Recycling of Li-Ion Batteries

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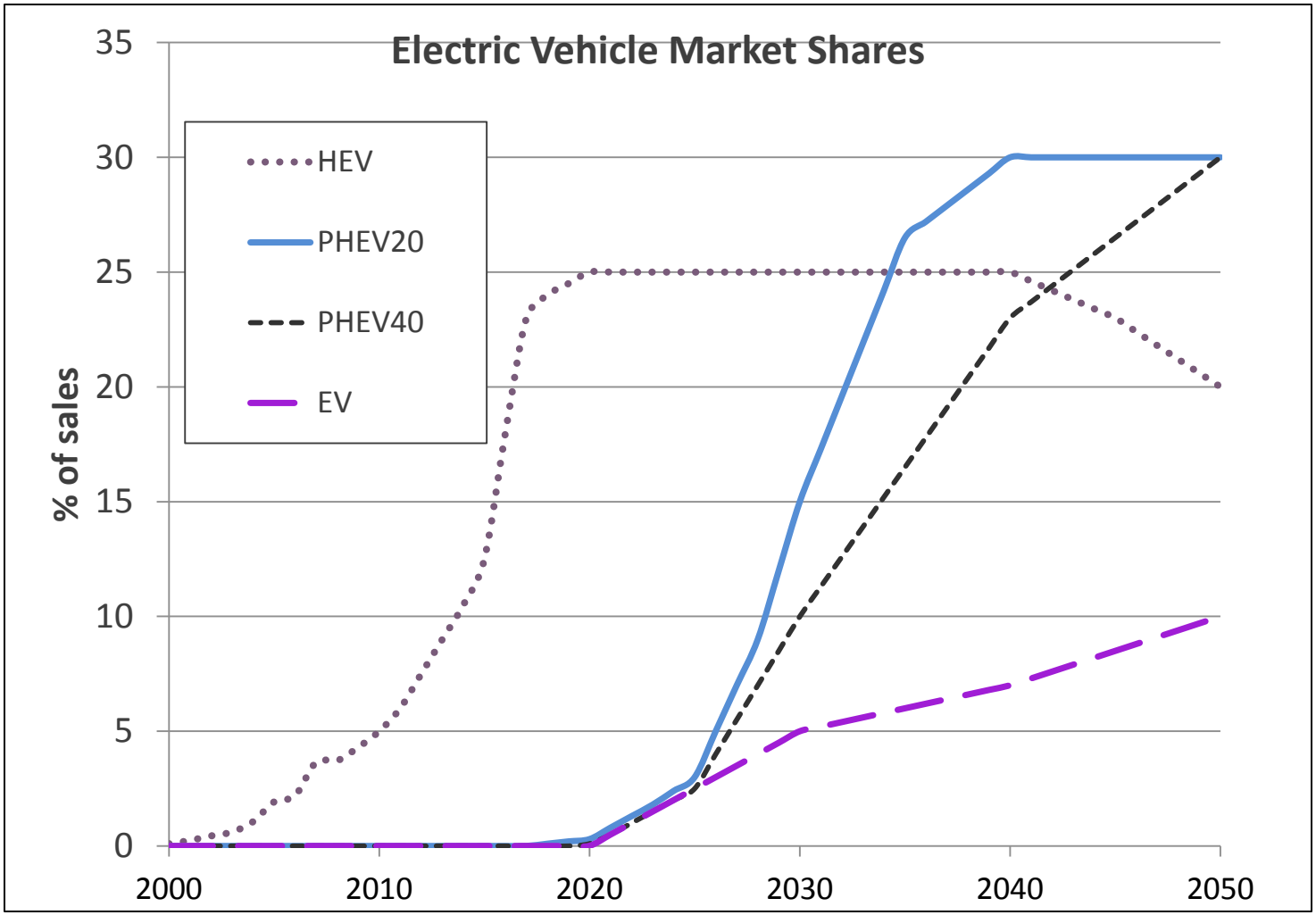
We don’t want to trade one crisis for another!

- Battery material shortages are unlikely
  - We demonstrated that lithium demand can be met
  - Recycling mitigates potential scarcity
- Life-cycle analysis checks for unforeseen impacts
- We need to find something to do with the used materials
  - Safe
  - Economical

We answer these questions to address material supply issues

- How many electric-drive vehicles will be sold in the US and world-wide?
- What kind of batteries might they use?
  - How much lithium would each battery use?
- How much lithium would be needed each year?
  - How much difference can recycling make?
- How does the demand compare to the available resources?
- Are there possible constraints on other key material supplies?
  - Will there be enough cobalt? Nickel? Manganese?

We chose an optimistic market penetration scenario



Source: Multipath Study Phase 1, Maximum Electric Scenario, http://www1.eere.energy.gov/ba/pba/pdfs/multipath_ppt.pdf

Then we looked at battery composition

System → Electrodes ↓	NCA Graphite	LFP (phosphate) Graphite	MS (spinel) Graphite	MS TiO
Positive (cathode)	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	$LiFePO_4$	$LiMn_2O_4$	$LiMn_2O_4$
Negative (anode)	Graphite	Graphite	Graphite	$Li_4Ti_5O_{12}$

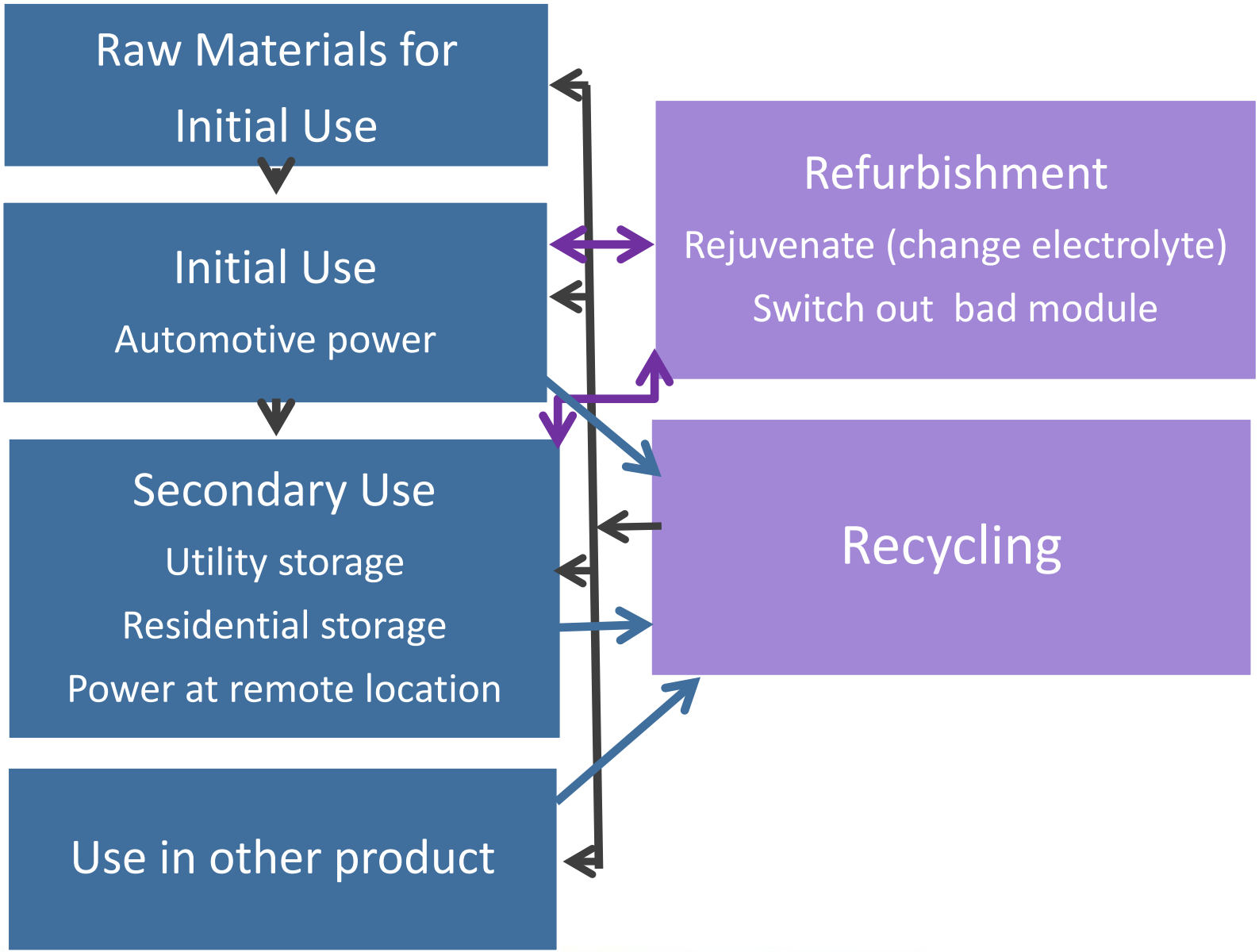
- **We considered four battery chemistries**
- **All contain lithium in cathode**
- **One uses lithium in anode as well**
- **Electrolyte contains lithium salt ($LiPF_6$) in solution**

