AGING OF LI-ION BATTERIES AND HOW TO DEAL WITH IT

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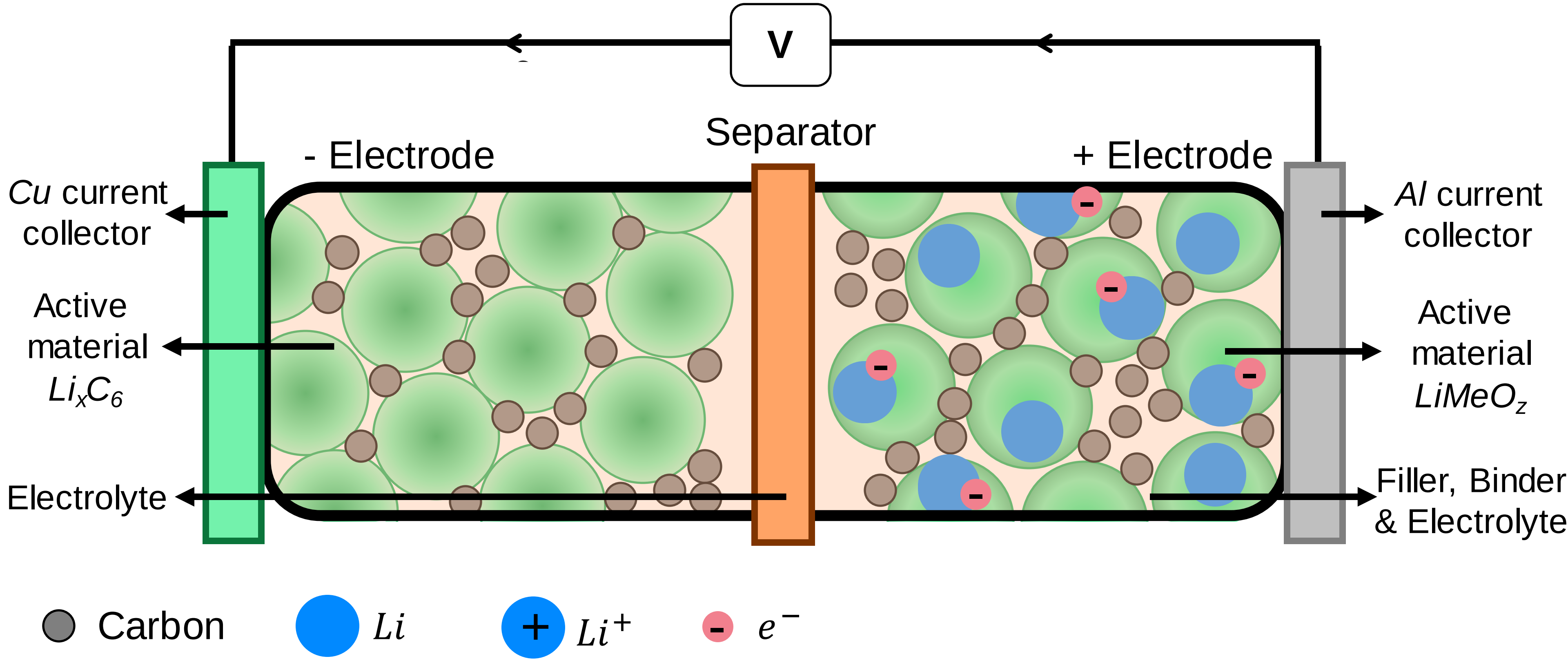
AGING OF LI-ION BATTERIES AND HOW TO DEAL WITH IT

- Li-Ion battery
- Aging Mechanisms
- Modelling fresh and aged cells
- Testing
- Parameter estimation
- Using the model

LI-ION BATTERY PRINCIPLE



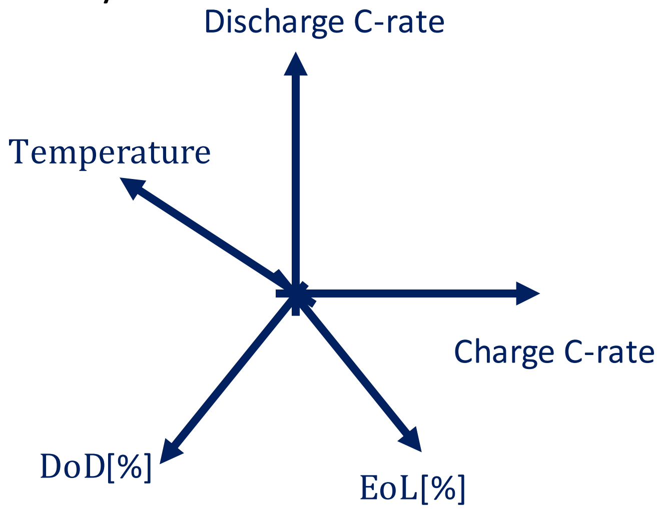
KEY BATTERY SPECS FOR STATIONNARY BATTERIES

