Tutorial 2.2. – Batteries for Electric and Hybrid Vehicles

Li-Ion Batteries Ageing

Sources and Analysis

Main Li-Ion Ageing Mechanisms

- Instability of SEI (Dissolution) and progressive Lithium loss
- Increase of Internal Resistance of the cell (e.g. drying of separator)
- Stability and Dissolution of some positive active materials (Mn especially) at high Temperature

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Destructive Physical Analysis

Opening of a cycled cell

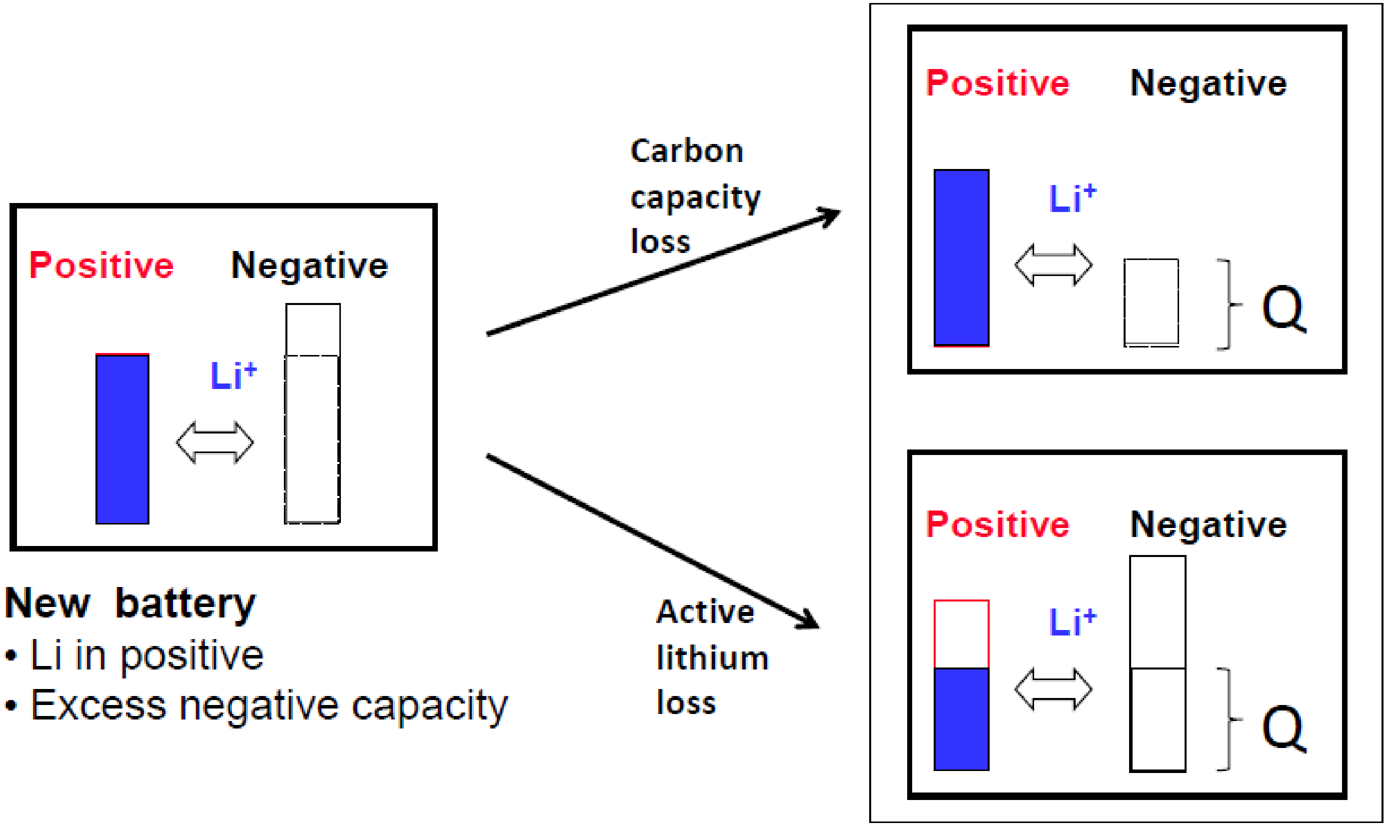
Negative tape

Positive tape

X-ray diffraction(XRD) also revealed that the crystalline sizes of (graphitic) negative became smaller upon cycling

