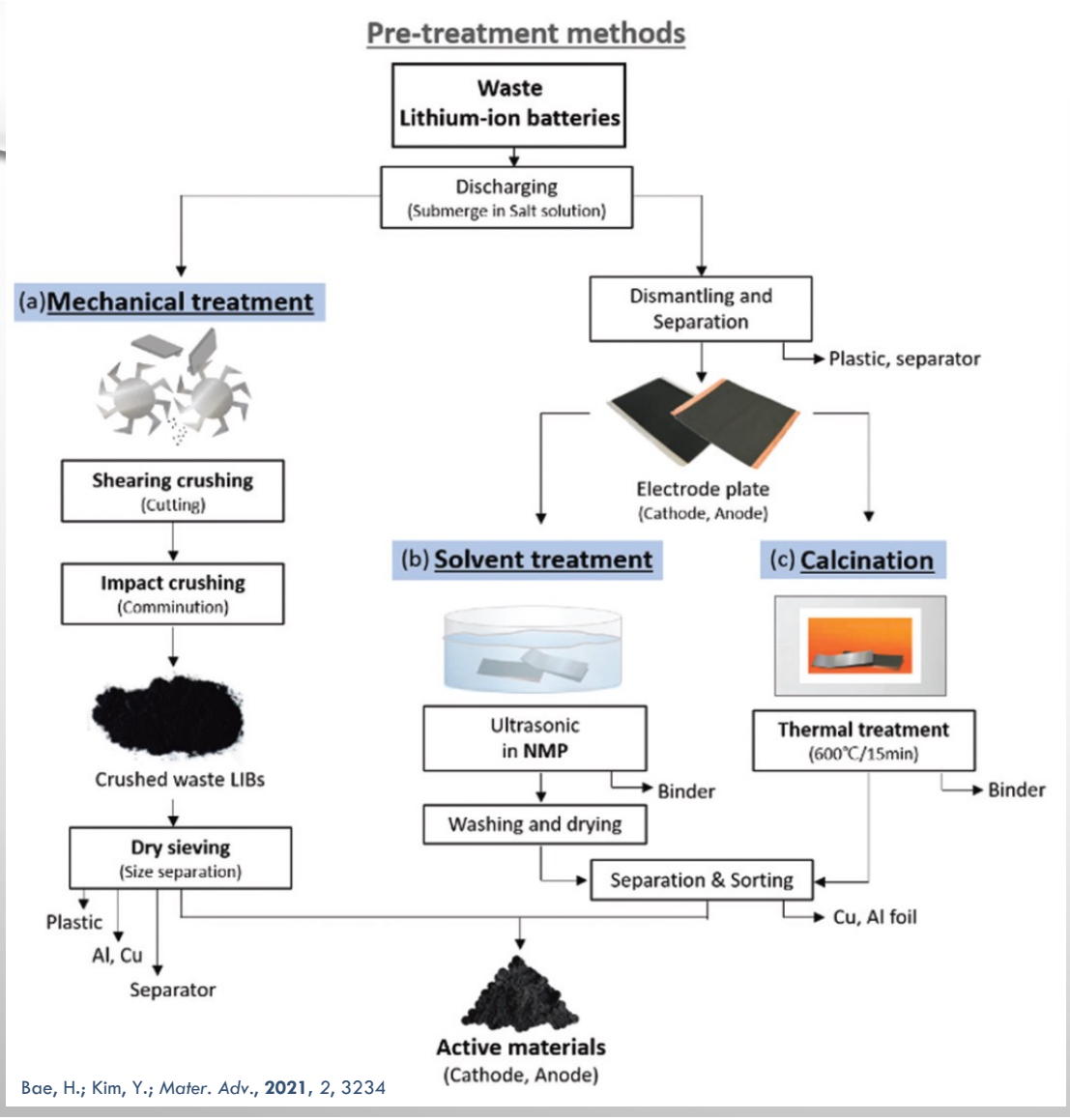


Source: Ycharts.com

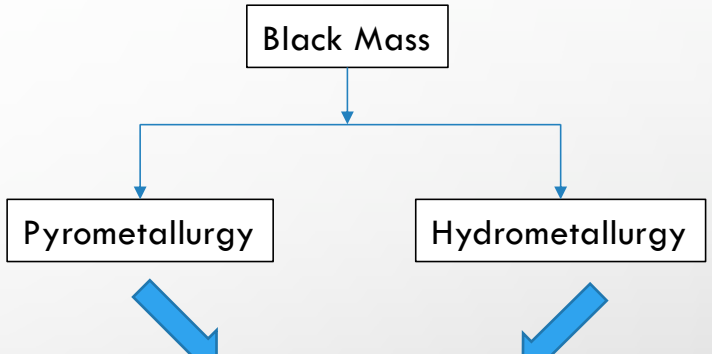


Source: Canary Media

- LIB recycling can be quite profitable with the right process technology
- Several recent startups emerged in the US and Canada