We calculated lithium required per battery pack

- **Total is sum of Li from cathode, electrolyte, and anode (for titanate)**

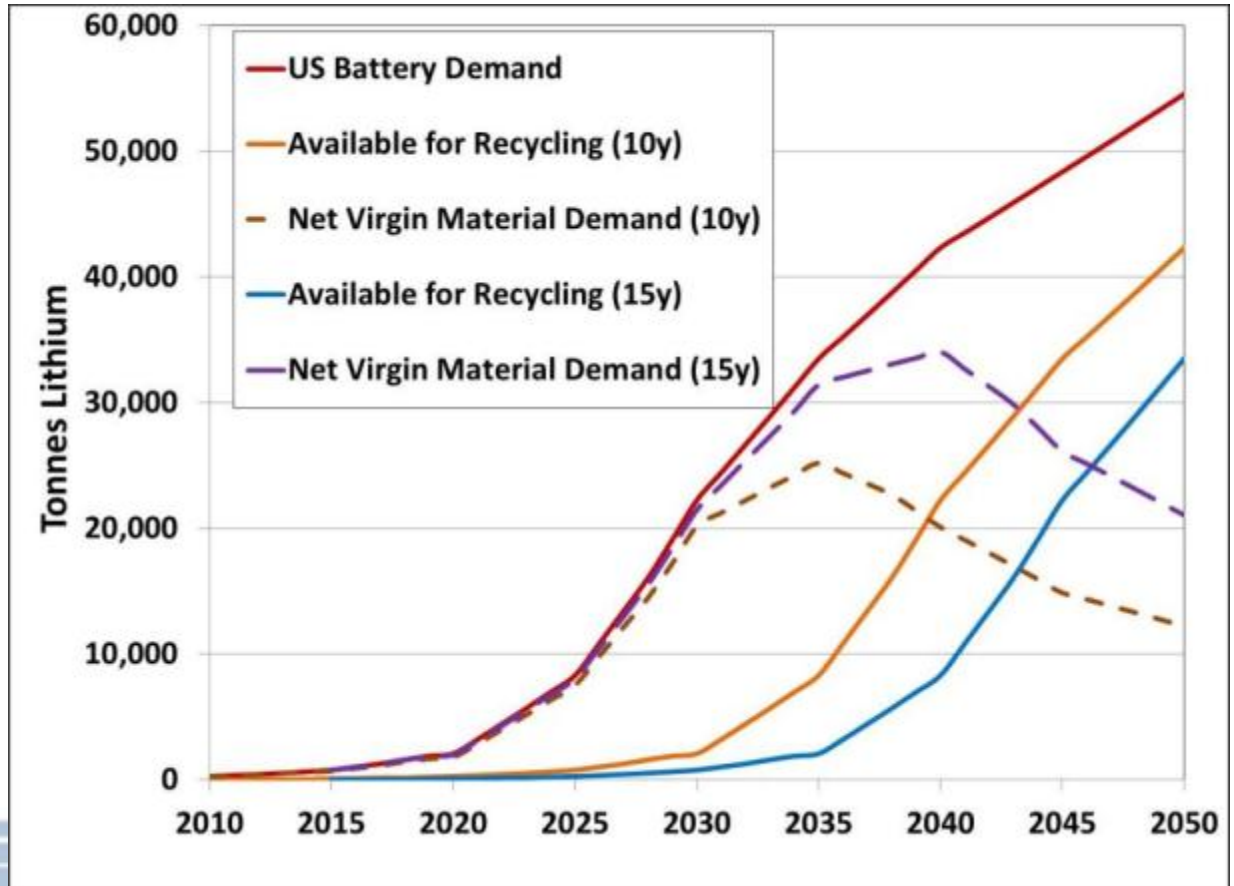
Battery Type	NCA-G				LFP-G				LMO-G				LMO-TiO			
Vehicle range (mi) at 300 Wh/mile	4	20	40	100	4	20	40	100	4	20	40	100	4	20	40	100
Li in cathode (kg)	0.34	1.4	2.8	6.9	0.20	0.80	1.6	4.0	0.15	0.59	1.18	3.0	0.29	1.2	2.3	5.8
Li in electrolyte (kg)	0.04	0.10	0.20	0.55	0.045	0.14	0.26	0.66	0.03	0.09	0.17	0.43	0.05	0.17	0.34	0.85
Li in anode (kg)	0	0	0	0	0	0	0	0	0	0	0	0	0.30	1.21	2.4	6.1
Total Li in battery pack (kg)	0.37	1.5	3.0	7.4	0.24	0.93	1.9	4.7	0.17	0.67	1.4	3.4	0.64	2.5	5.1	12.7

Battery materials could get used multiple times

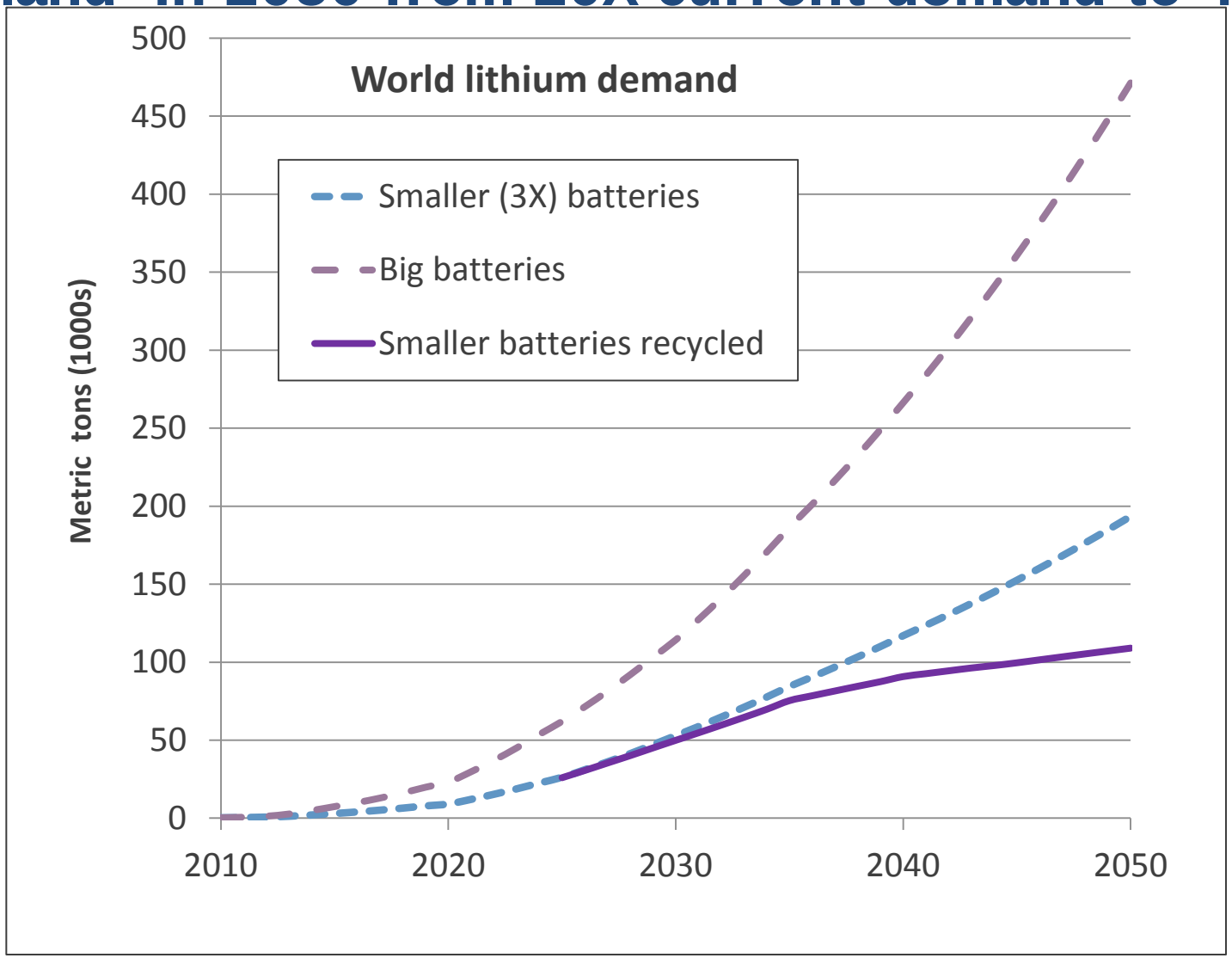


A word about battery reuse

- **Reuse takes battery directly back to lower-performance use**
- **Nissan will reuse batteries to store energy from PV panels or to store back-up power**
- **Reuse delays return of material for recycling and increases peak demand for virgin material**
  - Assumes virgin material would not be used for backup batteries



Recycling with smaller batteries reduces world demand in 2050 from 20X current demand to 4X



IEA assumed 12-18 kWh batteries

Known Li reserves could meet world demand to 2050, even under high demand scenario

	Cumulative demand to 2050 (Contained lithium, 1000 Metric tons)
Large batteries, no recycling	6,474
Smaller batteries, no recycling	2,791
Smaller batteries, recycling	1,981
	Reserve Estimates
USGS Reserves*	13,000
USGS World Resource*	29,000
Other Reserve Estimates	30,000+