A few typical values

Battery Specs	Unit	Remark	Home ESS	SME ESS	Utility ESS
Battery Pack					
Gross Energy capacity	kWh	Time to deliver power	5 (2-10)	20-200	>1000
Battery pack Weight	kg	Installation location	54	200-2000	> 10000
Cell gravimetric Energy density	Wh/kg		140 (LFP prism)	170 (NMC prism)	
Cell volumetric Energy density	Wh/l	Required space	280 (LFP prism)	350 (NMC prism)	
Discharge rate	C-rate	Discharging power	0,8C	1,5C	
Charge rate	C-rate	Charging time	0,5C	0,8C	
Operating temperature range	°C	Indoors	v	v	v
Cycle Lifetime	#EqCyc	Application requirements	10000?	6000?	8000?
Calendar Lifetime	Years	min 10 years	v	v	v

LIFETIME SPECIFICATIONS

- Examples in datasheets:
  - 10 years performance warranty (EoL capacity 70%) => is this 3650 cycles?
  - 10000 cycles (at ?? which conditions)
  - >3200 Cycles 25°C, 80% EoL, 0.5C/1C
  - 6000 Cycles @ 100% DoD | 70% EoL | 23°C +/-5°C 1C/1C
- Lifetime in number of cycles specified for:
  - Depth of discharge
  - C-rate for charging
  - C-rate for discharging
  - Temperature
  - End of Life condition

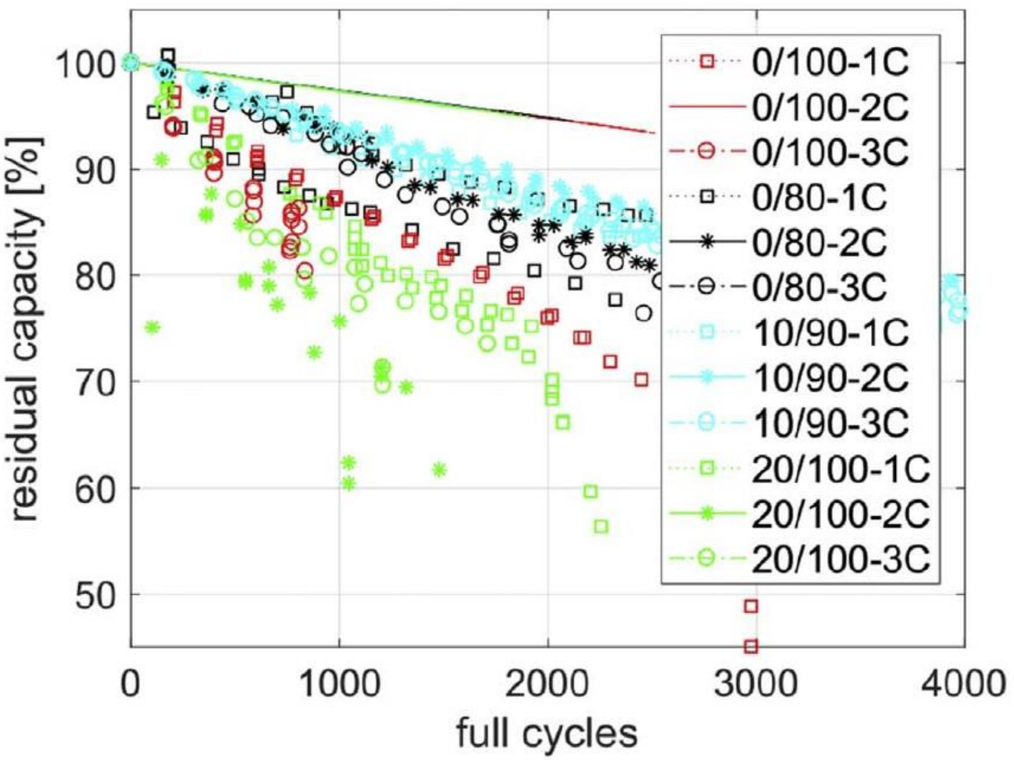


- **What if my application profile and conditions are different?**

DEGRADATION DEPENDS ON …

- DoD
- C-rate charging
- C-rate discharging
- Temperature

AND Li-Ion batteries degrade,
Even if they are not used!
=> avoid high SoC (and low SoC)