  - Top 5 by funding: Ascend Elements, Redwood Materials, Li-Cycle, Aqua Metals and Lithion Recycling
  - Each company uses proprietary process technologies



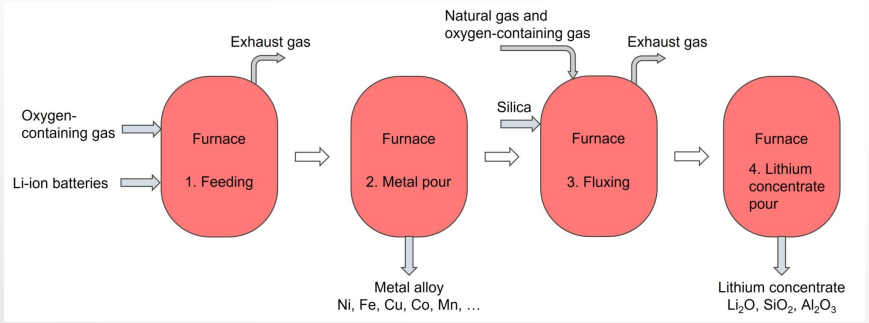
Bae, H.; Kim, Y.; *Mater. Adv.*, **2021**, *2*, 3234

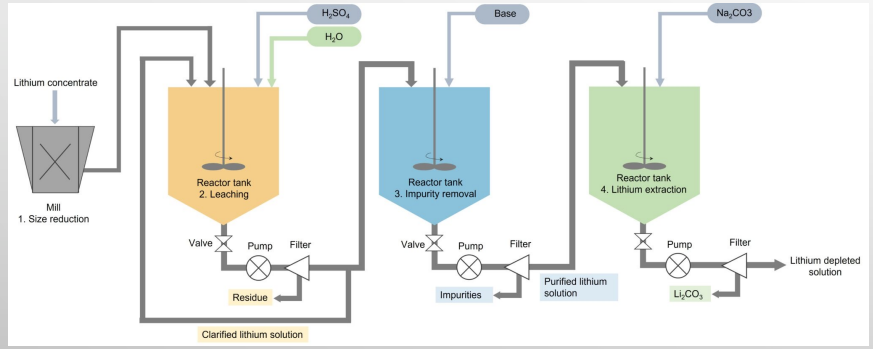


Li salts – Li_2CO_3

Co, Ni, Mn, Cu...