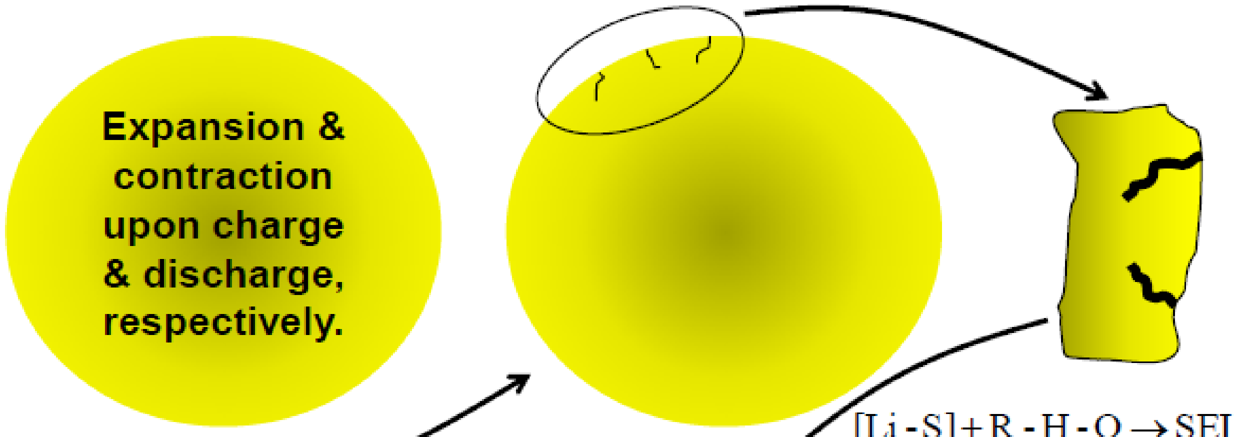
Deterioration of the negative was observed, while the positive was very robust

Schematic for Battery Aging



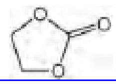
New battery
- Li in positive
- Excess negative capacity

HRL LABORATORIES GM — Overall qualitative degradation model



SEI forms on newly exposed surfaces (cracks)

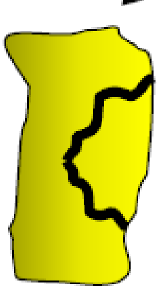
$[Li\text{-}S] + R\text{-}H\text{-}O \rightarrow SEI + \text{gasses} + \ldots$

$[Li\text{-}S] +$  $\rightarrow S + LiCO_3 \downarrow + H_2C = CH_2 \uparrow$

Increased disorder and cracking.

d_{002} peak-width at half max amplitude increases with cycling. Supported by Raman analyses.

- Consistent with loss of active lithium.



Electrode isolation and loss of active material when cracks join

- Consistent with additional loss of negative capacity

Modification for cycling and degradation

Capacity loss = f (Ah_throughput, T, Rate)

