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cea

Lithium-ion battery aging:

Representative EV cycling profiles compared to calendar life

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Supported by EVAAP EDTA European Commission

Outline

- Context and objectives
- Calendar & cycling aging experiments
- Aging results
  - Full cells
  - Post-mortem characterization
- Conclusion

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Context and objectives

- Lithium-Ion battery : promising candidate for electric transportation
- However performances decline with use and time…

Battery Aging

Cycling aging

(= driving and charging mode)

Calendar aging

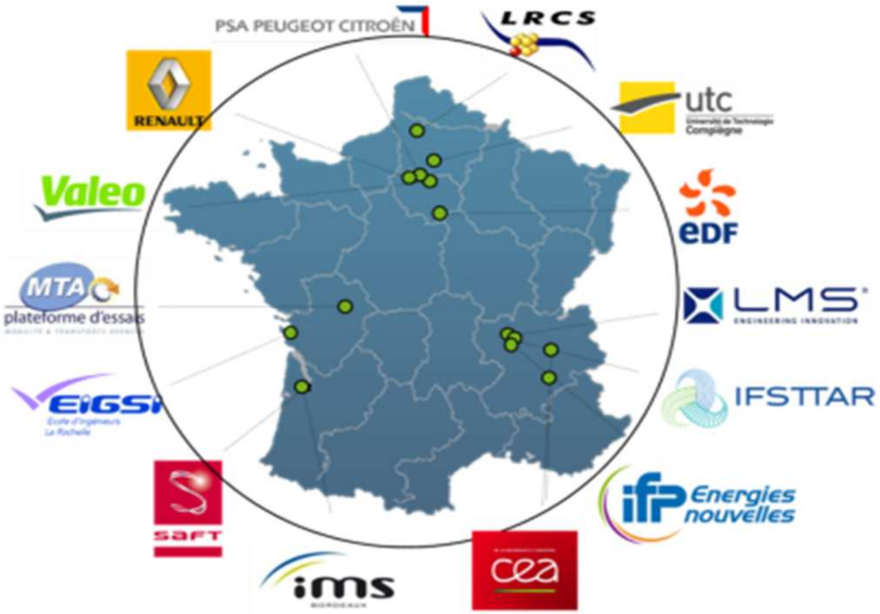
(= parking mode)

Passenger vehicles spend about 90% of time in parking mode!

10 to 15 years are required !

Context and objectives

- The research project SIMCAL (2010 – 2013) :



  - Consortium of 14 partners in both academy and industry
  - Calendar aging data for 6 Li-Ion technologies
  - In-depth understanding of aging mechanism upon storage (<u>mainly</u> loss of lithium cyclable due to SEI growth)

Question : how cell lifetime is affected by using the battery **once a day** like in a typical automotive application?

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Aging experiments

- Aging experiments performed on:
  - Commercial 12 Ah cell (purchased in 2010)
  - Cell chemistry: LI $NiCoMnO_2$ |Graphite
  - Measured capacity (25°C, 1Cnom):
    12.7 ± 0.12 Ah

End-of-discharge voltage (V)	**2.70**
End-of-charge voltage (V)	**4.20**

Aging temperature test set to 45°C

1. Calendar aging conditions:
   3 SoCs: 30%, 65%, 100%

SIMCAL

Compared to …

2. Cycling aging conditions representative of an EV usage
   3 charging scenarios investigated

Experiments : calendar aging

1. Calendar tests :

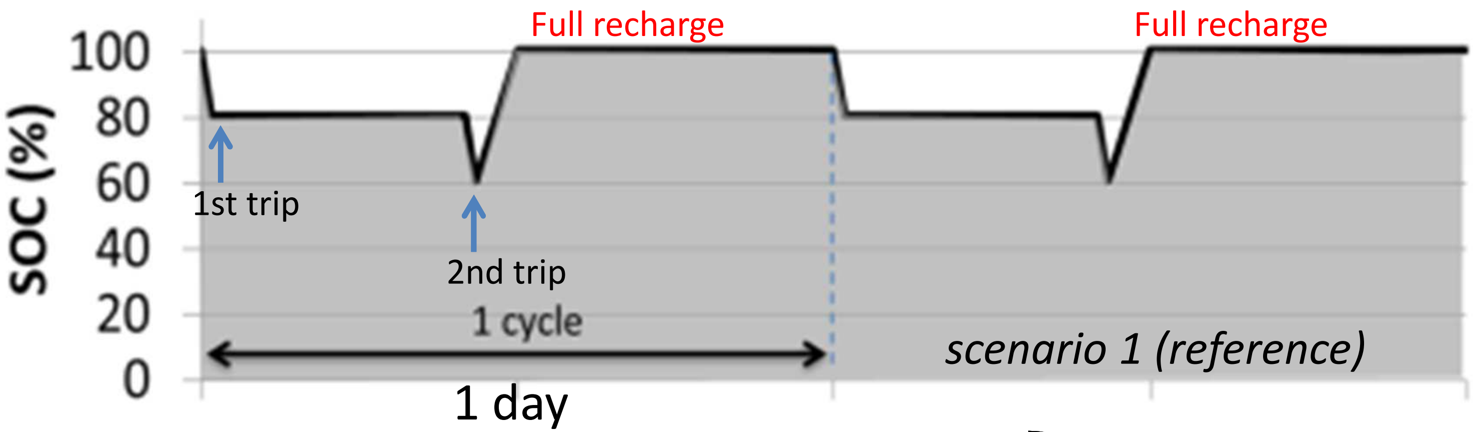
State-of-Charge (%)		
SOC1	SOC2	SOC3
30	65	100