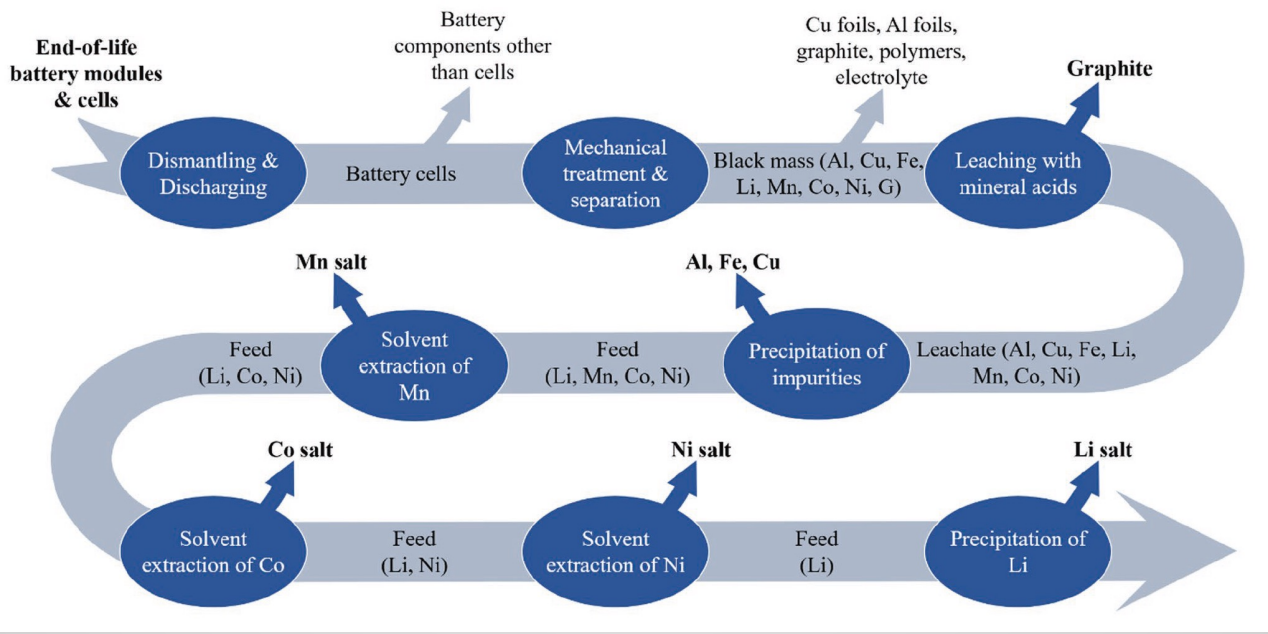
Pyrometallurgy – General process





- Organics burned off in furnace at ~1500 °C
  - Plastics, electrolytes, graphite removed
  - Forms liquid metal and solid Li oxide phases
- Liquid metal poured off solid Li concentrates
  - Metallic elements further separated by melting point
- Silica flux added to Li concentrates
  - Heated to flux/fluidize solids before pouring Li concentrates out from furnace
- Li salts extracted from crushed Li concentrate
  - Li^+ leached from concentrate with aqueous acid
  - Extract neutralized with base to precipitate impurities
  - Sodium carbonate added to precipitate Li_2CO_3