$$Q_{loss} = A(I)\exp\left(-\frac{E_a}{RT}\right)Q_T^z$$

$E_a = 30{,}000$ J/mol or 7.2 kcal/mol

I = Current, C-rate

$A = 17{,}390 + 1361 I$

Q_{loss} = Capacity loss, %

Q_T = Total charge throughput, Ah

$R = 8.314$ J/mol·K

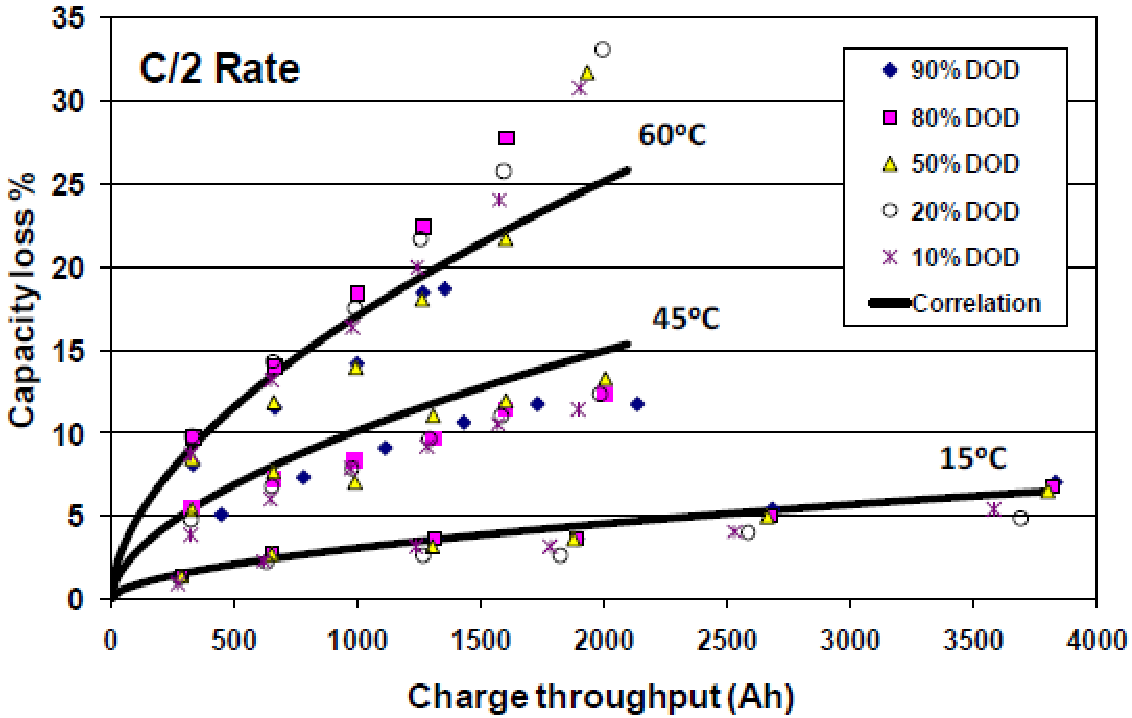
T = Temperature, K

$z = 0.56$

The 1 C-rate corresponds to a current in Amps numerically equal to that of the nominal cell capacity in Ah

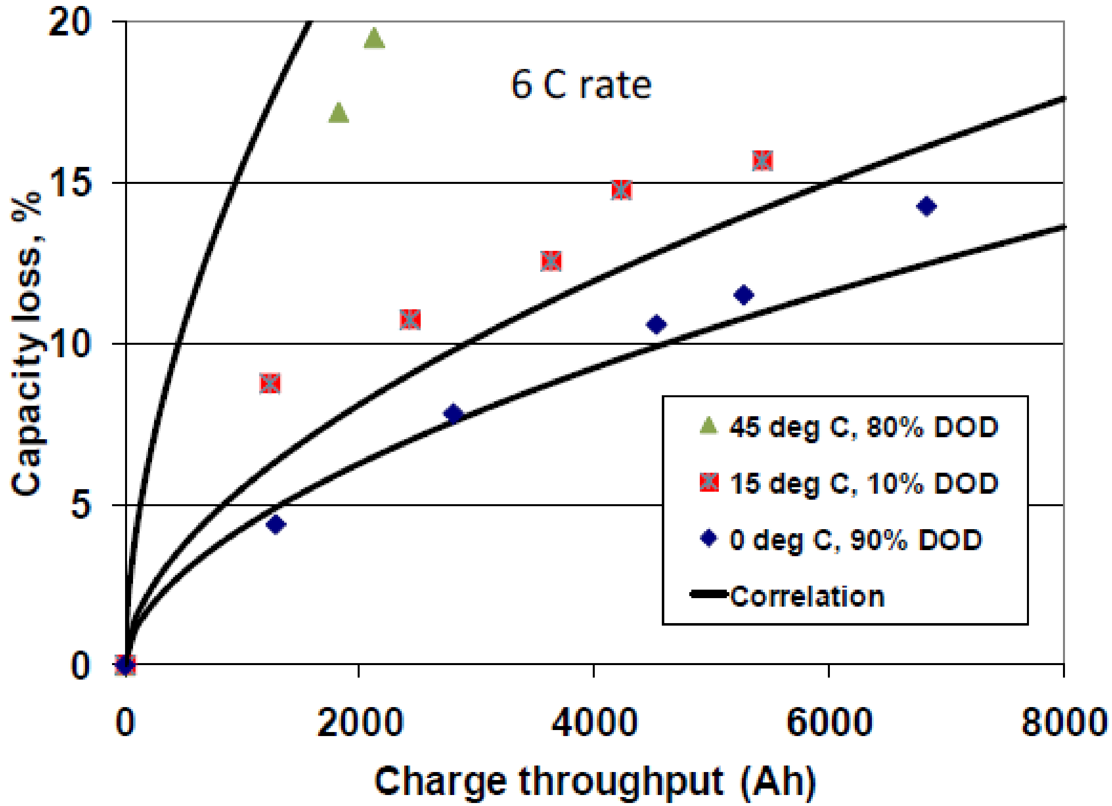
- **Correlation performance**
  - Good: Low rates, below C/2
  - Fair: High rates, 6 and 10 C