- **Open Circuit**
- **3 cells for each storage condition**
- **Duration: 24 months**

Experiments : cycling aging

2. Cycling tests performed

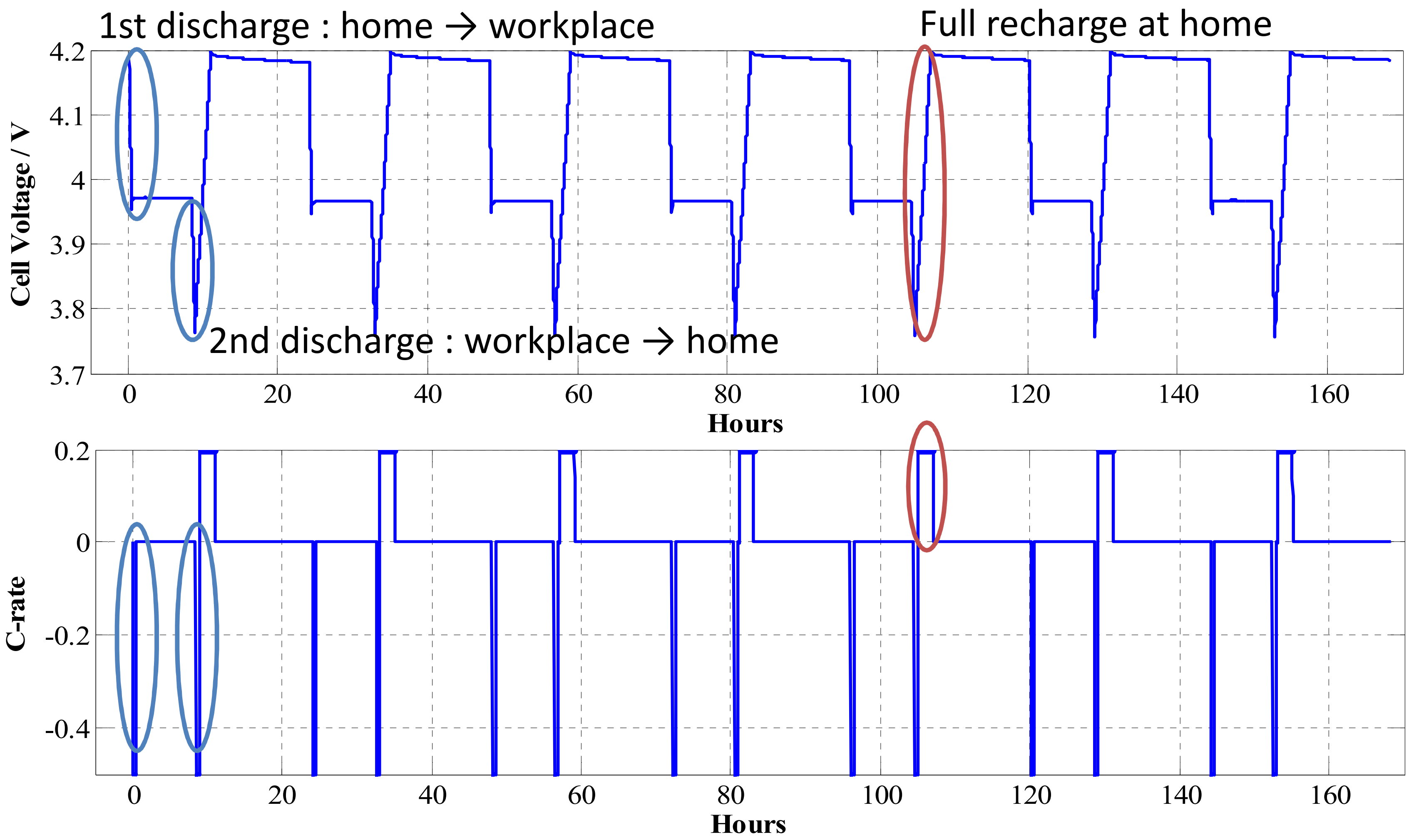
- Mimic a cell usage of a pure EV (home ↔ workplace)
- Each trip = 20 % of DoD -> 40% DoD /day