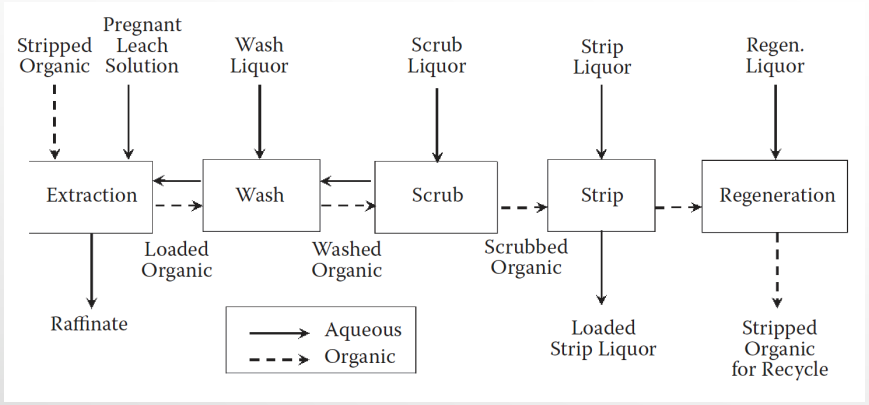
Hydrometallurgy – General process

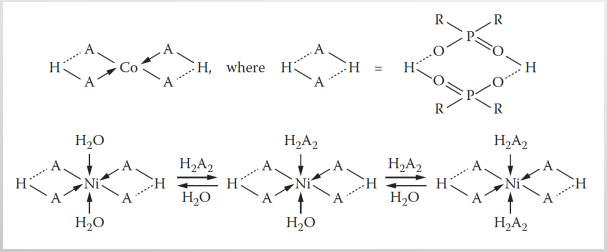


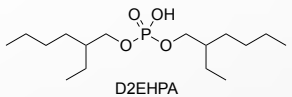
Neumann, J.; Petranikova, M.; Meeus, M.; Gamarra, J.D.; Younesi, R.; Winter, M.; Nowak, S.; *Adv. Energy Mat.*, **2022**, *12*, 2102917