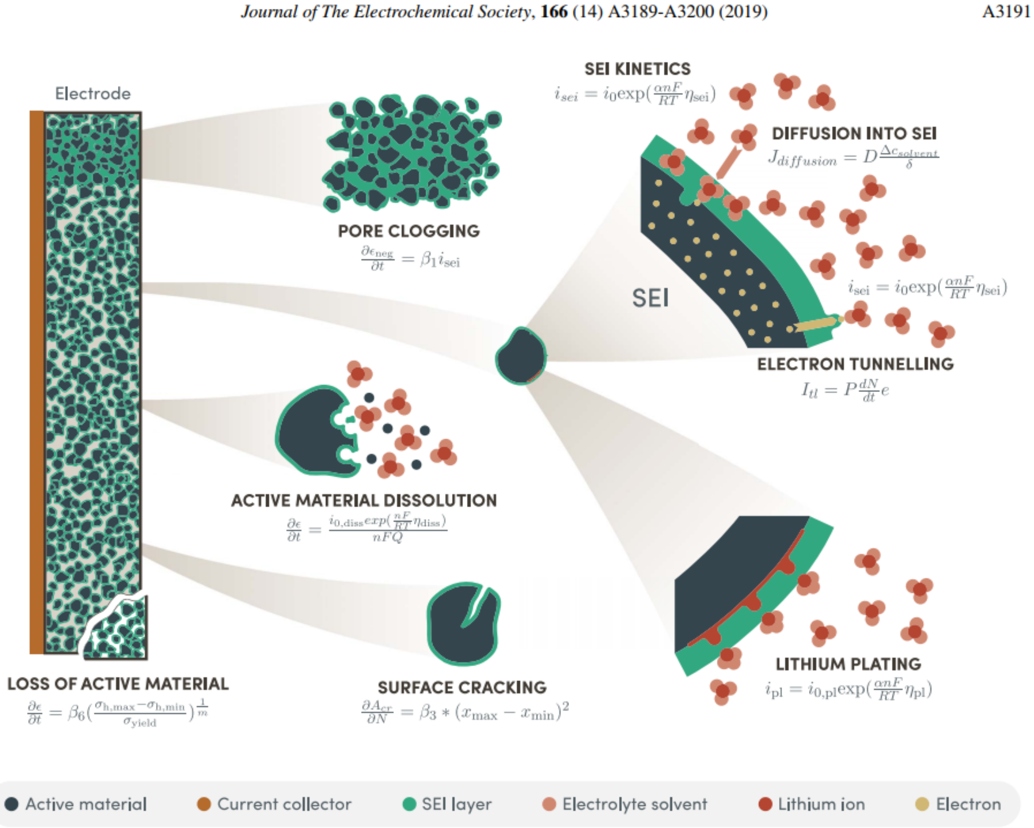


Reniers, J. M., Mulder, G., Ober-Blöbaum, S., & Howey, D. A. (2018). Improving optimal control of grid-connected lithium-ion batteries through more accurate battery and degradation modelling. Journal of Power Sources, 379, 91-102.

LI-ION DEGRADATION MECHANISMS

Main degradation mechanisms

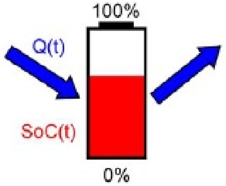
- SEI growth
- Surface cracking
- Loss of active material



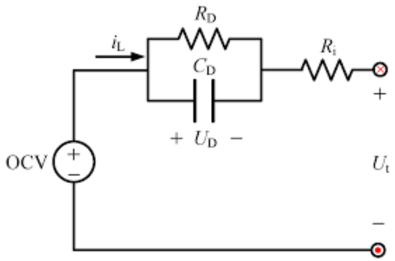
Reniers, J. M., Mulder, G., & Howey, D. A. (2019). Review and performance comparison of mechanical-chemical degradation models for lithium-ion batteries. Journal of The Electrochemical Society, 166(14), A3189-A3200.

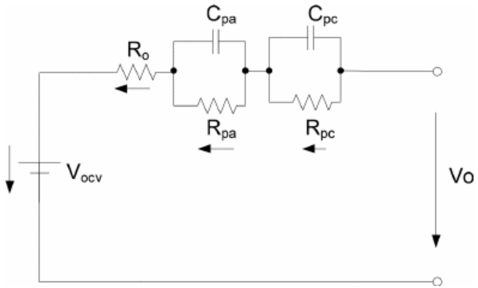
HOW TO MODEL A FRESH BATTERY? HOW TO ADD AGING?