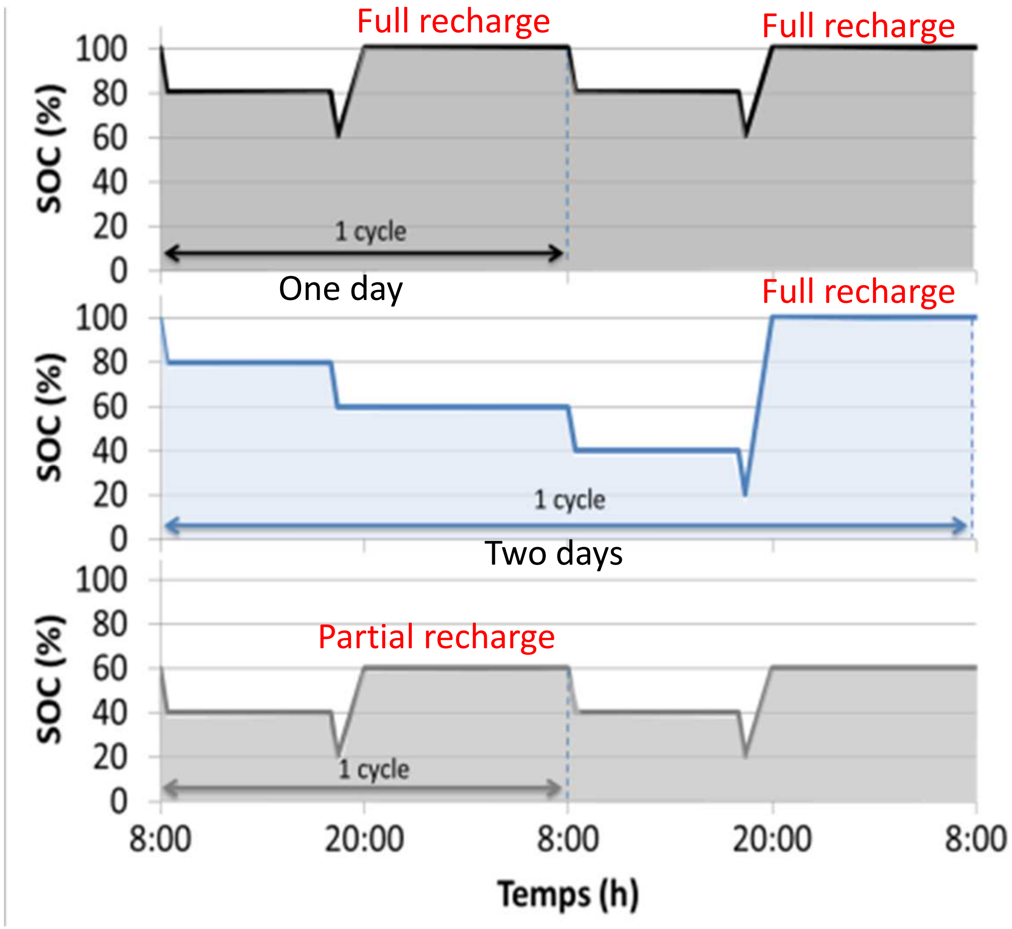
- Driving mode : <u>C/2 constant current discharge</u>
- Charging mode : C/5 constant current
- Profile repeated every day during 4 weeks