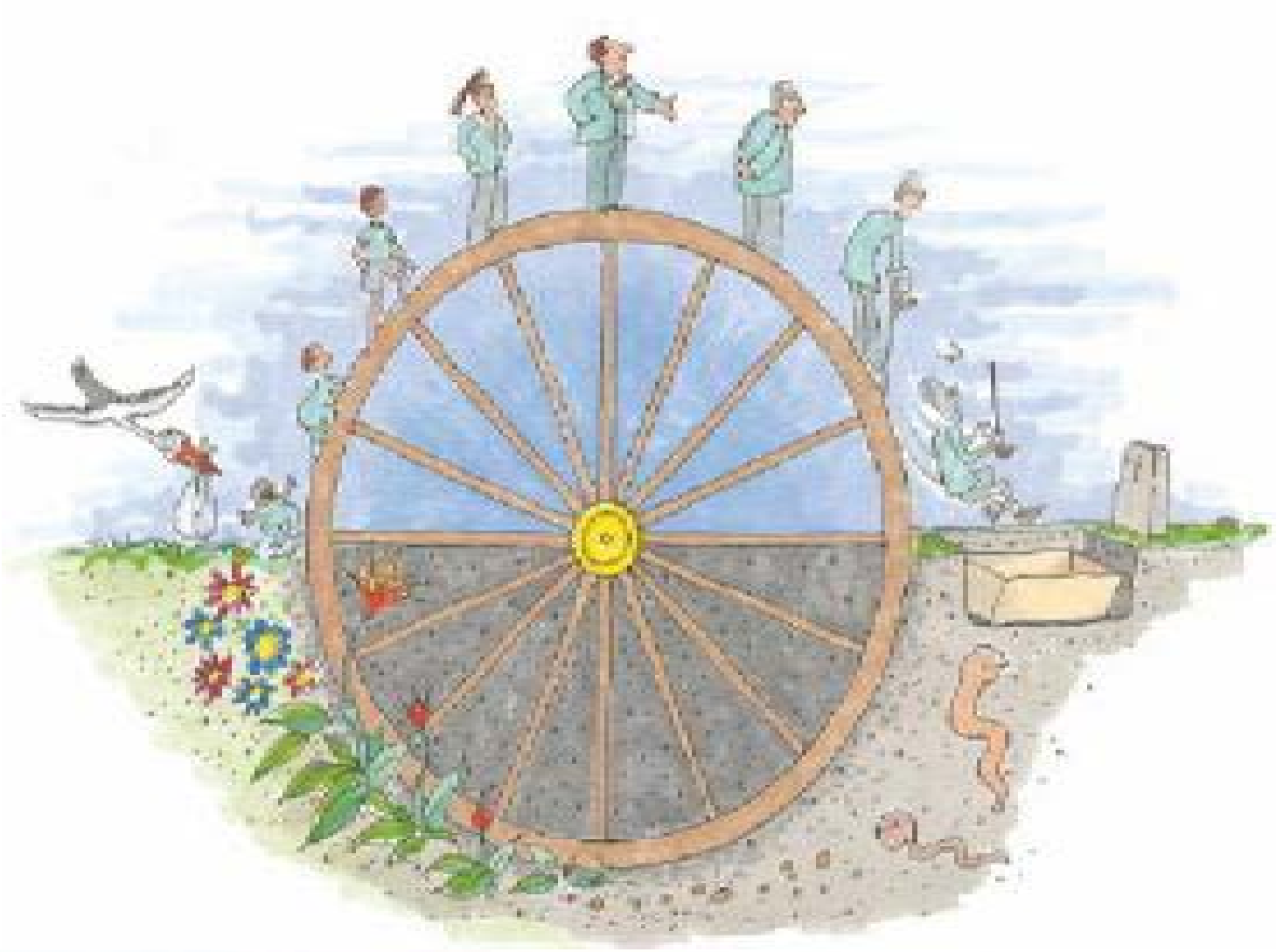
*Revised January 2011
http://minerals.usgs.gov/minerals/pubs/commodity/lithium/mcs-2011-lithi.pdf

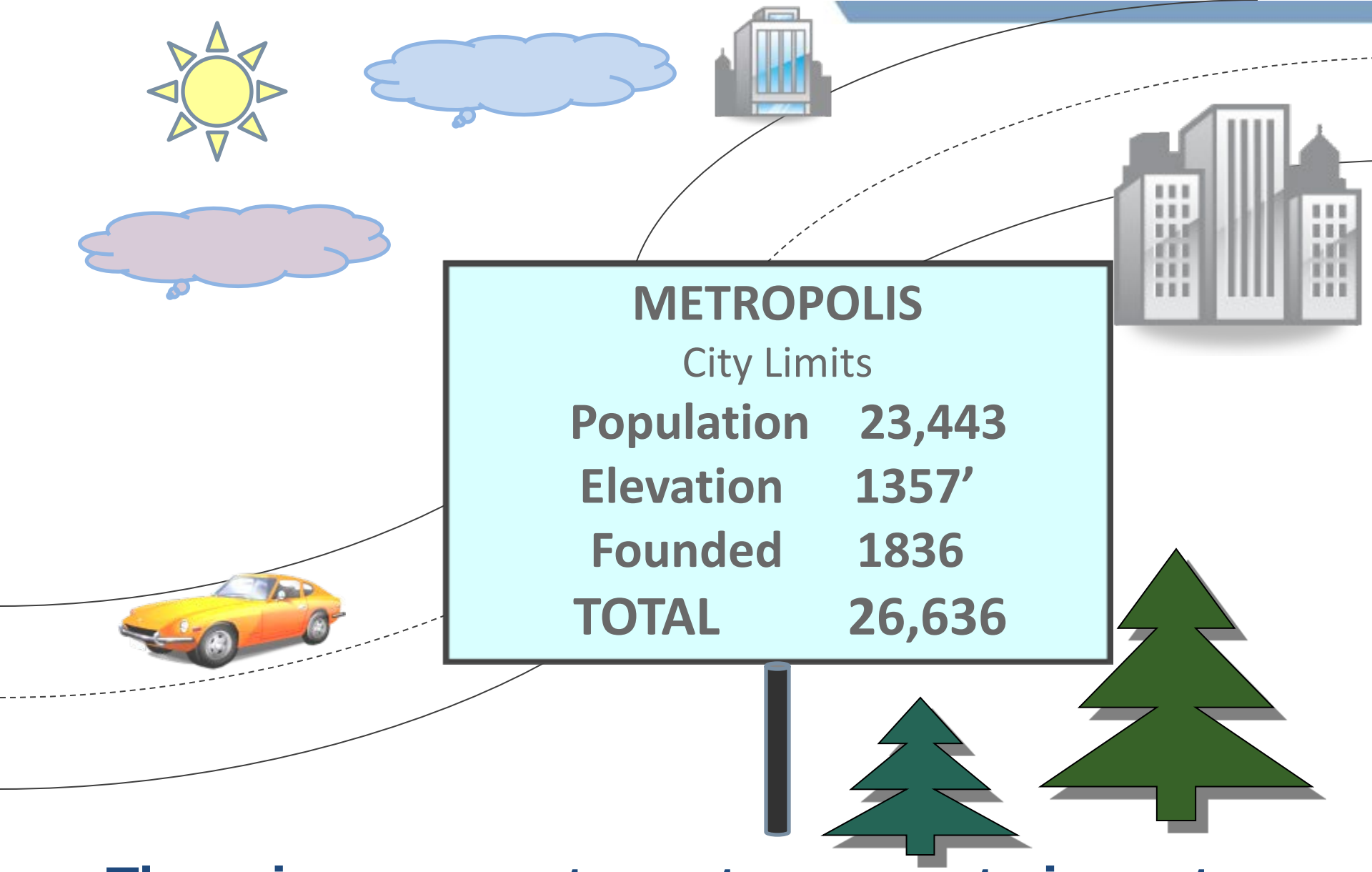
U.S. cobalt use could make dent in reserve base by 2050

Material	Availability (million tons)	Cumulative demand	Percent demanded	Basis
Co	13	1.1	9	World reserve base
Ni	150	6	4	World reserve base
Al	42.7	0.2	0.5	US capacity
Iron/steel	1320	4	0.3	US production
P	50,000	2.3	~0	US phosphate rock production
Mn	5200	6.1	0.12	World reserve base
Ti	5000	7.4	0.15	World reserve base

Lifecycle analysis compares all process impacts

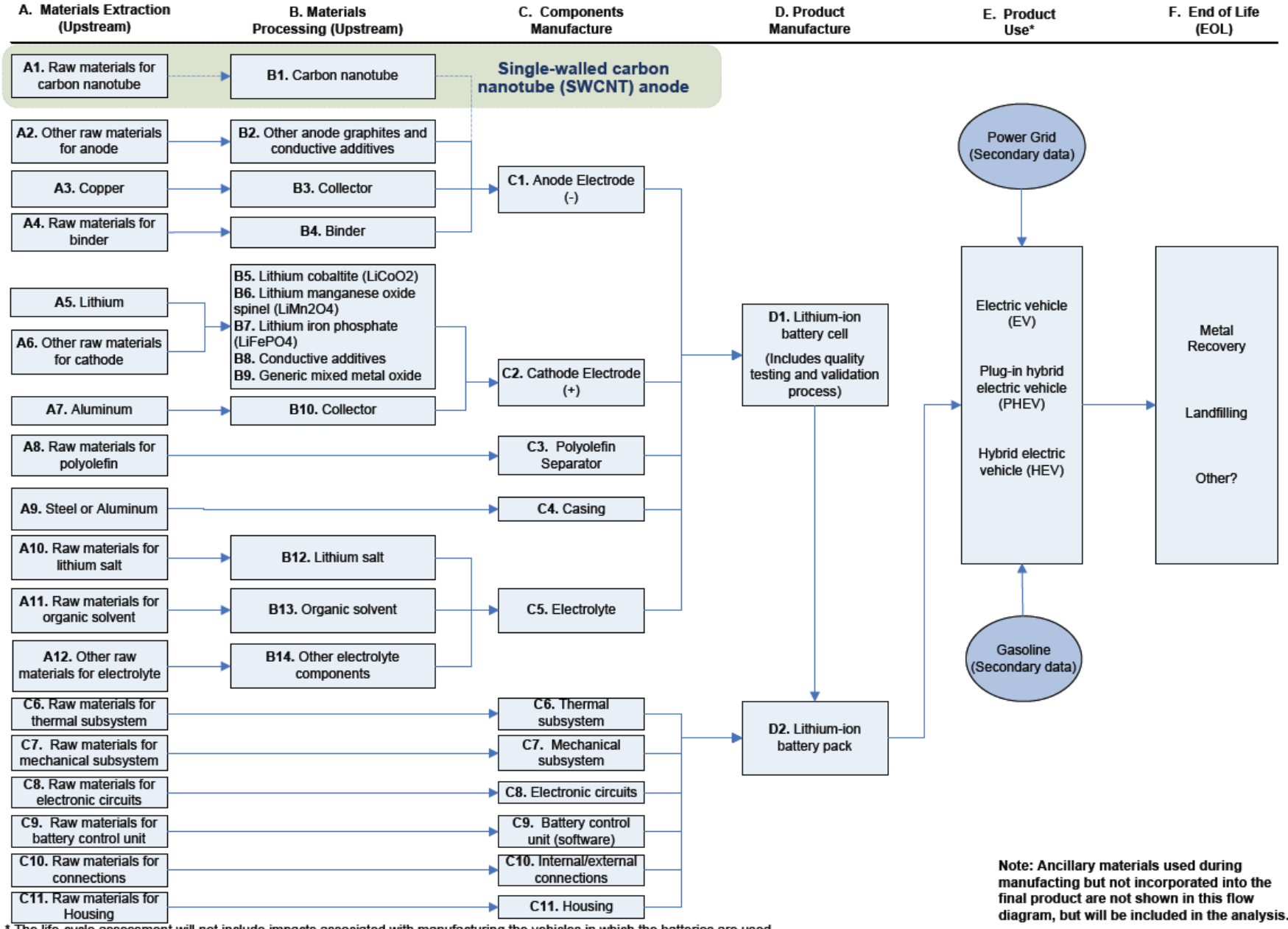
of a product's life cycle, from raw material acquisition through production, use, end-of-life treatment, recycling, and final disposal if any.