- Bucket:
  degradation usually limited to
  linear degradation in 1 condition



- Equivalent Circuits:
  parameters for each condition
  degradation modelling requires
  (non-physics based) additions



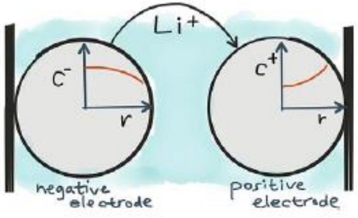


- Empirical/mathematical:
  usually fitted on a limited data set
  degradation requires addition of functions

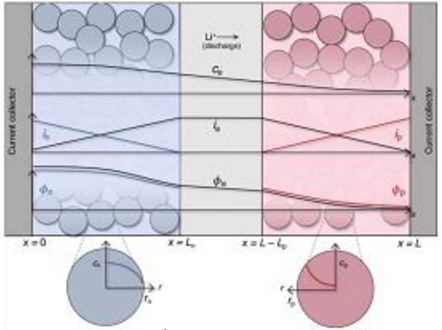
$$U = f\ (I, SoC, T)$$

HOW TO MODEL A FRESH BATTERY? HOW TO ADD AGING?

- Reduced complexity electrochemical models like Single Particle Model (SPM) physico-chemical degradation mechanisms
  => good compromise between accuracy and complexity



- Accurate high complexity electrochemical models like Doyle–Fuller–Newman (DFN) physico-chemical degradation mechanisms
  => usually for improving cell design



Wang, A. A., O'Kane, S. E. J., Planella, F. B., Houx, J. L., O'Regan, K., Zyskin, M., ... & Foster, J. M. (2021). Parameterising continuum level Li-ion battery models & the LiionDB database. arXiv preprint arXiv:2110.09879.

SINGLE PARTICLE MODEL ELECTROCHEMICAL MODEL

Solid-phase diffusion

$$\begin{cases} \frac{\partial c_i(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_i r^2 \frac{\partial c_i(r,t)}{\partial r}\right) \\ D_i \left.\frac{\partial c_i(r,t)}{\partial r}\right|_{r=0} = 0 \\ D_i \left.\frac{\partial c_i(r,t)}{\partial r}\right|_{r=R_i} = -\frac{i_i(t)}{F} = -\frac{I(t)}{V_i a_i F} \\ c_i(r,0) = c_{i,0}(r) \end{cases}$$

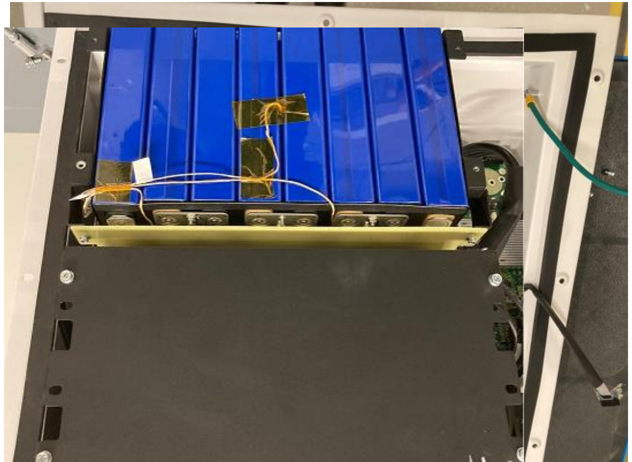
Voltage[a]

$$\begin{cases} v(t) = U_+\left(c_+(R_+,t)/c_+^{\max}\right) - U_-\left(c_-(R_-,t)/c_-^{\max}\right) \\ \quad + \eta_+\left(c_+(R_+,t), I(t)\right) - \eta_-\left(c_-(R_-,t), I(t)\right) - \frac{R_c}{V_- a_-} I(t) \\ \eta_i\left(c_i(R_i,t), I(t)\right) = \frac{R_g T}{\alpha F}\sinh^{-1}\left(\frac{I(t)}{2V_i a_i i_{i,0}\left(c_i(R_i,t)\right)}\right) \\ i_{i,0}\left(c_i(R_i,t)\right) = F k_i \sqrt{c_i(R_i,t)\, c_{\mathrm{el}}\left(c_i^{\max} - c_i(R_i,t)\right)} \end{cases}$$