} Realistic current rates for EV

Experiments : cycling aging

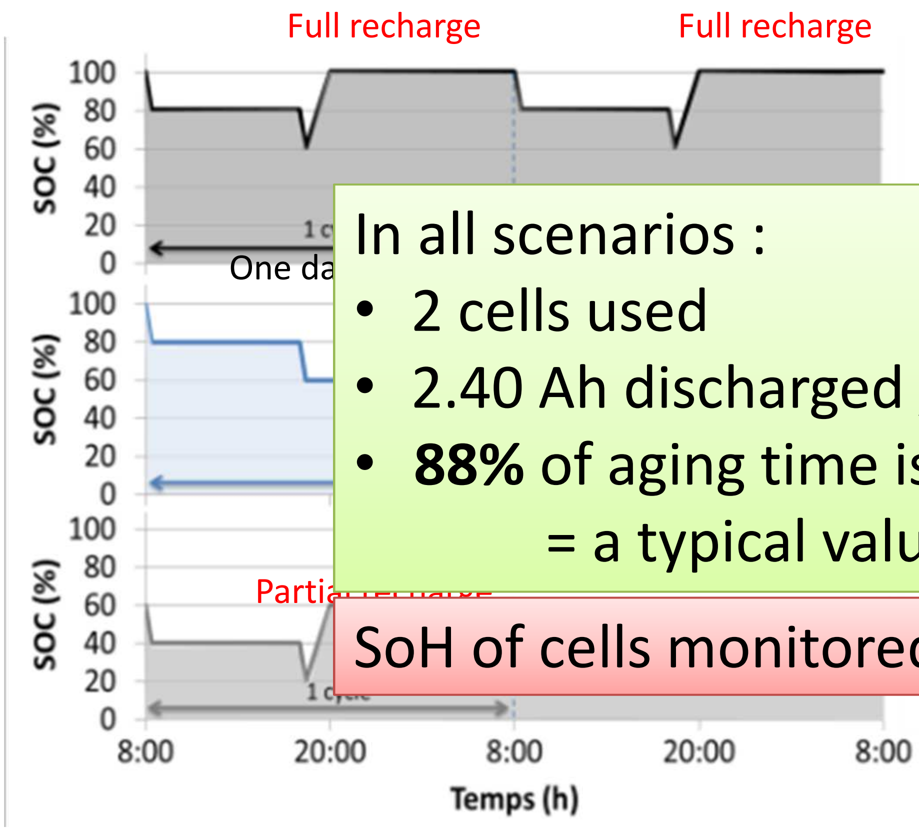


Experiments : cycling aging



- <u>3 "charging scenarios"</u>
  - In scenario **1** (previous slide) : battery fully recharged *every day, , DoD=40%*
  - In scenario **2** : recharged only *when SoC=20%, DoD=80%*
  - In scenario **3** : the battery is operated between SoC range *60 % - 20 %.*

Experiments : cycling aging



- <u>3 "charging scenarios"</u>

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ly

operated between SoC range *60 % - 20 %.*

In all scenarios :
- 2 cells used
- 2.40 Ah discharged / day = 40% SoC window)
- **88%** of aging time is spent at rest
  = a typical value for an EV application

SoH of cells monitored at **25°C** every 4 weeks

Characterization protocol (25°C)

Test	Test description
Capacity test	Fully discharge cell to 2.7V at **1C** rest 30 min Full charge to 4.2 V at **1C**, hold at 4.2V until the current drop below C/20 (CCCV) Discharge and charge three times Second and third capacity values are used to define the SoH

- Periodicity:
  - Calendar aging experiments : every 8 weeks
  - Cycling aging experiments : every 4 weeks
- Other tests : Electrochemical Impedance Spectroscopy & relaxation test

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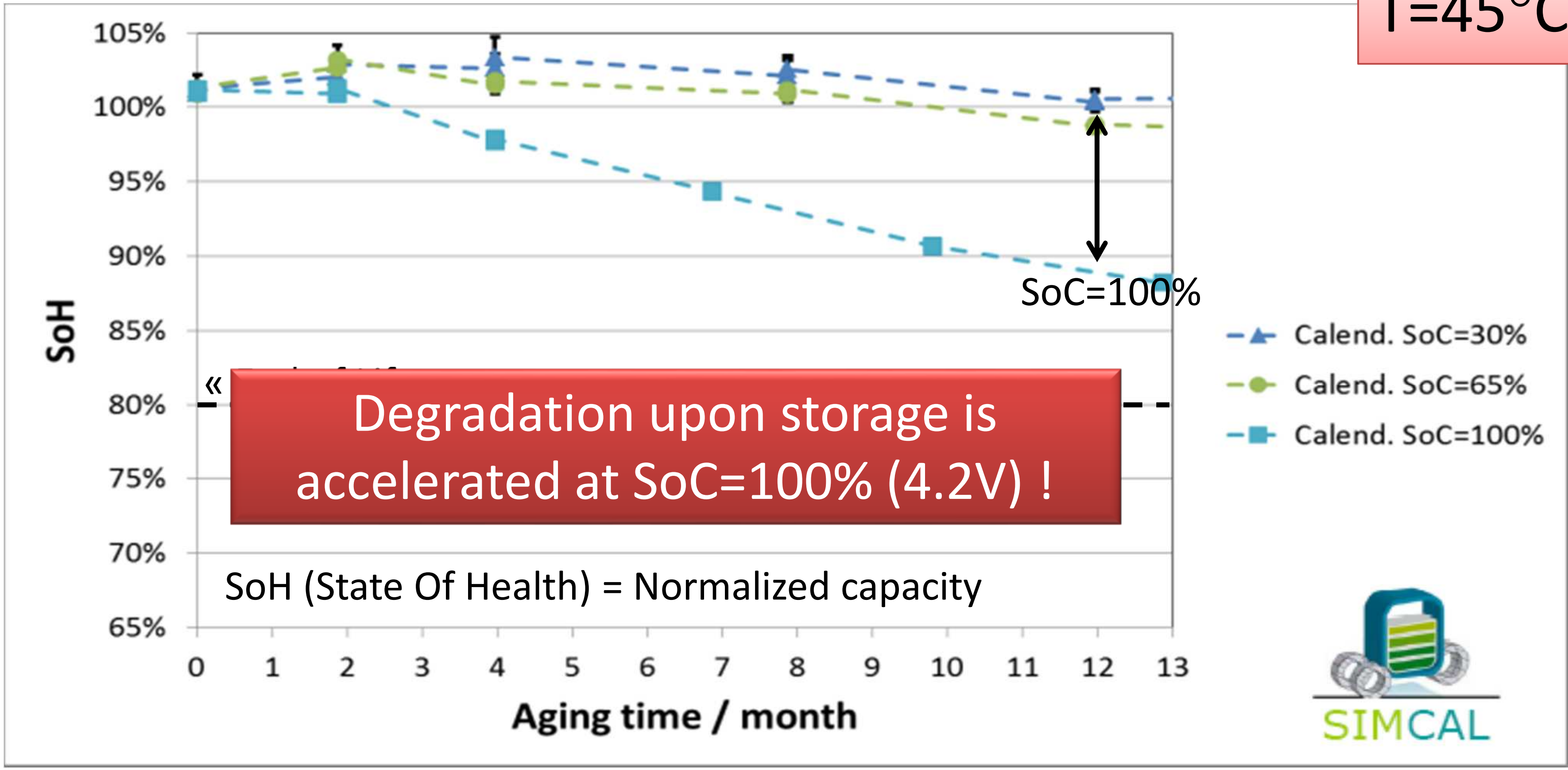
Aging results : full cell capacity