There is no correct way to aggregate impacts into a single “score.”

Generic Process Flow Diagram for Passenger Vehicle Energy Systems, Focusing on Lithium-ion Batteries

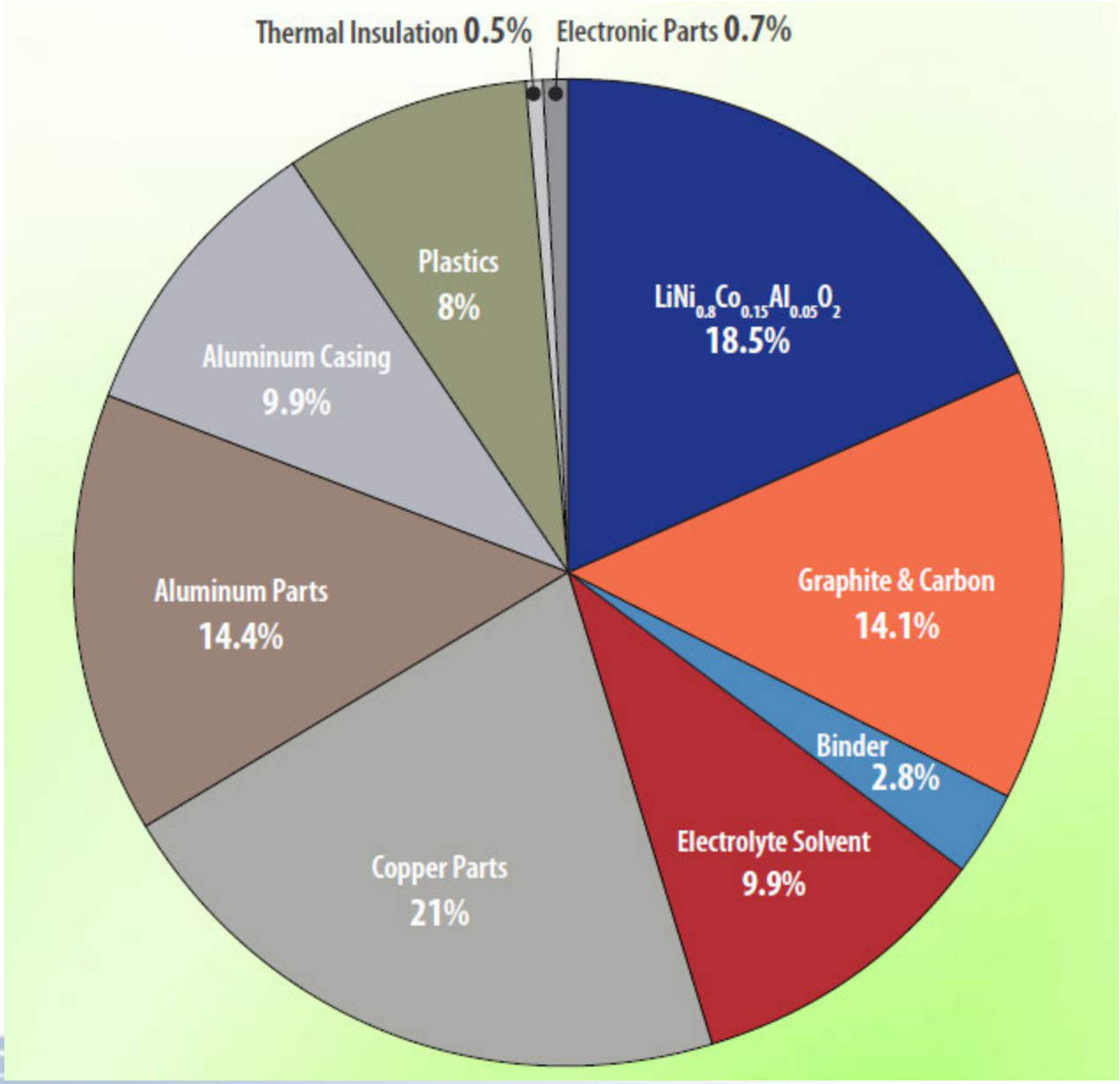


Note: Ancillary materials used during manufacting but not incorporated into the final product are not shown in this flow diagram, but will be included in the analysis.

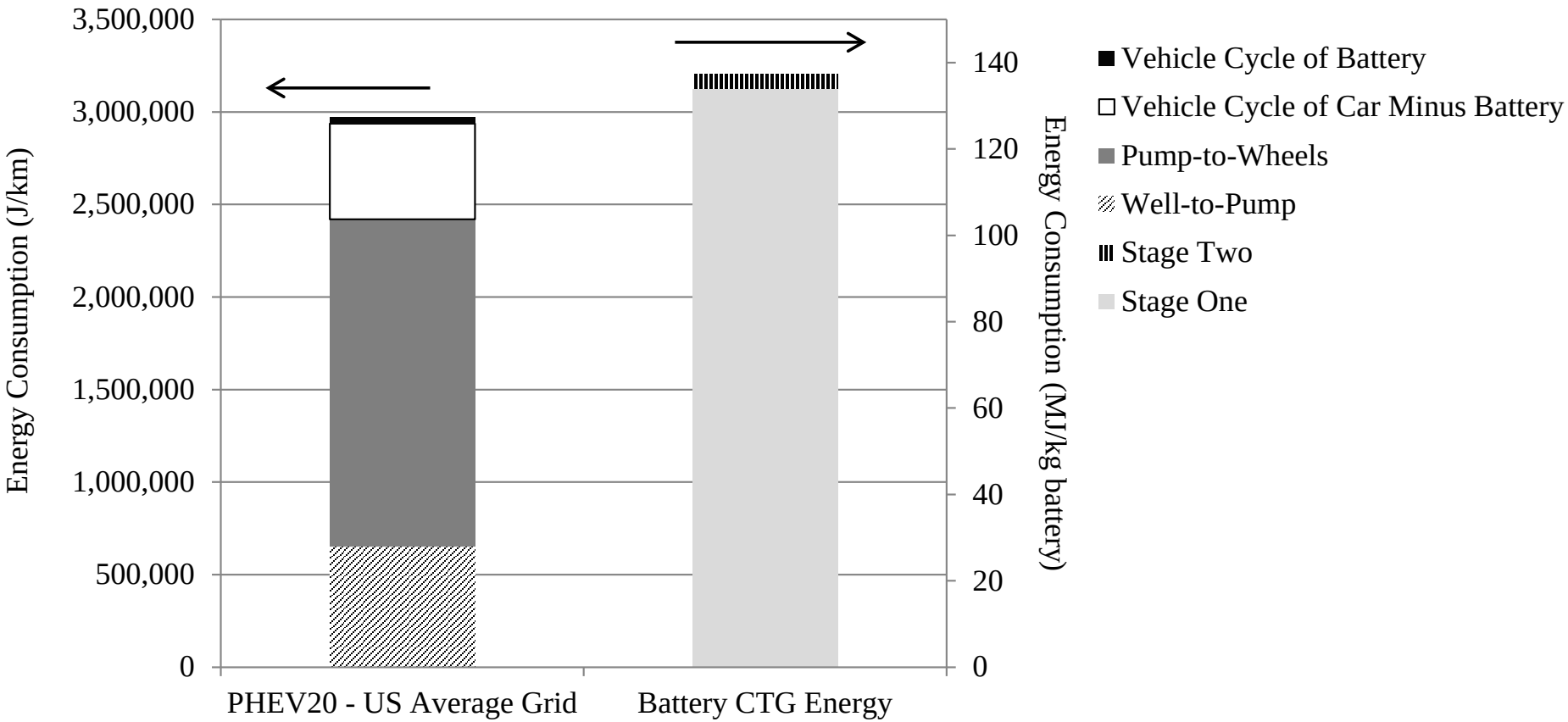
* The life-cycle assessment will not include impacts associated with manufacturing the vehicles in which the batteries are used.

Sources: EPA, Design for Environment, Nanotech Partnership; Components of lithium ion rechargeable batteries, NEC/TOKIN (http://www.nec-tokin.com;
Olapiriyakul, S, Caudill, RJ. *A Framework for Risk Management and End-of Life (EOL) Analysis for Nanotechnology Products*: A Case Study in Lithium-Ion Batteries. IEEE.
Ganter, MJ, Seagar, TP, Schauerman, CM, Landi BJ, Raffaelle, RP. *A Life Cycle Energy Analysis of Single Wall Carbon Nanotubes Produced Through Laser Vaporization*. Rochester Institute of Technology.
Electropedia, Battery and Energy Technologies, Lithium Ion Battery Manufacturing (http://www.mpoweruk.com/battery_manufacturing.htm accessed on June 7, 2010)

The bulk of battery materials are well characterized; we concentrated on the others



Battery materials are responsible for only 2% of energy but 20% of life-cycle SOx!