+ thermal model + degradation mechanisms

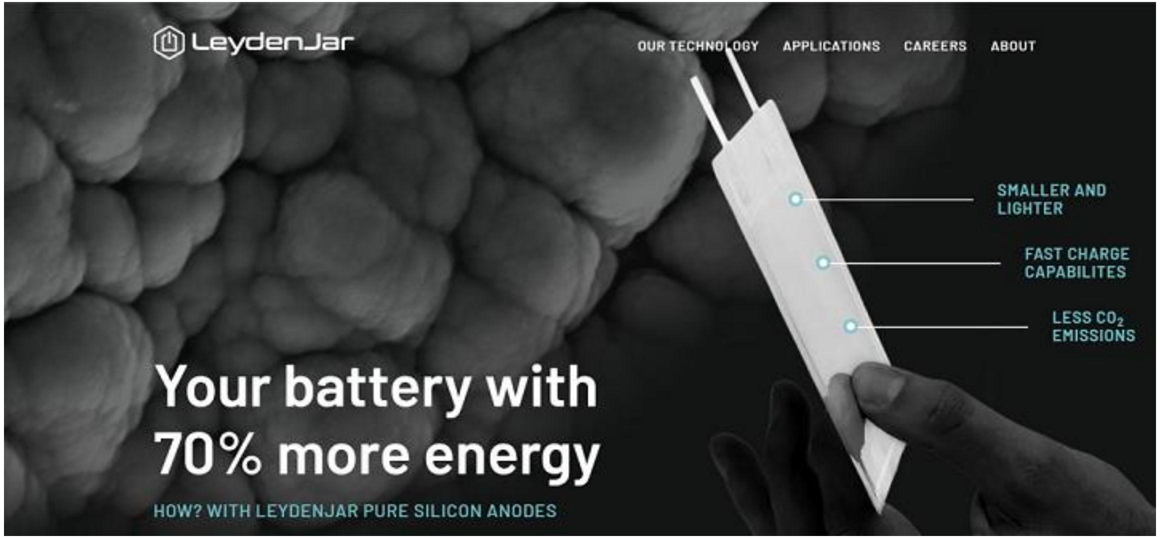
BATTERY TESTING

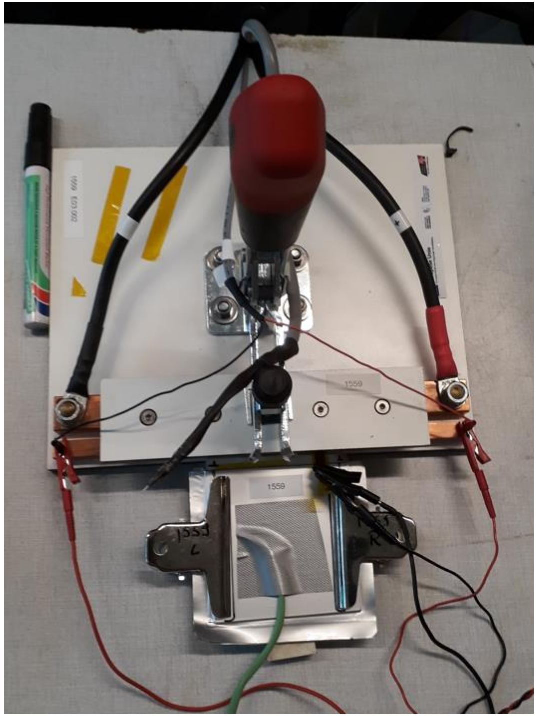
- Commercial Battery Kstar BluE-Pack 5.1 S 3680D 5.12kWh 230V 1ph
  - Passive air convection cooling. Multi-days test with additional temperature sensors.
  - Up to 35°C in room temperature conditions.
- CATL cells aging tests
  - 18 CATL cells cycling aging tests at 35°C at various C-rates & SoC windows.
  - 16 CATL cells calendar aging tests at various temperatures and SoC