1. Calendar aging results

T=45°C



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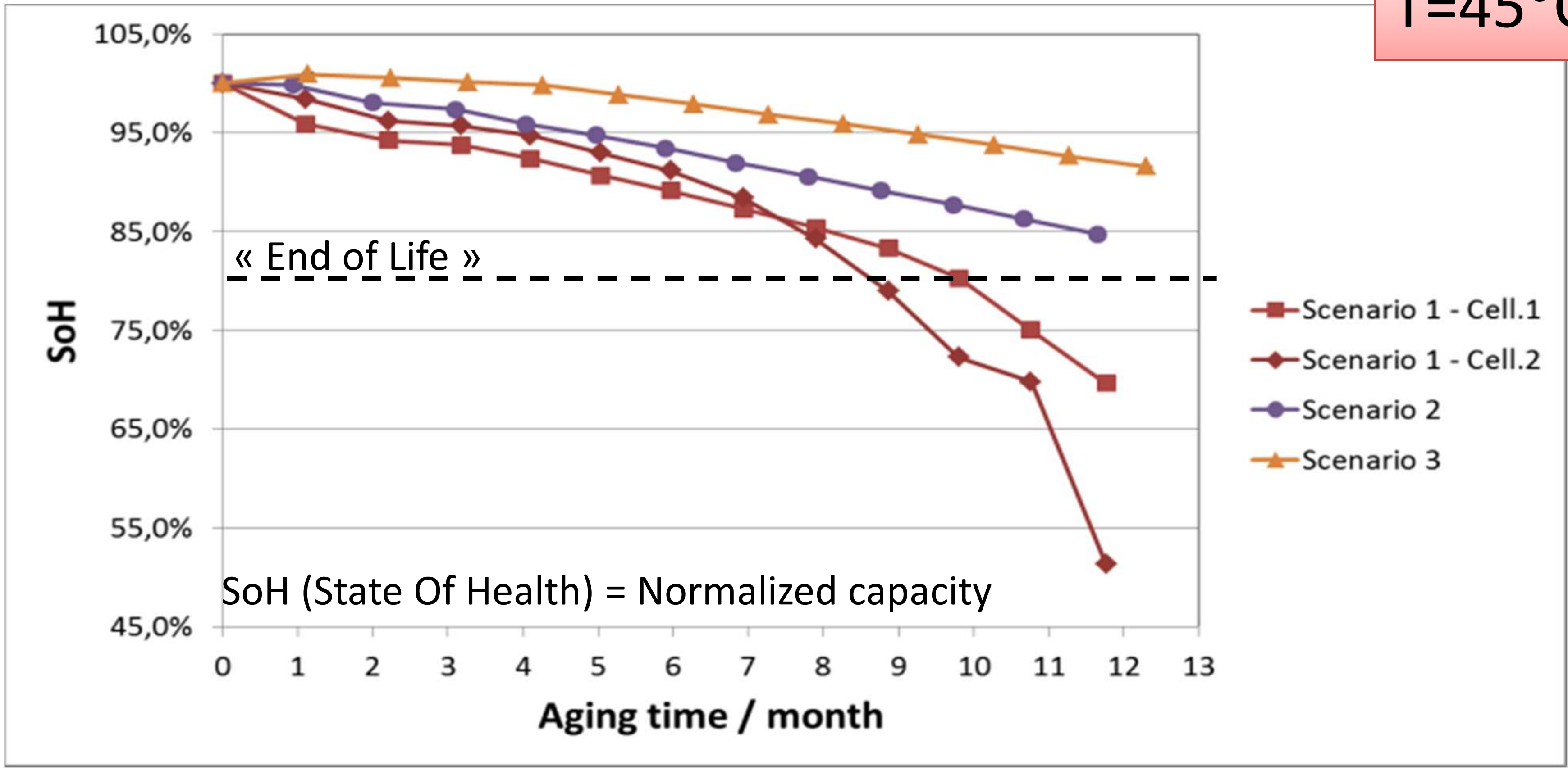
Aging results : full cell capacity