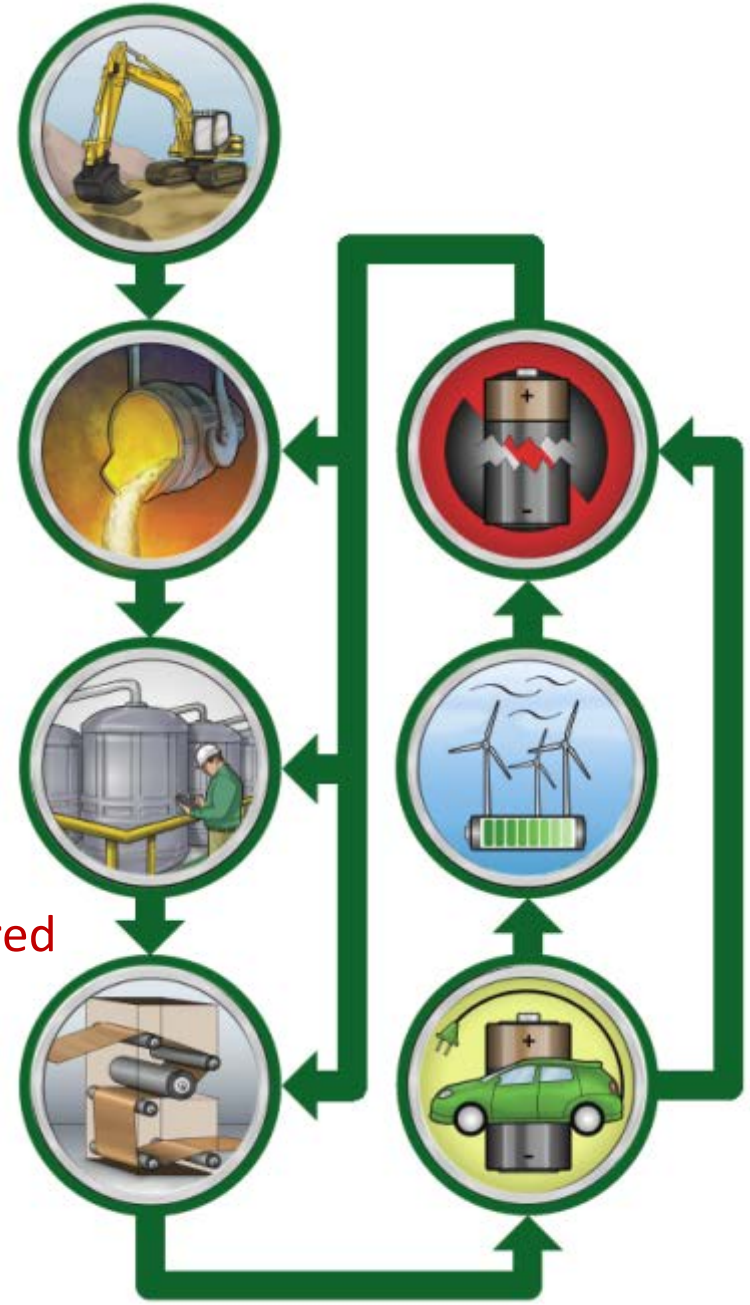


Battery impacts rise with all-electric range.

Why think about recycling?

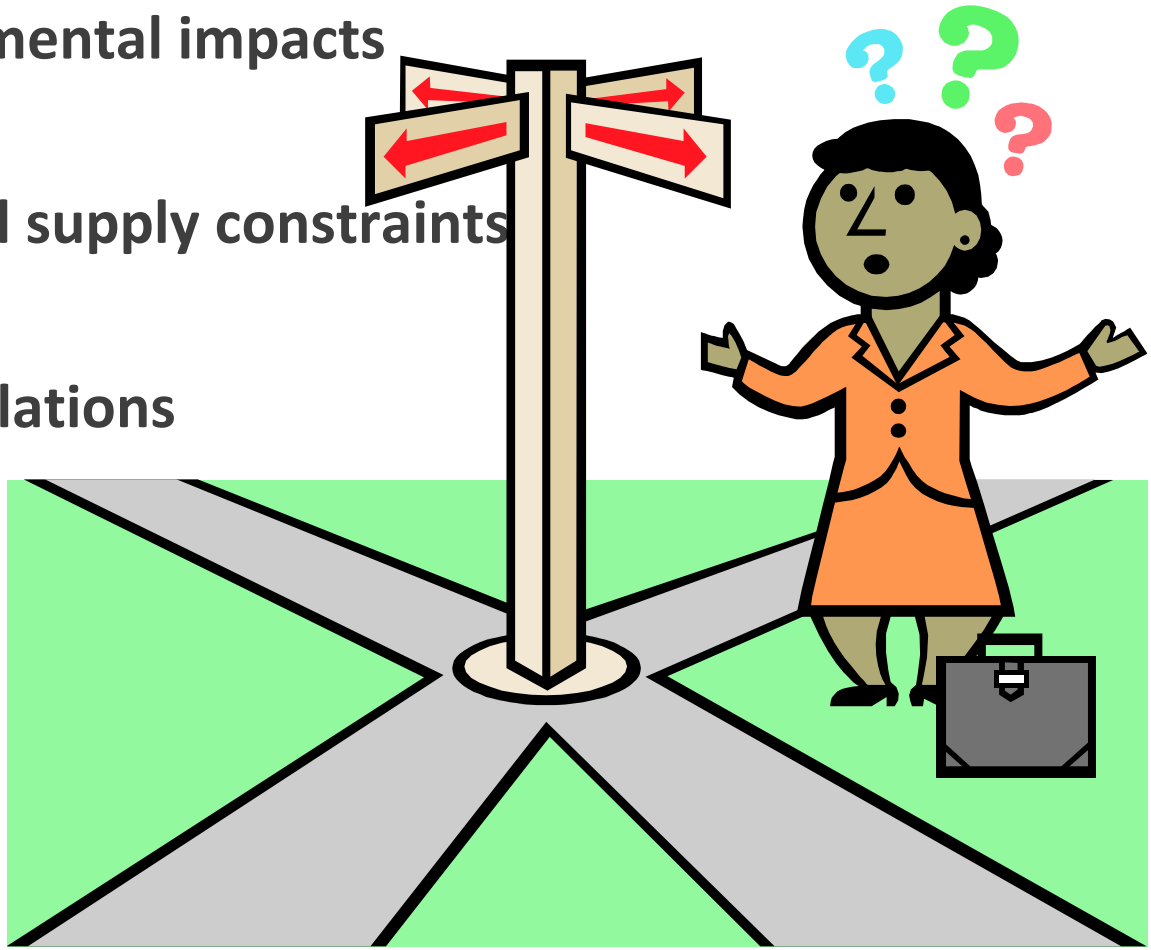
- Material scarcity alleviated
- Recycled materials cheaper
- Production impacts avoided
  - Energy use
  - Emissions
  - Mining impacts
- Legally required

- But not all recycling processes are created equal
- Which is best?
  - LCA identifies "greenest" processes
  - May not be most economical
    - Economics depends on what is recovered
  - There may be other issues as well



Recycling processes will be compared using several interconnected criteria

- Reduction of environmental impacts
- Energy savings
- Alleviation of material supply constraints
- Economics
- Compliance with regulations
- Feed requirements
- Utility of products
- Scale



The key factor in Li-ion battery recycling is economics

- Value of elements contained may be low
- Value of active materials is high
- Objective is to recover highest value possible product

Cathode	Price of Constituents ($/lb)	Price of Cathode ($/lb)
$LiCoO_2$	$9.90	12.00[3,4]
$LiNi_{.3}Co_{.3}Mn_{.3}O_2$	$6.10	$8.80[4]
$LiMnO_2$	$1.35	$4.50[2]
$LiFePO_4$	$0.75[1]	$9.10[2]

Sources:
1 Battery Recycling Technology, T. Ellis and J. Hohn, RSR Technologies (adjusted)
2 Modeling of Manufacturing Costs of Lithium-Ion Batteries for HEVs, PHEVs, and EVs, D. Santini, K. Gallagher, and P. Nelson
3 http://www.asianmetal.com/news/viewNews.am?newsId=782720
4 Chinese prices of cathode material for lithium-ion batteries rise, Metal-Pages (8/17/11)

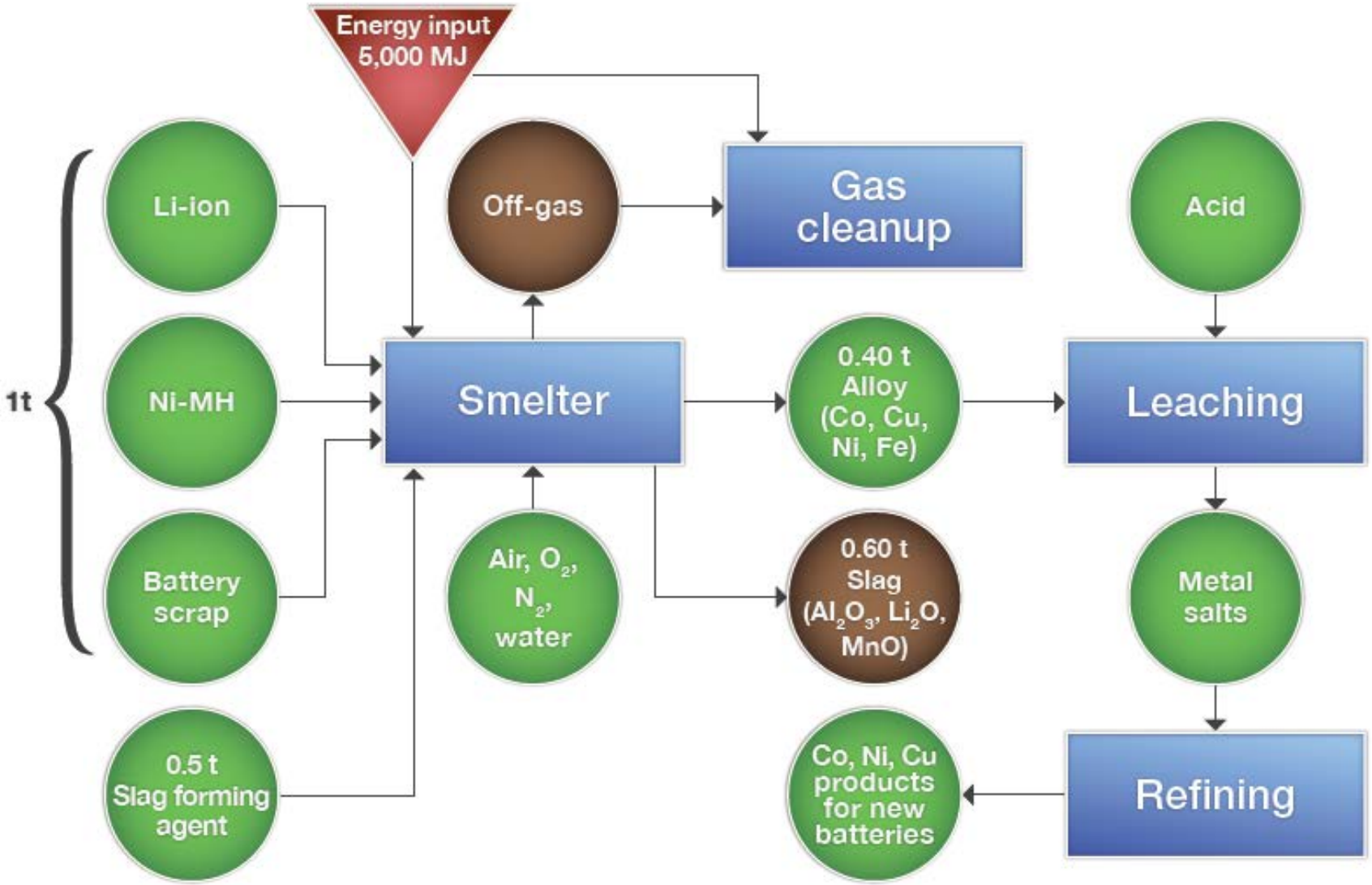
Rest-of-battery recycling will help economics