Principles of Solvent Extraction

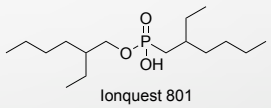
Organophosphorus acids



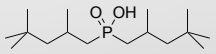




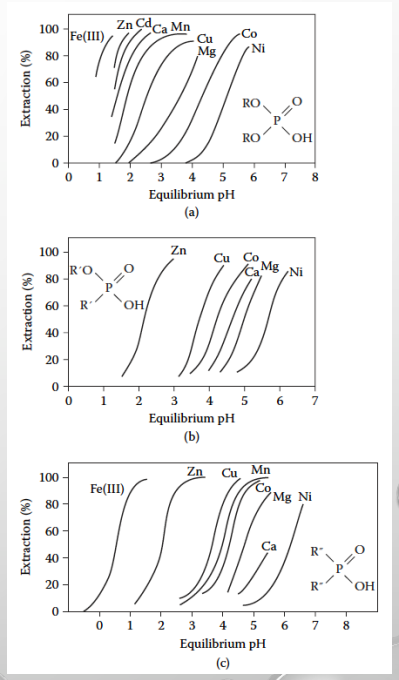
D2EHPA
dialkylphosphoric acid



Ionquest 801
dialkylphosphonic acid

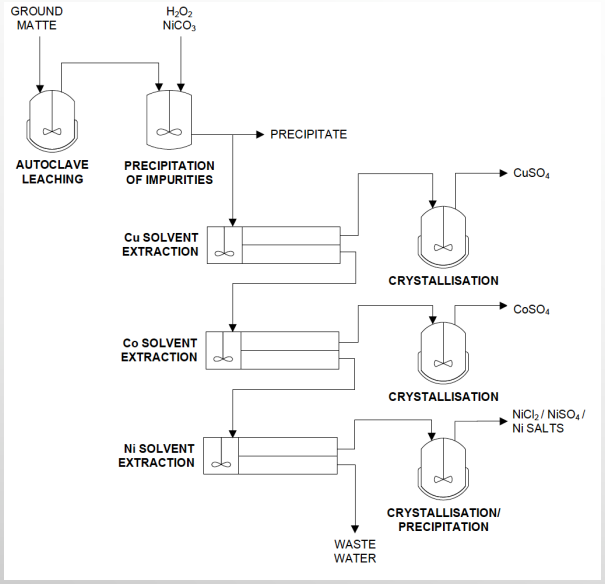


CYANEX 272
dialkylphosphinic acid

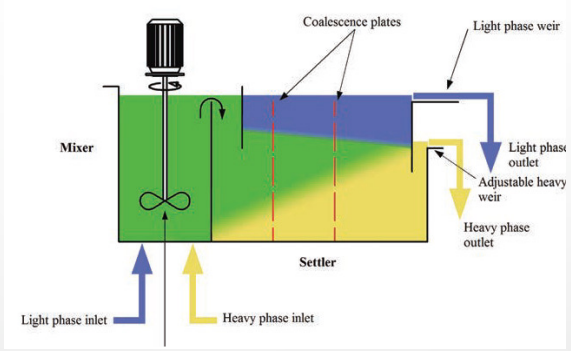


Sole, Kathryn; Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials, 141-200

Equipment for Hydrometallurgy and Solvent Extraction

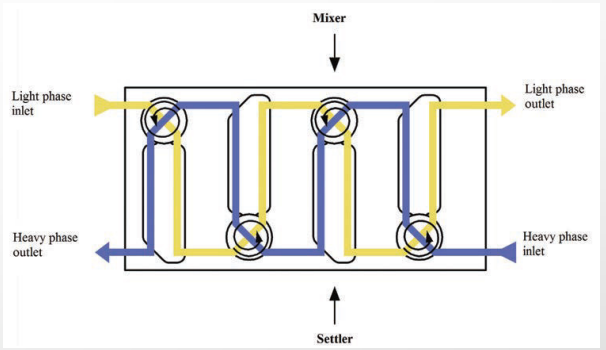


Simplified flowsheet of Nickelhütte Aue GmbH
Brückner, L.; Frank, J.; Elwert, T.; *Metals*, **2020**, *10*, 1107



Mixer-settler unit

De Deitrich mixer-settlers

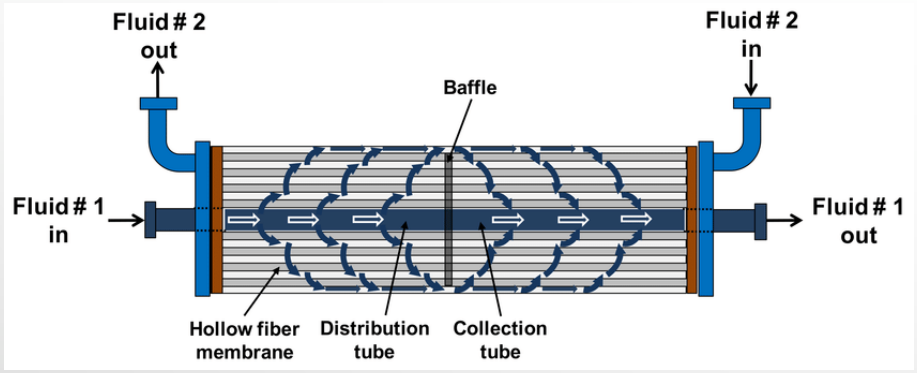


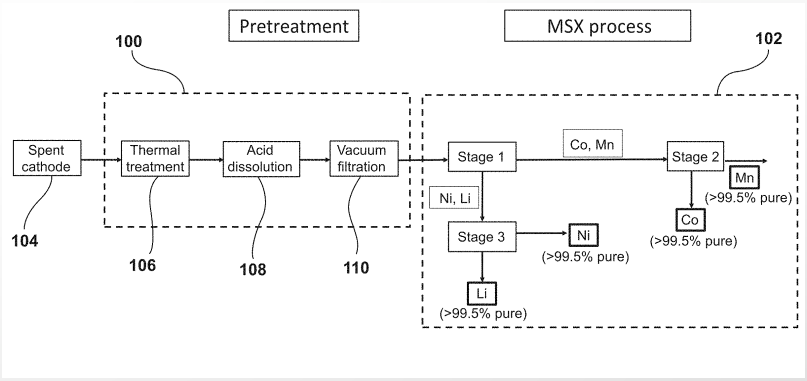
Countercurrent bank of mixer-settler stages

Rousselet-Robatel eight-stage battery

Membrane Supported Extraction

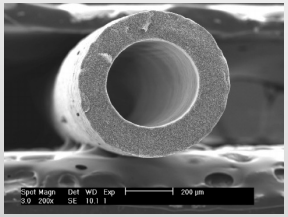
Overview



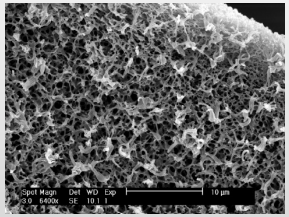


Bhave, R.R.; Islam, S.Z.; Wagh, P.A.; US 2021/0376400 A1

Thousands of hollow fibers in a module



Fiber cross-section (scale: 200 microns)