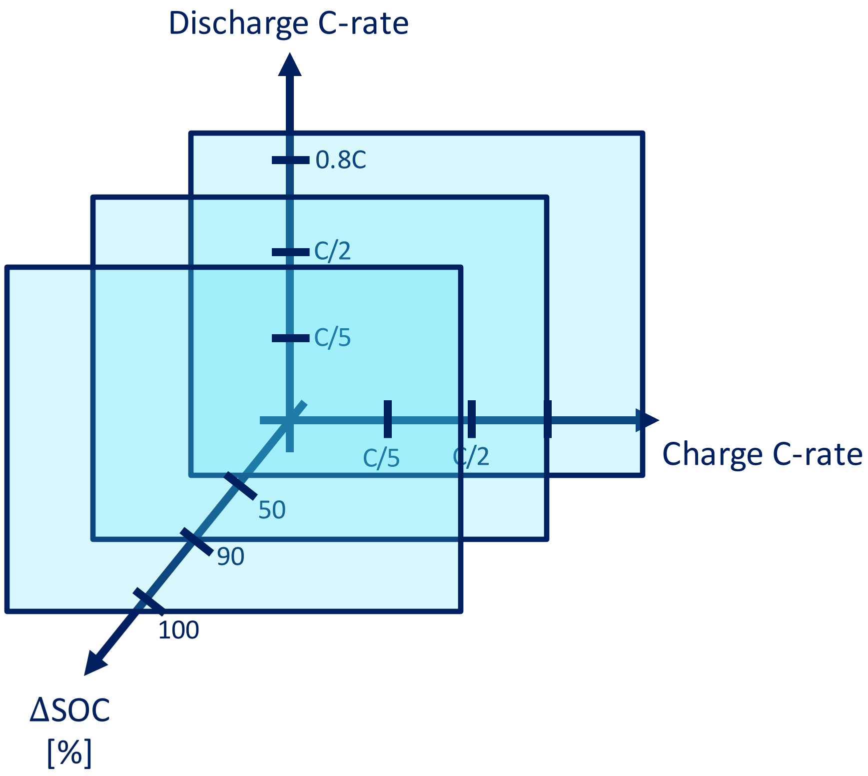
BATTERY TESTING

- Prototype cells with pure Si-anode from LeydenJar





FLEXINET LI-ION BATTERY CYCLE TESTS



ΔSOC = 50

CH\DCH	C/5	C/2	0.8C
C/5	x		
C/2		x	

ΔSOC = 90

CH\DCH	C/5	C/2	0.8C
C/5	x		x
C/2	x	x	x

ΔSOC = 100

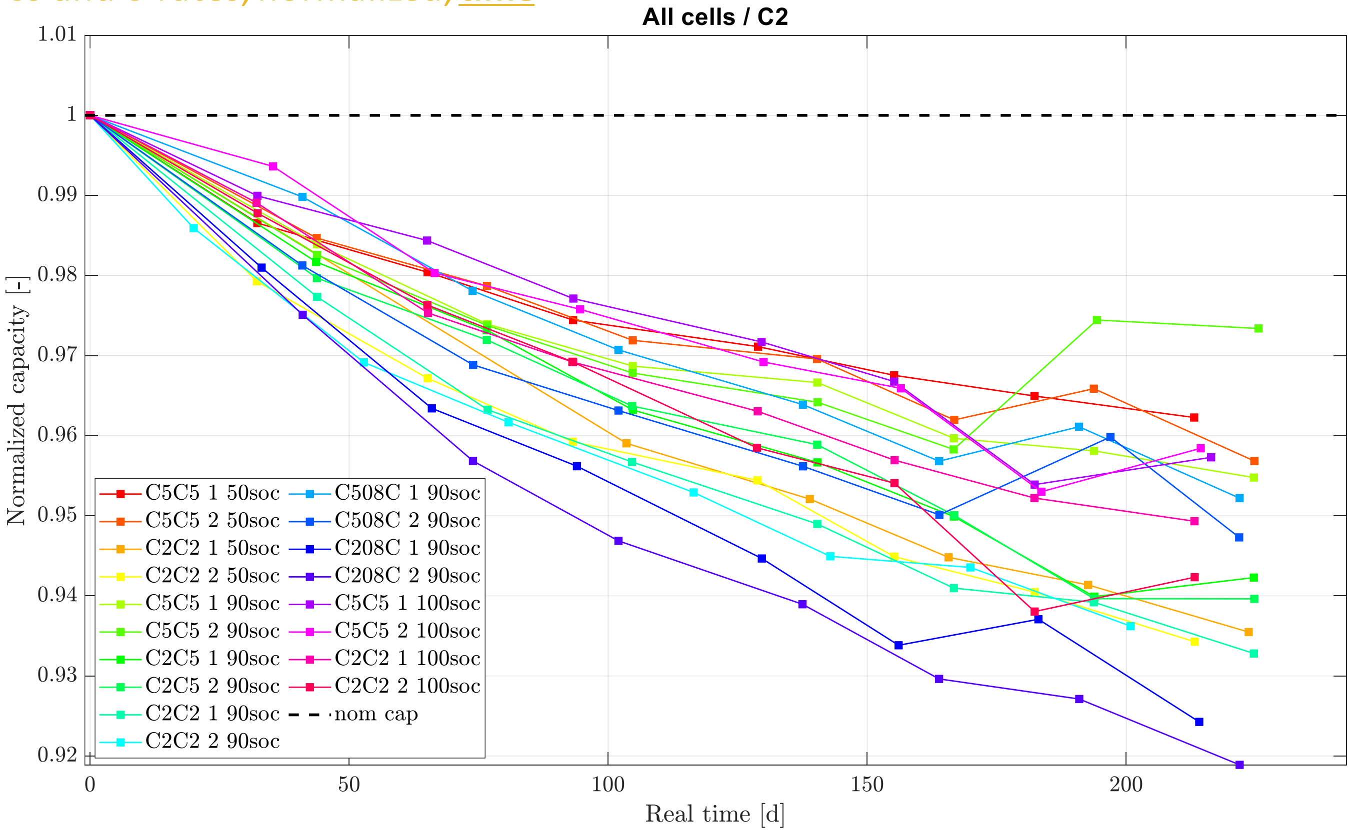
CH\DCH	C/5	C/2	0.8C
C/5	x		
C/2		x	