2. Cycling aging results

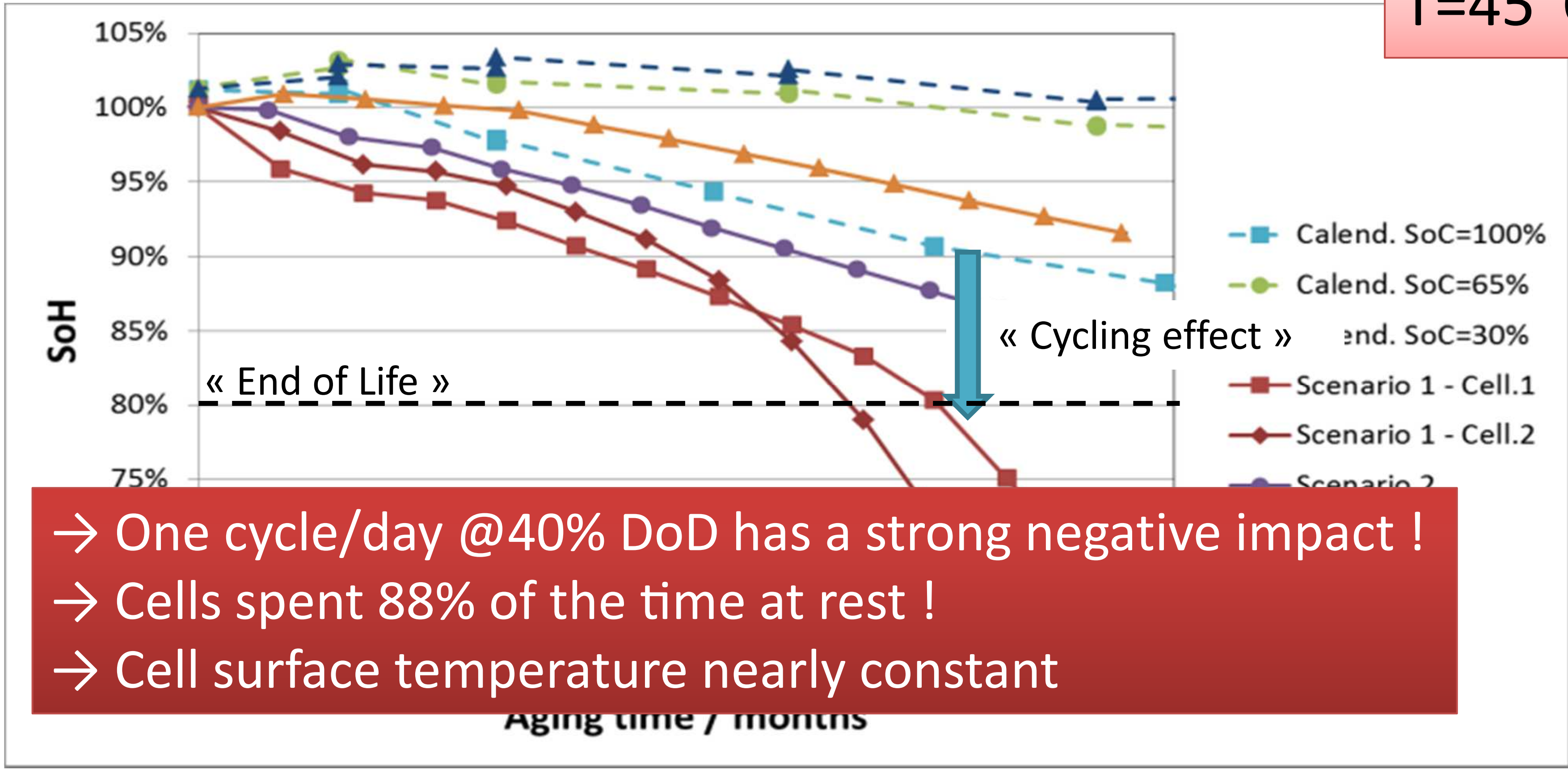
T=45°C



Aging results : full cell capacity

3. Cycling vs calendar aging

T=45°C



→ One cycle/day @40% DoD has a strong negative impact !