Correlation and Experimental Data



- Trends are captured qualitatively
- Note…no clear DOD influence

Correlation and Experimental Data, 6 C rate



Trends are captured qualitatively

Calendar and cycling degradation

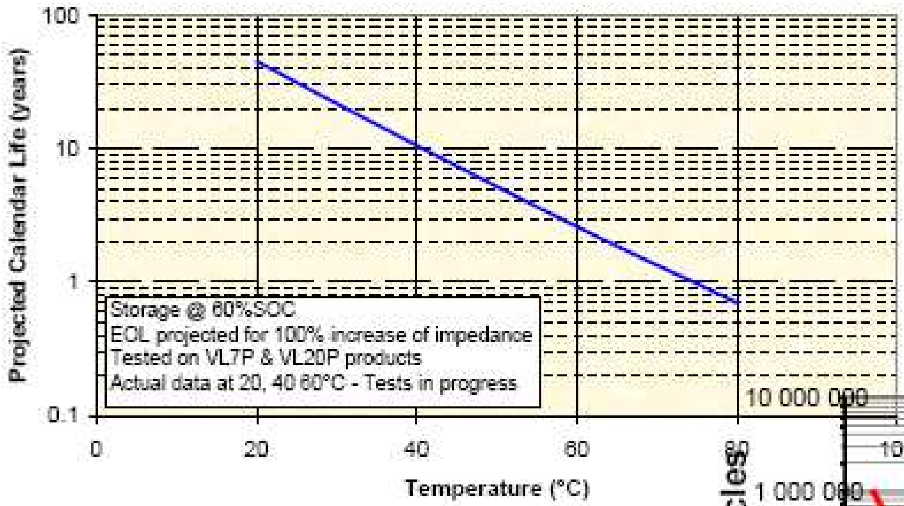
- We expect the following correlation to work well (qualitatively) for both calendar life and cycling degradation of state-of-the-art graphite|iron phosphate cells

$$Q_{loss} = \underbrace{A_1 \exp\left(-\frac{E_{a,1}}{RT}\right)t^{z_1}}_{\text{Calendar life}} + \underbrace{A_2(I)\exp\left(-\frac{E_{a,2}}{RT}\right)Q_T^{z_2}}_{\text{Cycle life}}$$