Limits coming from KStar specs

Each test has 2 cells and 2 types of experiments (characterization & cycling)

FLEXINET LI-ION BATTERY DEGRADATION

Across SOCs and C-rates, normalized, **time**



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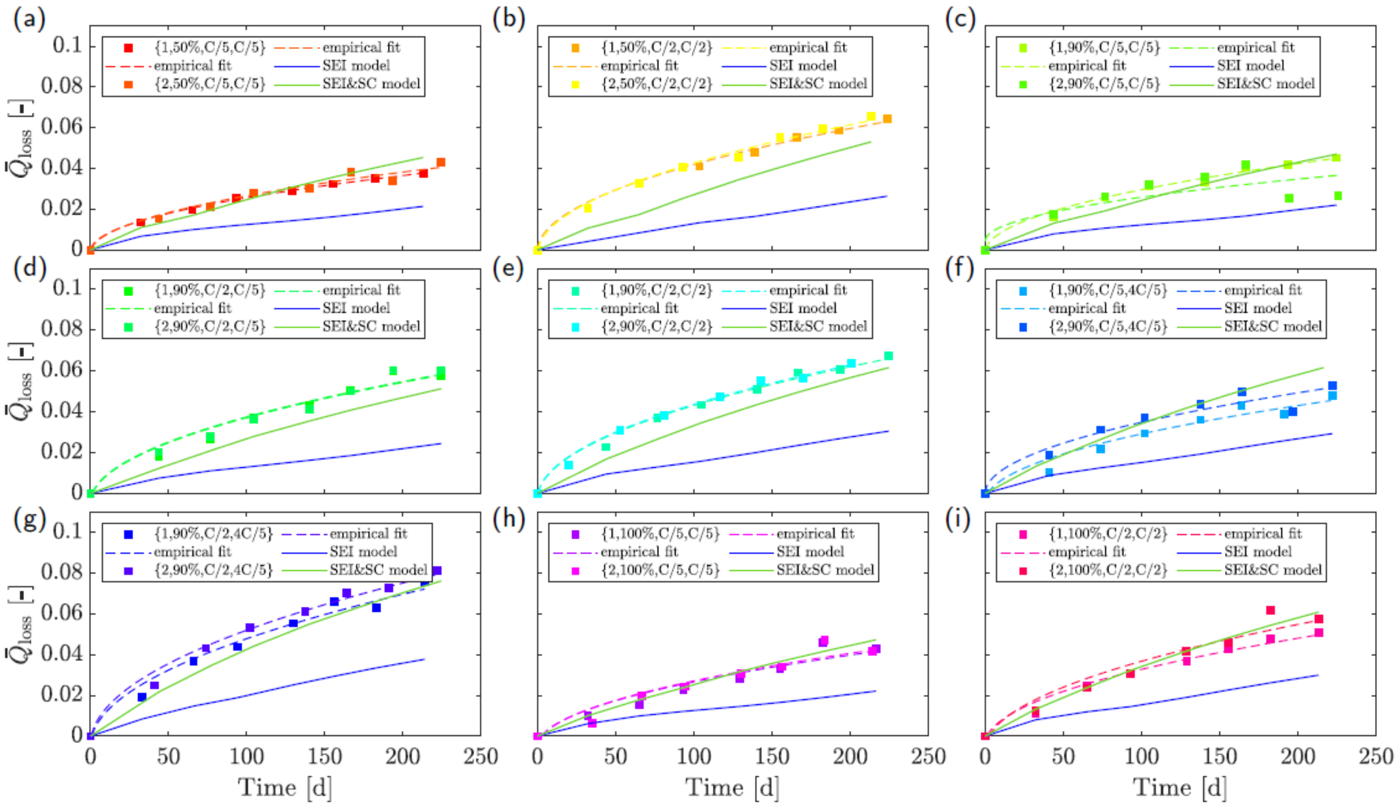
PARAMETER ESTIMATION IN DIFFERENT CONDITIONS – CAPACITY LOSS VS TIME