→ Cells spent 88% of the time at rest !

→ Cell surface temperature nearly constant

Aging results : full cell capacity

Aging Test	End-Of-Life @ T=45°C (months)	Acceleration factor Cal. 45°C, SoC=100%
Calendar : 45°C, SoC=100%	20^{m}	1
Scenario 1 **Charge every day to 100%**	**9^{m}**	**> 2**
Scenario 2 Charge every 2 days to 100%	15^{e}	1,3
Scenario 3 Charge every day to 60%	24^{e}	0,8

* End-Of-Life : 20% of capacity loss

Capacity fade rate

m : measured
e : estimated by extrapolation of present test results

SoC management can be effective for preserving battery lifetime

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Post-mortem characterization

- Characterize degradation on electrode individually
- Disassembled in a glove box

Electrode sampling
Ø = 14 mm

Physical characterization (XRD[1], SEM[2], ICP-MS[3])

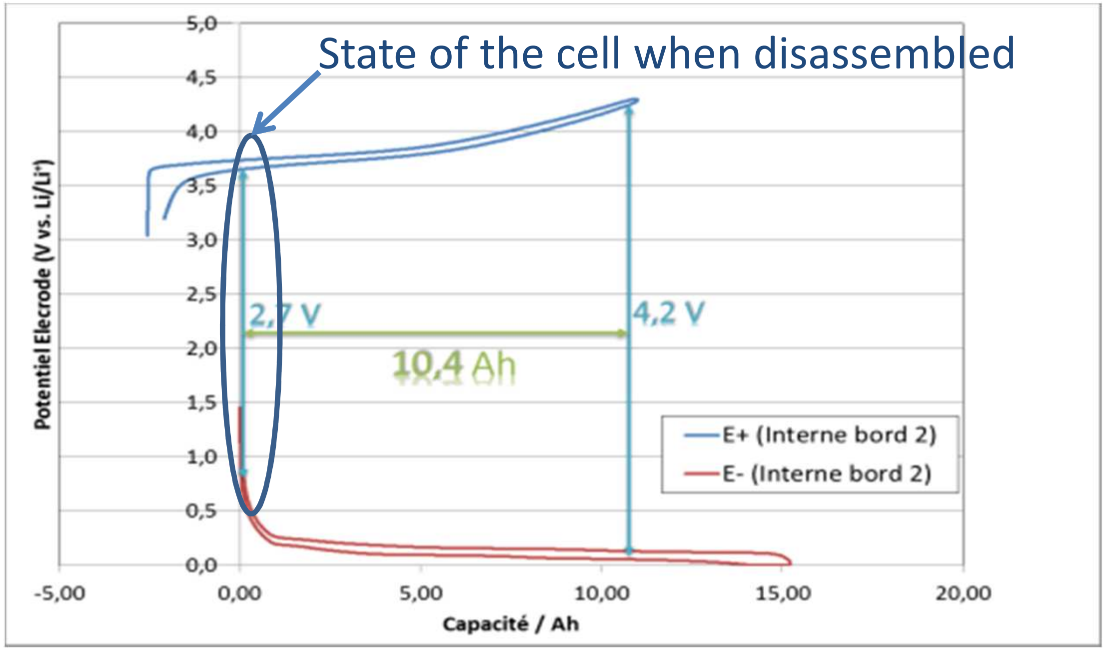
Electrochemical characterization

4 cells disassembled (1 ante-mortem + 3 from each cycling scenario)
- Cell #2 for scenario 1 (most aged cell)
- 9 XRD, 9 SEM, 8 ICP-MS analyses
- 50 assembled half-cells

[1]X-Ray Diffraction, [2]Scanning Electron Microscopy, [3]Inductively Coupled Plasma Mass Spectrometry

Post-mortem characterization

- Electrochemical characterization of the electrodes
  1. Initial lithium content of the electrodes at discharge
  2. Capacities of the electrodes (4 cycles at C/10)

