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## Recycling the Tough Stuff  Beyond BM

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# RECYCLING THE TOUGH STUFF BEYOND BM

- ELECTROLYTES
- CARBON (aka GRAPHITE, CONDUCTIVE, AND ANODE)
- MANGANESE
- THE OTHER LITHIUM BATTERIES ?

# ELECTROLYTES- WHAT THEY ARE

- Inside almost all rechargeable batteries including solid state.
- Necessary for conducting Li ions through separator.
- Electrolytes are flammable and volatile.
- Maximized to achieve optimized conductivity at >4.1 V (Max is 10-11 mS/cm at RT.
- Electrolytes that have been modified for FR perform lower conductivity.

# ELECTROLYTES- WHAT THEY ARE

- The electrolytes usually consist of about :
- 1/3 **ethylene carbonate (EC)** (necessary for the SEI formation)
- bp 243 C; closed cup fp 143 C

**Highly Flammable**

- 1/3 **dimethyl carbonate (DMC**)

  bp 90 C; cc fp 23 C;
- 1/3 **ethyl methyl carbonate (EMC)**

  bp 101C; ccf fp 24 C and/or
- **diethyl carbonate (DEC)**

  bp 126 C: cc fp 24 C

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- **The Salt: 9-11% LiPF6** primarily (water sensitive); There are a few newer more expensive conductive salts such as LiFSI; primary batteries may use Li Imide and other Li salts based on per-fluorosulfonates). There are about 1-5% proprietary additives also present which are sensitive to water.

# Est. Value of the Electrolyte Pure Components

**$ Cost per Lb. in volume**

May 2025 prices

- **Ethylene Carbonate (EC) 0.31-0.50**
- **Dimethyl Carbonate (DMC) 0.41**
- **Ethyl Methyl Carbonate (EMC) 0.41**
- **Diethyl Carbonate (DEC) 0.64**

**The solvents are low cost**

**Difficult to economically justify recovery and purification**

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- **Lithium Hexafluorophosphate (LiPF6) $8.00-$17.00 depending**
- **Moisture sensitive; unstable above 70 C**

**Battery impurities present ;recovery as pure salt not practical**

# Electrolytes: What Happens in Recycle Processes for the BM

- **Pyrolysis-** The cells rupture and the electrolyte burns off. The Kynar binder burns and some burning of the carbon occurs. The resulting BM can be sent to the smelter. No Li recovery.
- **Pyrolysis then Hydrometallurgical**- Recovery of the metal salts and Li. No electrolyte recovery
- **Wet Shredding- Hydrometallurgical** – The electrolytes are destroyed rapidly in the basic pH process water to produce the corresponding alcohols, ethanol, ethylene glycol and methanol which can be a flammable hazard and are not recovered. The LiPF6 is also hydrolyzed forming Li, PO4, and F ions during BM hydrometallurgical extraction to form solutions of NMC sulfates.

No recovery of the electrolyte except for the Li component from the subsequent process water after removal of contaminates.

**DMC + 2LiOH + H2O→2 CH3OH + Li2CO3**

**HYDROLYSIS**

**They hydrolyze to their respective alcohols**

# Electrolytes: What Happens in Recycle Processes for the BM (cont.)

- **Vacuum dry shredding-**Shredding under vacuum and condensing/recovery of the solvents as a mixture. The mixture of the volatile solvents-DMC, EMC and DEC can be used for fuel. It can also be fractionally distilled into the purified separate organic carbonates. This is expensive and the overall yields will be lower. (This is being demonstrated in Germany now. Volkswagen was one of the first. Not really commercial, yet?) It does not lend itself for continuous operation and appears to be CAPEX intensive.) The pure commercial organic carbonates are relatively inexpensive. The Li is extracted in subsequent hydro processing for NMC.
- **Extracting the opened discharged cells with liquid CO2 or other solvents under nitrogen-** This is not commercial is labor and CAPEX intensive. The resulting electrolyte /solvent mixture is isolated by distillation. The LiPF6 will be too contaminated to meet specifications.

# Electrolytes: Disposal or Recovery ?

- **The recovery of the electrolyte components does not appear to be commercially desirable for either the LiPF6 nor the organic solvents and the additives.**

- **Most BM extraction processes are focused on and will in the future focus on the recovery of Ni, Co, and Li. The Mn is recovered as by-product or co-product.**

# Carbon: The Forms and Sources

**The BM from NMC hydro shredding** yields roughly 38-42% insoluble (filter cake) on a dry basis after reductive acid extraction.   This contains all of the carbon plus binder plus any unextracted metals. (<3%)

1) Anode carbon (graphite, synthetic carbon, ?silicon, ?carbon nanotubes) It is about 5 to 15 microns. Roughly 85% of this cake.

2) Conductive carbon such as black pearls. It is  sub micron.

   Roughly 6% of this solid filter cake.