Calendar life

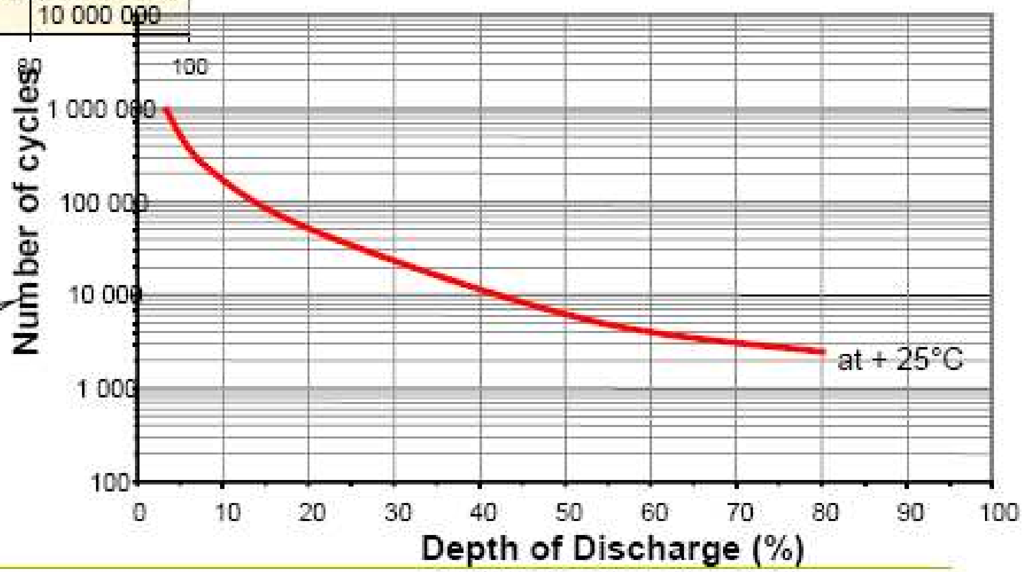
Cycle life

Le système Batterie = Durée de vie du Li-ion (source Saft)



Durée de vie = fct (temp.)

Durée de vie calendaire



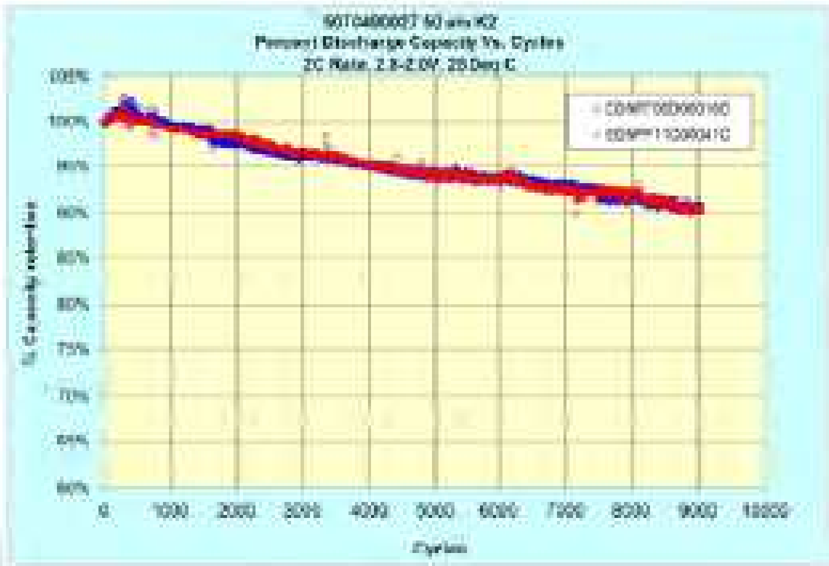
Durée de vie = fct (DOD.)

Durée de vie en cyclage

50 Ah energy storage cell cycling performance

50Ah cells 100% DOD cycling test at 25°C in 2.0 – 2.8 V voltage windo
(EIS battery voltage range) and 2C charge/discharge rate

- 90% capacity retention after 9,000 cycles observed.
- Suggest at least 18,000 cycles at 80% capacity retention



Accelerated Calendar Life Test

- Arrhenius plot of lg(capacity fade) as a function of 1/T
  - As displayed the mean fade values for the 25ºC, 40ºC and 55ºC lie on the same line suggesting no change in activation energy.
  - The large activation energy, 58 kJ/mol, calculated from the slope suggests strongly suppressed cell degradation mechanisms.