- In Europe, 50% of cell materials must be recycled as of 9/26/11
  - Collection is assumed
- The rest of the battery is included in the 95% auto recycling requirement
  - This may include enough valuable materials to make recycling the battery pay, even if $LiFePO_4$ cathodes are used
- The responsibility for recycling belongs to the company that makes the consumer product

Smelting processes avoid metal ore processing

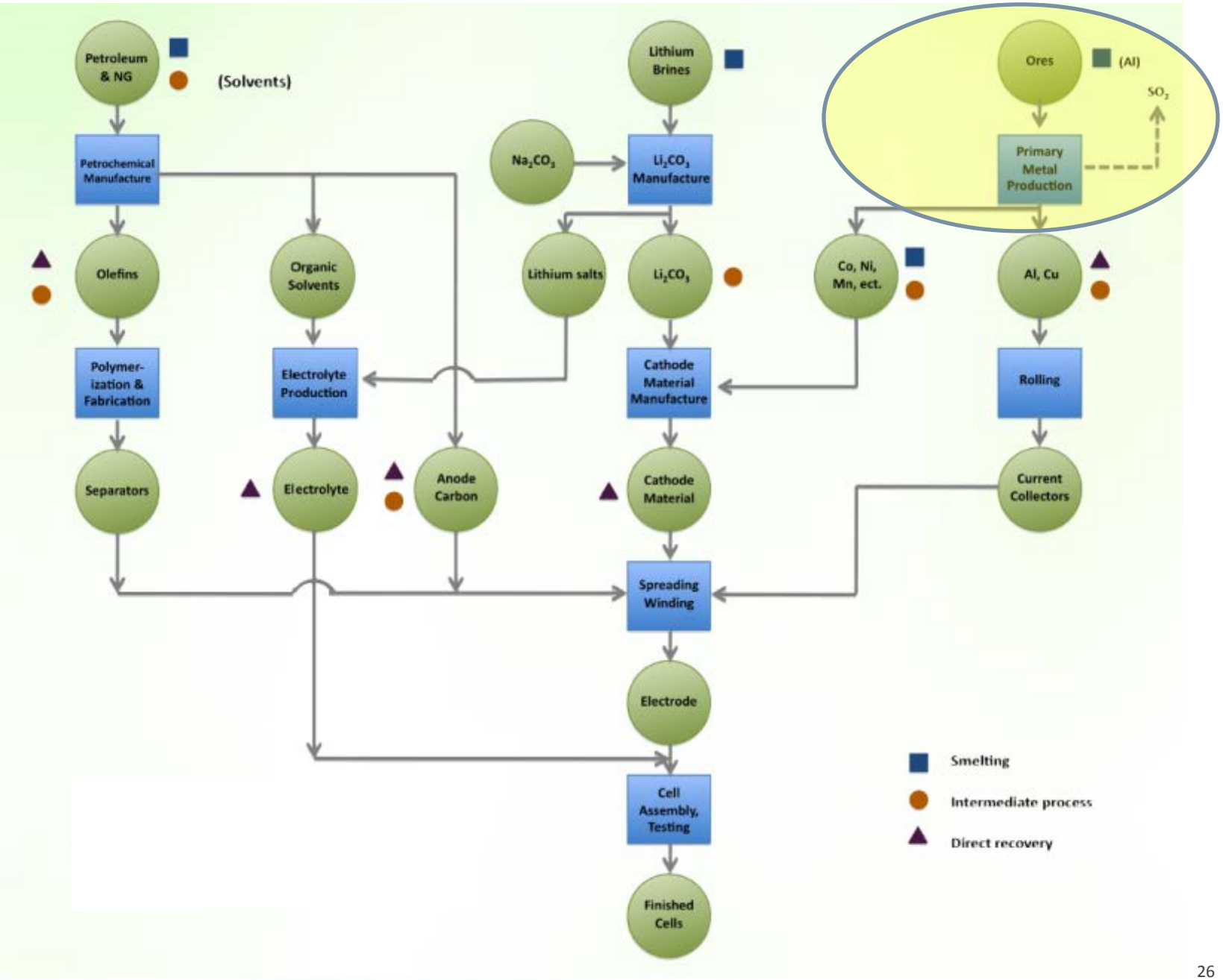
- **These can take just about any input, high volume**
- **High-temperature required**
  - Organics are burned for process energy
- **Valuable metals (Co, Ni, Cu) recovered and sent to refining**
  - Suitable for any use
  - 70% of cobalt production energy saved; sulfur emissions avoided
  - Fabrication still needed
  - Less Co → less value
- **Volatiles burned at high-T**
- **Li, Al go to slag**
  - Could be recovered

Commercial smelting process recovers metals



In Finland, batteries are collected and sent to a small plant

They are sorted and chopped up


Petroleum & NG
(Solvents)
Lithium Brines
Ores
(Al)
SO_2
Petrochemical Manufacture
Na_2CO_3
Li_2CO_3 Manufacture
Primary Metal Production
Olefins
Organic Solvents
Lithium salts
Li_2CO_3
Co, Ni, Mn, ect.
Al, Cu
Polymer-ization & Fabrication
Electrolyte Production
Cathode Material Manufacture
Rolling
Separators
Electrolyte
Anode Carbon
Cathode Material
Current Collectors
Spreading Winding
Electrode
Cell Assembly, Testing
Finished Cells
Smelting
Intermediate process
Direct recovery

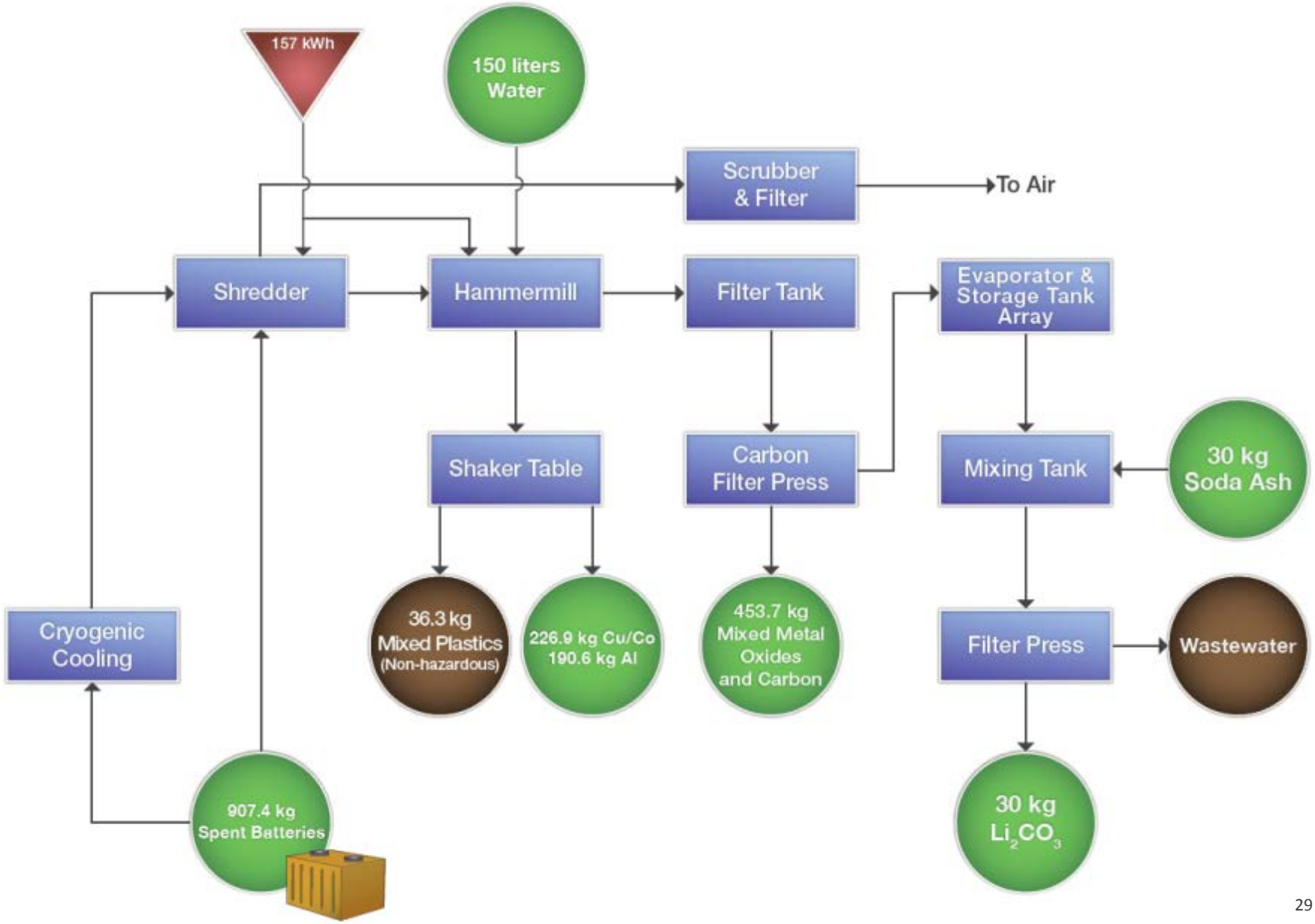
What if another cathode is used instead of $LiCoO_2$?