3) Kynar (PVDF) binder. Roughly 6% of this cake

# Carbon from Hydro Shredding /Processing

- If the extracted carbon cake from hydro-processing the BM is pure enough, it can be sold as commercial conductive carbon which is added to plastics, flooring and other applications for antistat purposes.  A significant market.
- Small amounts of silicon if not previously extracted should not matter.
- If the recovered carbon is to be recycled back for anode application, it should be of the same composition as the original battery source-production scrap, etc. for current battery production anode.
- The particle size needs to be brought back to the original 5-15 microns.

# Don’t Forget the Binder in the Carbon Cake

- The binder should be removed.
- Pyrolysis will remove the binder at >500 C, but the carbon will partially ignite unless under nitrogen or vacuum.
- In addition, PFA’s might form which must be checked out , and if present must be destroyed. Any pyrolysis of fluorine containing polymers might generate small quantities of PFA’s depending.
- There are some commercial processes for this latter step-CFX (Honeywell) and others.

# Carbon: The Forms and Sources (cont.)

- **Pyrolysis processing** yields a metals/ partially oxidized carbon cake which usually goes to the smelter. No carbon recovery.
- **Pyrolysis/Hydroprocessing** may produce an extracted carbon cake which the binder is removed (thermally-PFAS?). It is not known what shape the carbon is in for recycle to anode carbon. Possibly can be used for commercial conductive carbon use.

# Other BM Filter Cakes After Metals Extraction

**LFP:** Previously discussed; the Li is extracted out by several slightly different processes.

But the filter cake usually contains both $FePO_4$ and carbon. Redissolving the cake to remove the anode carbon and reprecipitation of the $FePO_4$ just ramps up the cost. LFP recycling remains problematical presently not profitable without a processing fee.

Flotation recycling can remove the carbon and obtain the intact LFP minus some Li. Should be slightly profitable.

US Patent 12,021,207 (06/25/24)

# Recycling Other Lithium Batteries

- **Lithium batteries with <u>lithium metal</u> anodes, primary and secondary, are** usually crushed and delivered immediately into water ***carefully.*** The Electrolyte is not recovered and is hydrolyzed in the very basic water--- a potentially flammable situation. The Li should be recovered.

--<u>Secondaries Li metal anodes:</u> Low levels of carbon in the recoverable NMC filter cake from these secondaries. The carbon might be recovered as described earlier. Li can be recovered.

<u>--Primaries Li metal anodes:</u> Usually do not have NMC cathodes but do have carbon and/or manganese dioxide –(EMD) in the cathode. The electrolyte is not recovered, and the mixed cathode materials are not recovered since there currently is no Co or Ni present. Li can be recovered.

# Recycling Other Lithium Batteries (cont.)

**Lithium sulfur batteries**: Just coming on the scene; These have the potential of generating some hydrogen sulfide if not carefully processed.  They  are not compatible with a regular NMC or LFP recycling line.

The waste water also contains sulfide anion which is problematical and must be removed or oxidized to sulfur and removed/ filtered.

**OTHER TYPES:** Need to be discussed case by case with the recycler.

# Manganese?

- Up to now not much attention has been paid to isolating the manganese.  It is usually kept with the NC as NMC and smelted or processed hydrometallurgically NMC MMH or the sulfate.

- How will the newest high manganese candidate LiMnNC with 60+%  Mn be recycled?  This is an announced joint development from LG and GM.

- Manganese dioxide ore is very in low cost (10-15 cents/lbs.) compared to all other metal oxides but is  imported. ($MnSO_4$ is $0.45/lbs.)  EMD is about $1/lb

# Manganese?

- Since LiMnNC is still an NMC cathode, it should be recycled the same way.  However, the value of the recovered metals is much less because the amount of Ni and Co is much less; essentially less than half of the value/amount  in standard NMC (811).   The larger percentage of Mn will have to be removed  since it is a diluent to the value of the Co plus Ni and subsequent processing even if smelted.

# Removing Manganese (cont.)

- The technical literature is replete with processing to remove and to isolate Manganese as the oxide/dioxide.
- The BM obtained from a high 60%+ Mn -- LiNMC battery will probably require hydrometallurgical processing. From the solution of NMC sulfates obtained from these provesses, the Mn can be selectively oxidized and filtered off leaving the smaller amounts of Ni and Co in solution.
- There may be smelting schemes for making suitable alloys with this high manganese BM, but it will command a significant lower value probably breakeven if lucky.
- An alternative might be the use of flotation to isolate the intact LiMnNC cathode material from the anode carbon for direct reprocessing to pCAM/CAM for GM/LG.

# Recent US Recycling Patents by American Hyperform, inc.

- **11,316,208**

Optimum hydrometallurgical process for extracting BM using SO2 and sulfuric acid to produce solutions of NMC sulfate and carbon cake.

- **11,710,857**

Continuation of 11,316,208.

- **11,932,554**

CAM and pCAM from recycled Lithium ion and NIMH batteries

- **11,909,018**
- NIMH Battery Recycling

# Continued -

# Recent US Recycling Patents American Hyperform

- **12,201,207**

  Flotation Method for Recovering Lithium-ion Battery Cathode Material from Recycled Lithium-ion Batteries and Lithium-ion Production Scrap. (Adaptable for LFP recycling at the lowest possible cost recycling and the highest value product.)

- **Othe Applications Pending**

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