Li ion battery durability vs. a circular economy strategy
Global sustainability trend to encourage strategies supporting a circular economy for Li-ion batteries

- China battery recycling regulation
- EU – The Circular Economy Action Plan / The Green Deal
- World Economic Forum – Global Battery Alliance

A circular battery value chain assumes

- Extended life time of already existing batteries (repair and reuse)
- Substances and materials will be recovered and reused for manufacturing of new batteries in an endless closed loop
The demand for battery materials will continue to increase exponentially in a foreseeable future.

Availability of recovered materials for Li ion traction batteries will begin to increase approx 2030, but still at a modest scale compared to demand.

With existing regulatory strategies, recycled materials can become a significant portion of materials going into cell manufacturing post 2040.

Source: L. Gaines (2018) Argonne National Labs. Key issues for Li battery recycling
Review of Li ion cell chemistry

- The objective of the electrochemical cell is to transform chemical energy into electrical energy (discharge) and vice versa (charge).
- Li ion cell chemistry is an intercalation process.
- Reaction at discharge:
  - Cathode = reduction: \( \text{MO}_2 + \text{Li}^+ + e^- \rightarrow \text{LiMO}_2 \)
  - Anode = oxidation: \( \text{LiC}_6 \rightarrow \text{Li}^+ + e^- + \text{C}_6 \)
Electrode reactions

Electrode reactions occur at the interface between electrode and electrolyte and comprises multiple steps, e.g.
- Diffusion of ions to the electrode surface
- Adsorption
- Surface diffusion
- Charge transfer

Intercalation involves an insertion step when the Li ion takes place in the electrode material’s crystal lattice

Electrode reactions are strongly dependent on the chemical composition and the physical characteristics of the electrode surface
- Reaction rates
- Overvoltage (energy losses)

Crystal defects affect Li ion mobility in the electrode material

Intercalation process at the cathode-electrolyte interface

Adsorption: \( \text{Li}^+ + S + (1-\delta)e^- \rightarrow \text{LiS}^{\delta+} \)

Intercalation: \( \text{LiS}^{\delta+} \rightarrow \text{Li}^+(s) + S + (1-\delta)e^- \)
Cathode materials

- Predominantly transition metal oxides and phosphates
  - Layered: LiCoO$_2$ (LCO), Li(Ni$_{x}$Mn$_{y}$Co$_{1-x-y}$)O$_2$ (NMC)
  - Spinelles: LiMn$_2$O$_4$ (LMO)
  - Olivines: LiFePO$_4$ (LFP)

- "Invisible" components in the form of dopic agents and coatings
  - Dopning: Al, Fe, Mo, Ru, Zn, La, V, Cr, Mg, Zr, Sn, ...
  - Coatings: Al$_2$O$_3$, SiO$_2$, TiO$_2$, Li$_2$ZrO$_3$, V$_2$O$_5$, AlF$_3$, ...

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Recycling of Li ion batteries - Overview

- 3 main recycling processes:
  - Pyrometallurgical process
    - Treats battery waste as "ore" and feeds into the refining step
    - Recovers Co, Ni and Cu
  - Hydrometallurgical process
    - Metal components are recovered by leaching following an initial separation and grinding step
    - The multi-step leaching process involving cyclic extraction using strong acids, complex binders and 2 phase separation
    - Recovered materials: Al and Cu foils (current collectors), Co, Ni, Mn and Li from cathode
    - Recovered substances are used as precursors to electroce materials
  - Direct recycling
    - Process is under development
    - All materials can be recovered
    - The materials are recovered as close to their final engineering/manufacturing state as possible
    - Customized to specific cell chemistries/compositions
    - Economically justified for Co-poor chemistries

Research status:
Li ion battery material recovery
and use of secondary raw materials

- Relatively new research area
- Currently the focus of activities is centered in China and USA but rapidly growing in EU, based on scientific publications
- Existing studies are based on laboratory studies involving very well defined "waste streams", i.e. single cell model from one manufacturer
- Ageing of original cells prior to recycling is reportedly performed in laboratory environment
- Preparation of "waste material" is performed manually
- Recovered secondary raw materials have a different contamination profile compared to pristine raw materials
- Although recovery rates are reported, there is little or no information on the quality of the recovered secondary raw materials compared to pristine raw materials
- General experience is that high recovery rates usually are connected with a lower quality of the recovered materials, due to co-extraction of metals
- Manufacturing of high performance Li ion batteries relies on use of high quality, battery grade materials
- With the exception of Pb-acid batteries, the general experience is that only limited amounts of secondary raw materials can be used to manufacture new cells without introducing performance penalties
  - Rechargeable NiCd and NiMH less than 30%
  - For primary alkaline less than 10%
  - There is no evidence supporting that the performance of Li ion batteries would not be equally affected.
Challenges with recovered materials

**Substance recycling**

- Substance contaminants are expected in the recovered material:
  - Metallic contaminants: Cu, Al, Fe
  - Non-metallic contaminants: C, F, P
- Al and Fe can interfere with hydrometallurgic metal extraction
- Small amounts of contaminants can result in deteriorated electrochemical properties
  - Cu contamination is common in recycled Co – degrades energy density
  - Cu contamination also commin in Ni due to co-extraction
  - Al contamination contributes to increased nucleation, resulting in smaller but more numerous particles
  - Al contamination >0.6% contributes to increased rate of capacity fade (6-14% during 500 cycles)
- Material degradation compared to pristine materials due to accumulation of different contaminants in the end product

**Direct recycling**

- Due to the continual changes in Li ion chemistries, the recovered materials are likely to be obsolete and require additional engineering to be suitable for use
- Relies on strictly homogeneous waste streams (chemistry and manufacturer specific)
- The material morphology degrades during recycling
  - Uneven particles
  - Structural effects on both primary and secondary particles
  - Lower "tap density" resulting in lower energy density
- Risk of inhomogeneous coatings on particles and surface contaminants
- Successive increased degradation with multiple usage-recycling cycles
- Effectiveness of the recycling process is linked to SOH of waste material
- High sensitivity to Al and Cu microparticle contamination which degrades electrical performance
The consequences of an increased use of recycled materials in Li ion production on electric performance including durability, is difficult to foresee:

- A complex waste stream makes it challenging to recover substances and/or materials with high quality.
- Current research indicates that adverse effects on battery cycle life can be expected due to contamination and morphology effects.

The assumption of continued (linear) increase in Li ion traction battery energy density and cycle life may not be valid in a circular battery economy.

The Battery Durability GTR cannot be developed isolated from other battery sustainability regulation:

- Needs flexibility to reflect battery technology development:
  - New cell chemistries/technologies
  - Performance impacts of material recycling in cell manufacturing

More research is needed to understand how different sustainability regulation and requirements may impact on battery durability performance and, hence, realistic performance targets for the Battery Durability GTR.