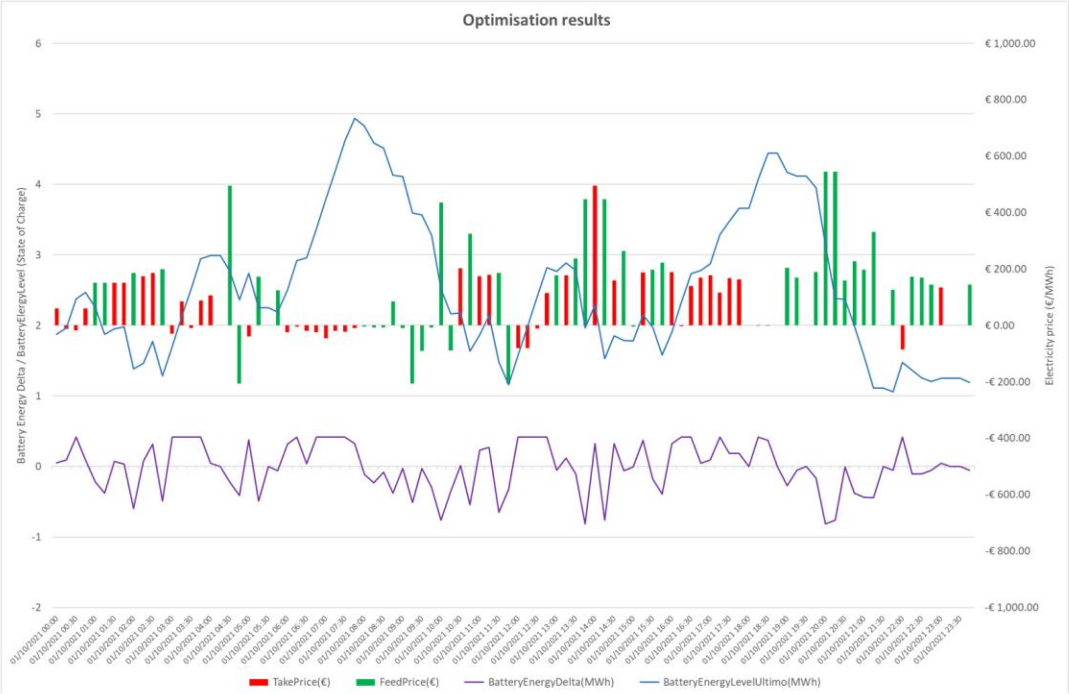


USING THE MODEL

- Battery Pack Manufacturers:
  - Predict future degradation of the real battery via simulating the battery degradation model with specific application profiles under specific conditions with the aim to dimension and optimize the Battery Pack
  - Determine warranty conditions & support Battery Pack Integrators
- Battery Pack Integrators
  - Anticipate for unforeseen (new) usage of the battery pack
- Battery Energy Storage System Operators:
  - Predict future degradation of the real battery via simulating the battery degradation model with various application profiles under various conditions with the aim to make better trade-offs when to use the battery (profit > cost of degradation)
  - Include the model in the control loop
    => both to improve ROI
- Battery Cell Manufacturers:
  - Use the model to improve understanding of degradation with specific application profiles under specific conditions with the aim to improve the cell design or cell manufacturing

FUNTIONALITY USE OF AGING MODELS

- Battery usage can help alleviate demand for flexibility and earn a return
- Electricity prices on flex markets are very volatile
- Rapid charging/discharging of battery will lead to high cycling of the battery and impact the aging of the asset
- Aging algorithms such as VITO's physics-based models will help understand the impact and improve the lifetime or the revenu (within the default lifetime) and thereby the return on investment



CONCLUSIONS

- Li-Ion battery aging depends on many factors
- Little information is publicly available on this
- Battery models help to deal with the aging of Li-Ion batteries
- All models require testing of cells (and modules) or live data acquisition to estimate their parameters
- The Single Particle Model is a good compromise between accuracy and complexity
- Method has been proven for both NMC and LFP batteries
- Method allows to increase ROI

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