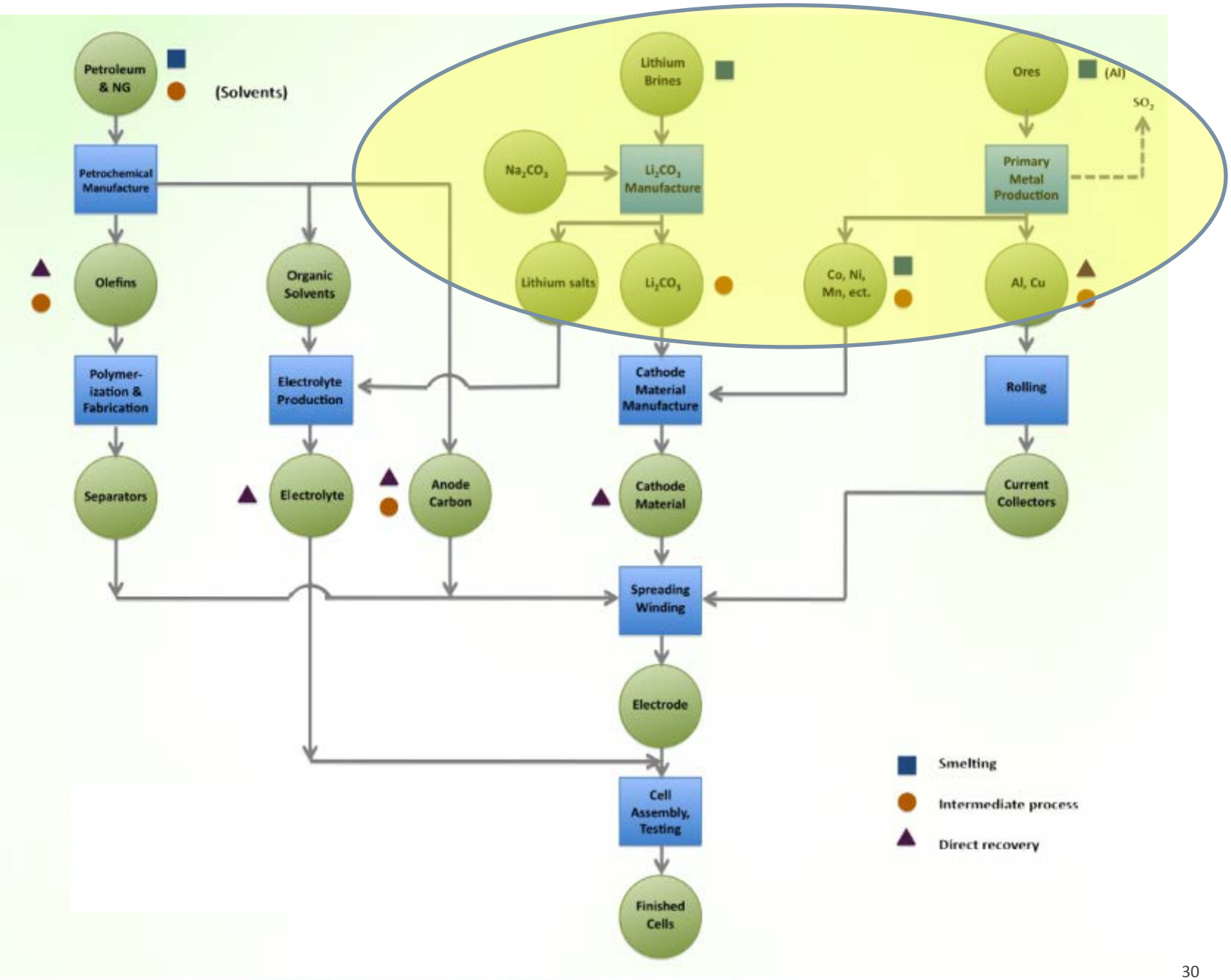
- **Value of product stream is reduced**
  - Cu is still recovered in smelter
  - Co plant probably won't want the shredded batteries
- **Ni reports to the product stream, where it is recovered**
- **Li, Al, Mn, and Ti from titanate anodes all go to the slag**
- **Heat available for smelter is reduced if titanate replaces carbon**
- **Fe from the $LiFePO_4$ will be partially in the metal fraction and partially in the slag with the phosphate**
- **Materials can be recovered from slag if value high enough, but process may have greater impacts than primary production**

DOE is funding a large-format battery recycling facility

- **New plant will recycle Ni-MH and Li-ion batteries**
- **Undisclosed process will separate/isolate constituents to produce battery-ready materials**
  - **From Ni-MH batteries**
    - Rare earths
    - Nickel
  - **From Li-ion batteries (possible)**
    - Anode materials
    - $LiCoO_2$
    - $LiFePO_4$
    - Electrolyte (EC, EMC, DC)

Toxco Ohio plant will use improved process to recover lithium as well as metals




Petroleum & NG
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Li_2CO_3 Manufacture
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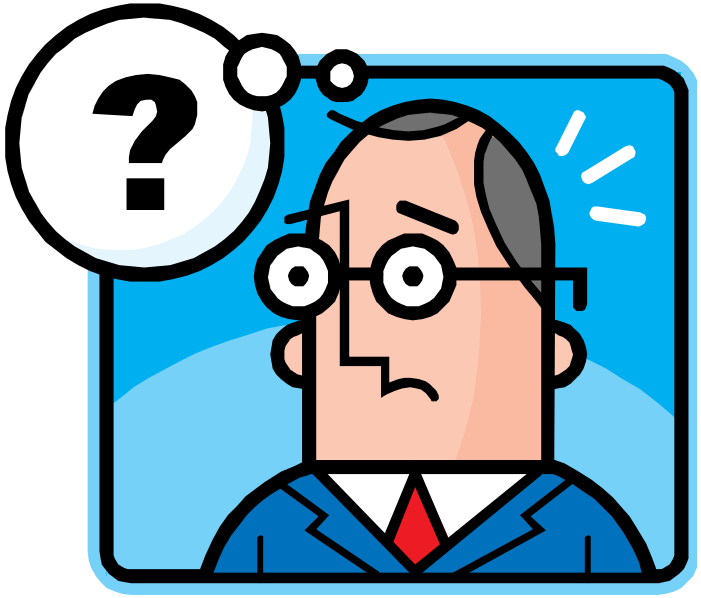
Al, Cu
Cathode Material Manufacture
Rolling
Cathode Material
Current Collectors
Spreading Winding
Electrode
Cell Assembly, Testing
Finished Cells
Smelting
Intermediate process
Direct recovery

What if another cathode is used instead of $LiCoO_2$?

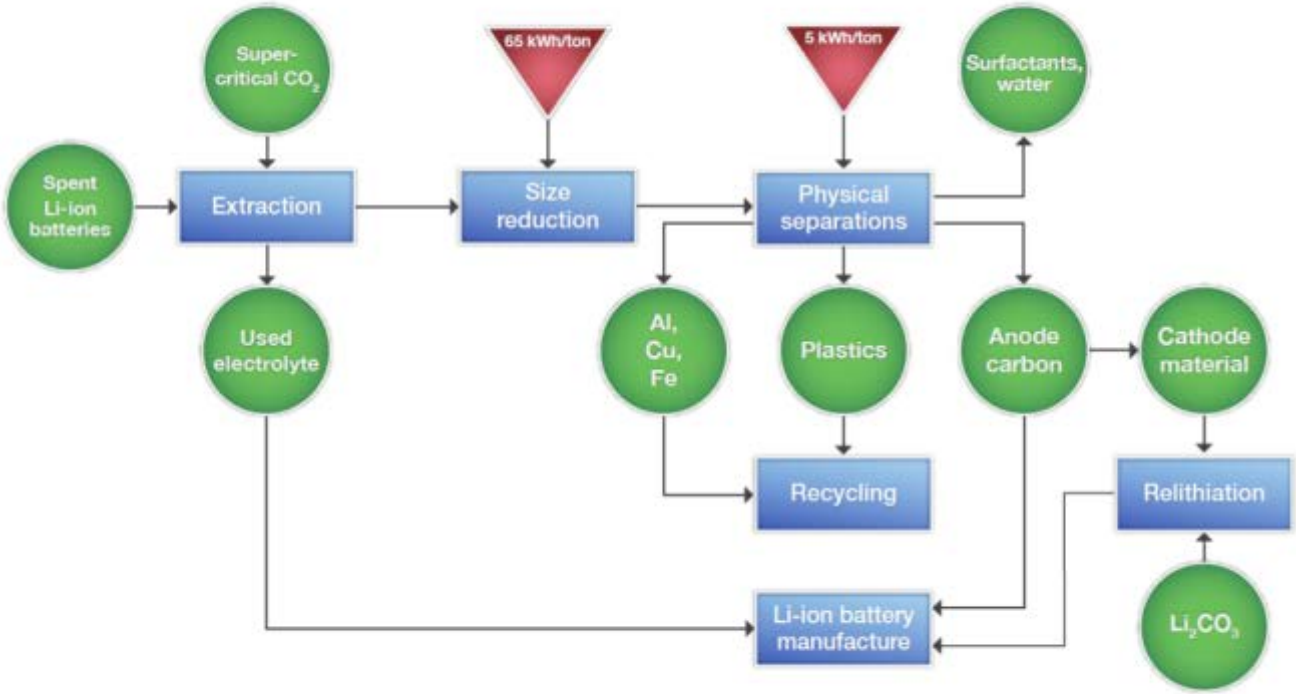
- Revenue from cobalt stream will decline
- New process design may be able to recover cathode materials
- Fate of Mn and Ni uncertain
- Iron phosphate could be a contaminant
- Titanate (anode) might require separate batch processing

- There is much work to be done here! Stay tuned.