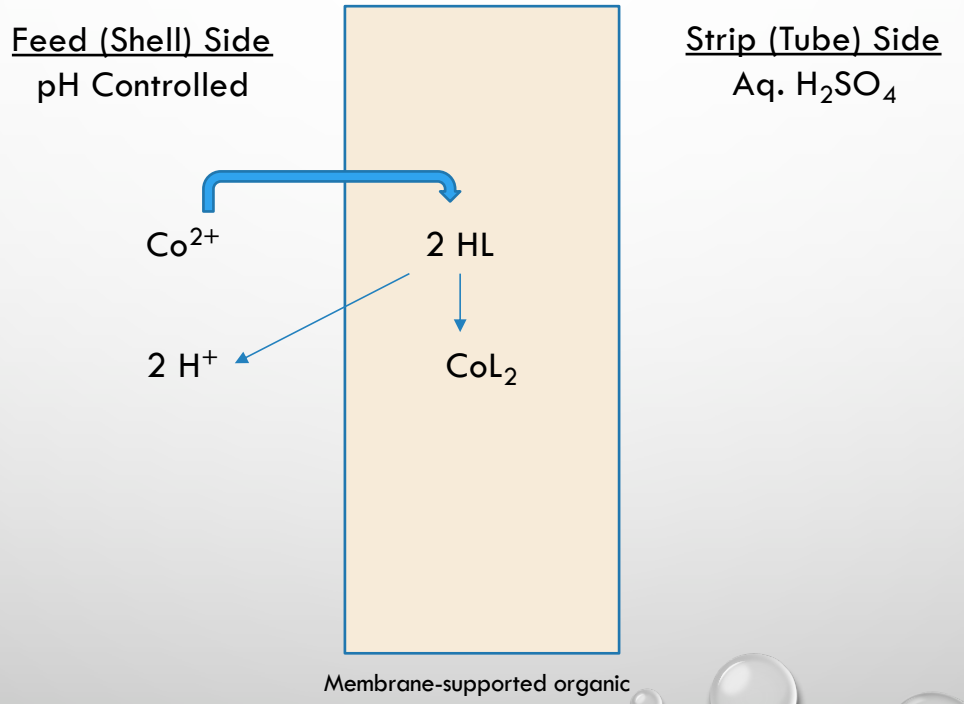


Surface of porous fiber (scale: 10 microns)

- Hydrophobic membrane pores are loaded with organic extractants
- Extraction and stripping steps occur in single device
- Modular design potentially useful for smaller scales

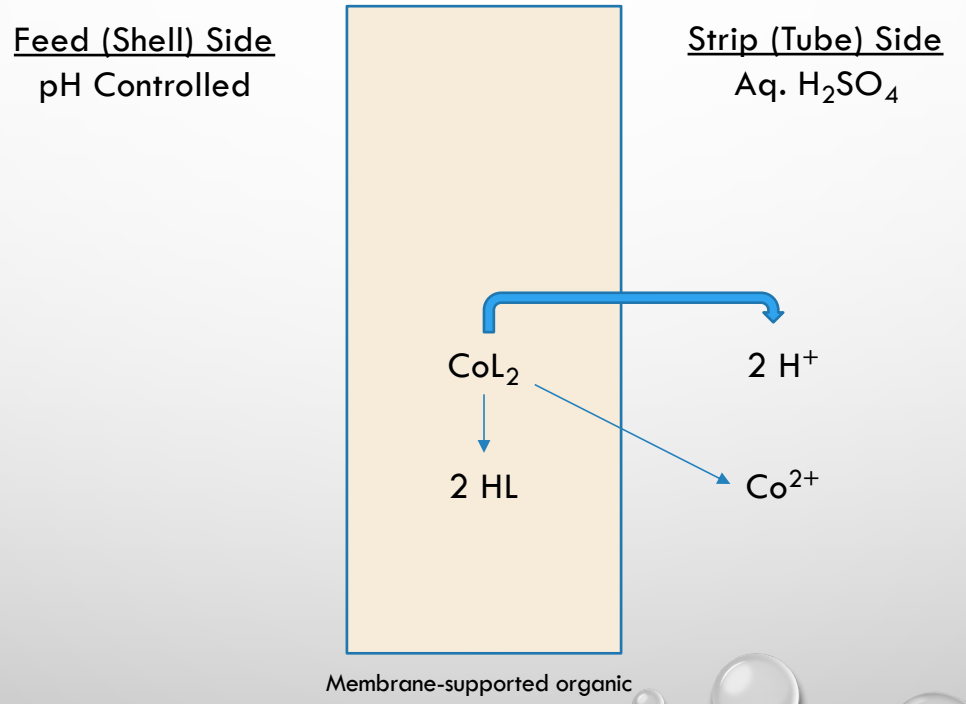
Membrane Supported Extraction

Mass transport across membrane



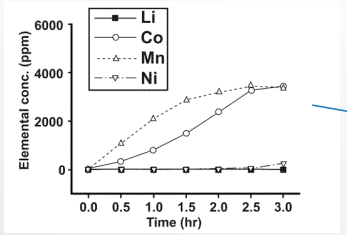
Membrane Supported Extraction

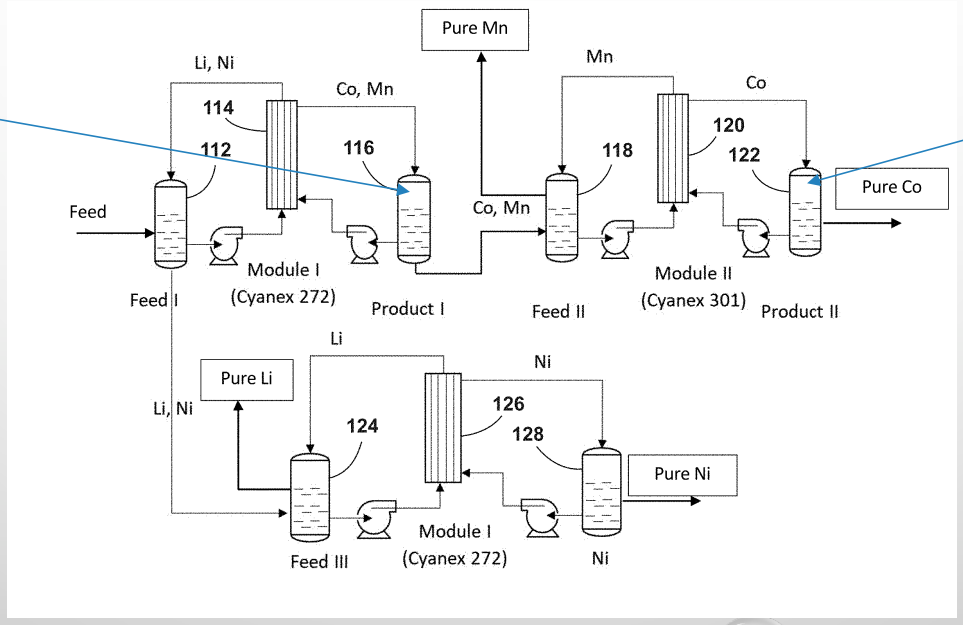
Mass transport across membrane

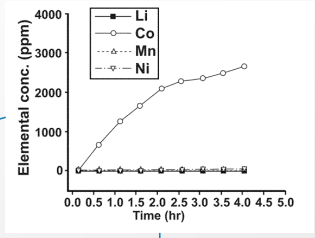


ORNL Membrane Supported Extraction Process

Batch Extraction Stages and Operation







Crystallizer

$CoSO_4 \cdot 7\ H_2O$

Bhave, R.R.; Islam, S.Z.; Wagh, P.A.; US 2021/0376400 A1

Summary

- Lithium-ion battery recycling will be a key part of the critical materials supply chain as vehicles continue to be electrified at an increasing rate going forward
- After discharge, disassembly and sorting, lithium-ion batteries can be recycled using a variety of innovative technologies
  - Largely based on pyrometallurgy or hydrometallurgy processes adapted from the mining industry
  - Various startup companies seeking to take advantage of high commodity prices
- Chemical engineers should remain deeply involved in commercializing green technologies