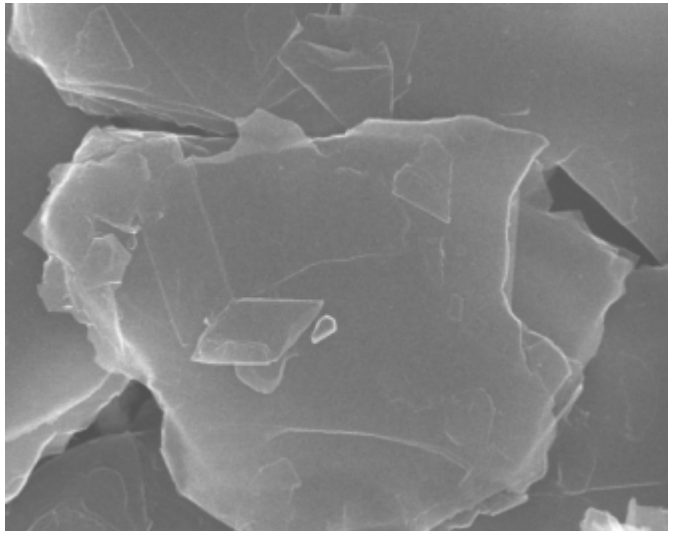
Recovery of battery-grade materials avoids impacts of production from raw materials

- **Requires as uniform feed as possible**
- **Components are separated to retain valuable material structure**
  - Costs lower than virgin materials
  - Purify/reactivate components if necessary for new batteries
  - Separator is unlikely to be usable, as form cannot be retained
- **Low-temperature process, low energy requirement**
- **Does not require large volume; could process prompt scrap**

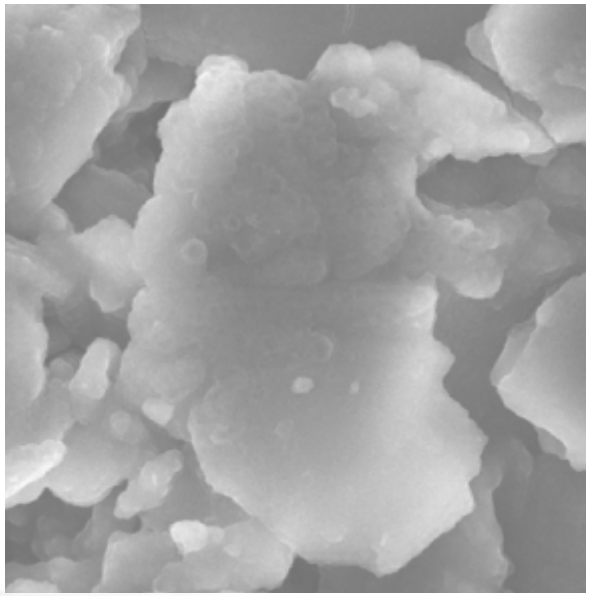


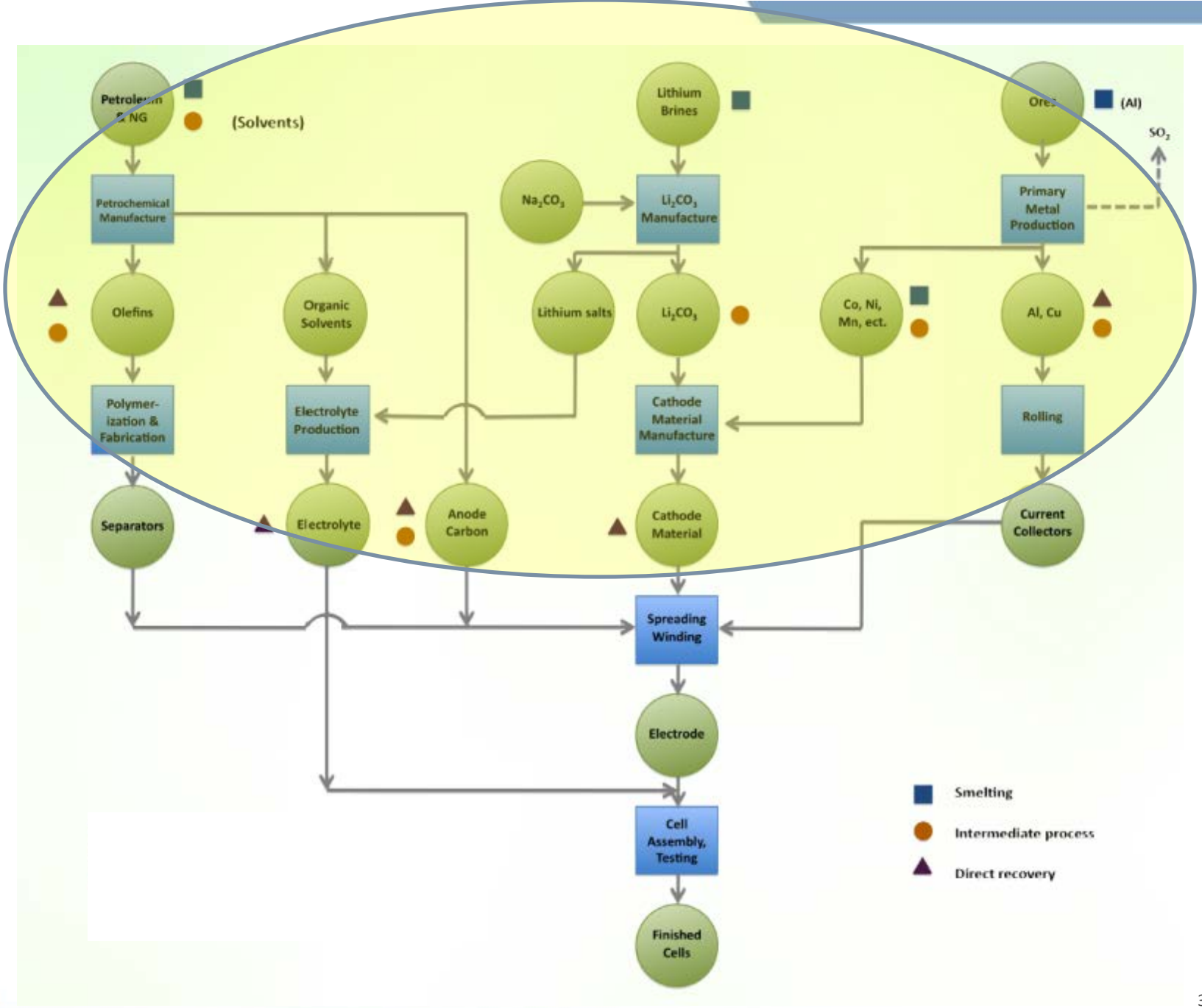
Active materials may be degraded after use

- Quality and performance must be verified
- Treatment to upgrade could be developed
- Material may be suited for lower-performance uses
- Number of re-uses might be limited for some materials
- Material may be obsolete when recovered



Graphite:
New and after 50% power fade

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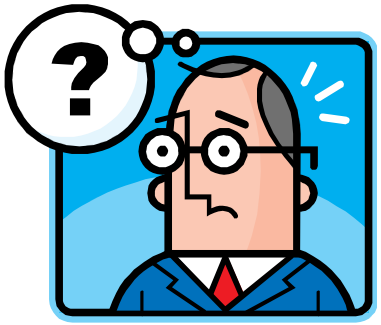
What if another cathode is used instead of $LiCoO_2$?

- Process should work, with minor modifications
  - Demonstration has been funded
  - Also demonstrated with Ni-MH
- Work in progress to separate mixed cathode streams
- High-value cathode material could still be recovered for possible reuse in new batteries
  - Even if cathode made from low-cost raw materials
  - But will the material be obsolete when it is recovered?
  - Could other high-value products be produced?



- We haven't even begun to think about Li-S or other developmental chemistries yet.

Recycling processes differ in important ways

	Pyrometallurgical	Hydrometallurgical	Physical
Temperature	High	Low	Low
Materials recovered	Co, Ni	Metals, Li_2CO_3	Cathode, anode, electrolyte, metals
Feed requirements	None	Separation desirable	Single chemistry required
Comments	New chemistries yield reduced product value	New chemistries yield reduced product value	Recovers potentially high-value materials; Could implement on home scrap

Plastics can be made into C-nanotubes

- **Argonne has developed a process for plastic bags**
  - Vilas Pol is developer
  - Process could be used for battery plastics
- **React with cobalt acetate catalyst at 700˚ C, cool 3 hours**
  - Recover catalyst when battery recycled
- **C-nanotube anodes are produced**
  - Now made from petroleum at ~$100/gram
  - Recycling process would be cheaper
- **Argonne solvent extraction process also could be used to recover battery plastics**
  - Could utilize plastic stream from Toxco/Kinsbursky or Eco-Bat

Several strategies could facilitate recycling

- Standard configuration enables recycling equipment
- Chemistry standardization reduces need for sorting
- Cell labeling enables sorting
- Design for disassembly enables material separation
- SAE working group is discussing recycling issues

Thank you!

- Work sponsored by USDOE Office of Vehicle Technologies
- Contact me: lgaines@anl.gov