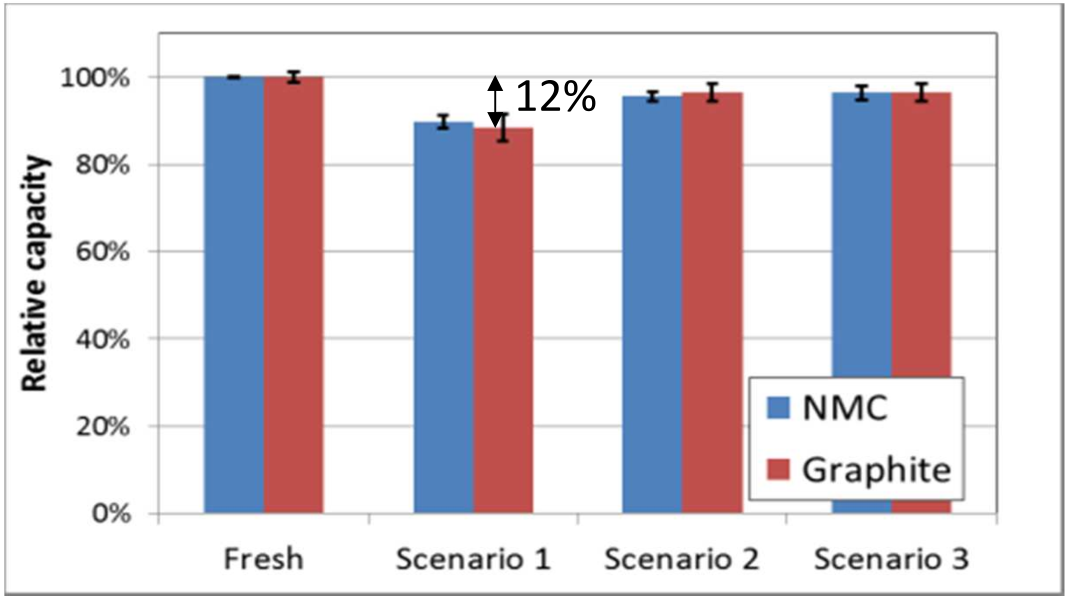


1. Negative electrode *is fully delithiated* when cell is disassembled

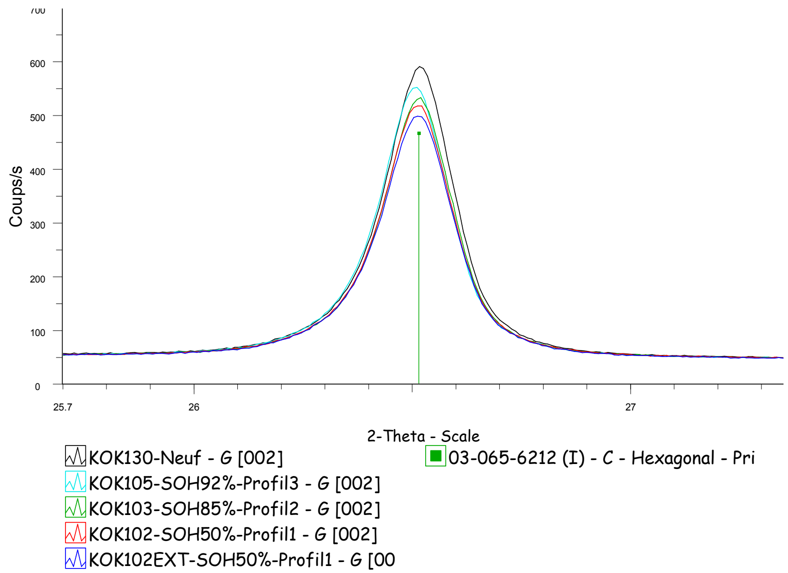
2. Initial lithiation of positive electrode provides <u>cell internal imbalance</u>

Post-mortem characterization

- Aging on electrode materials ?



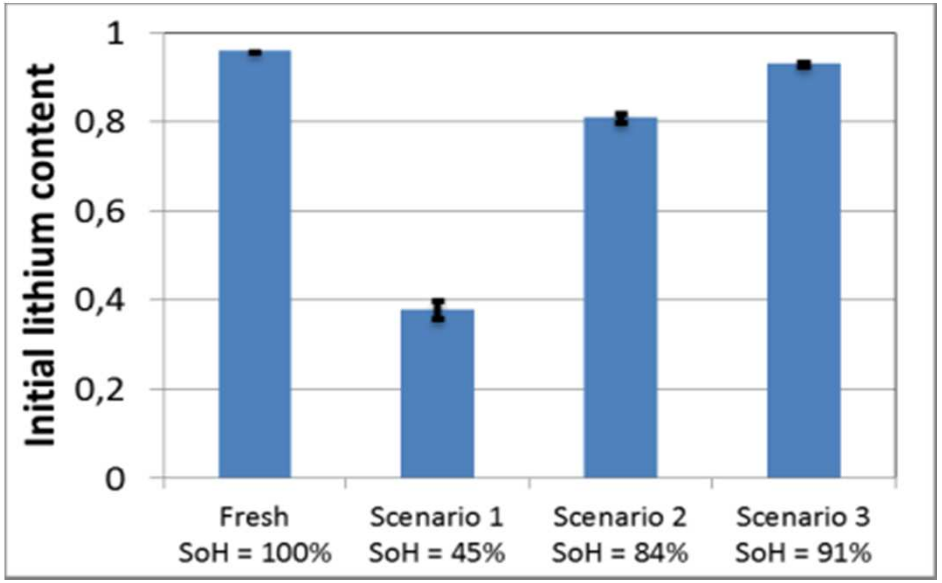
XRD on graphite electrode

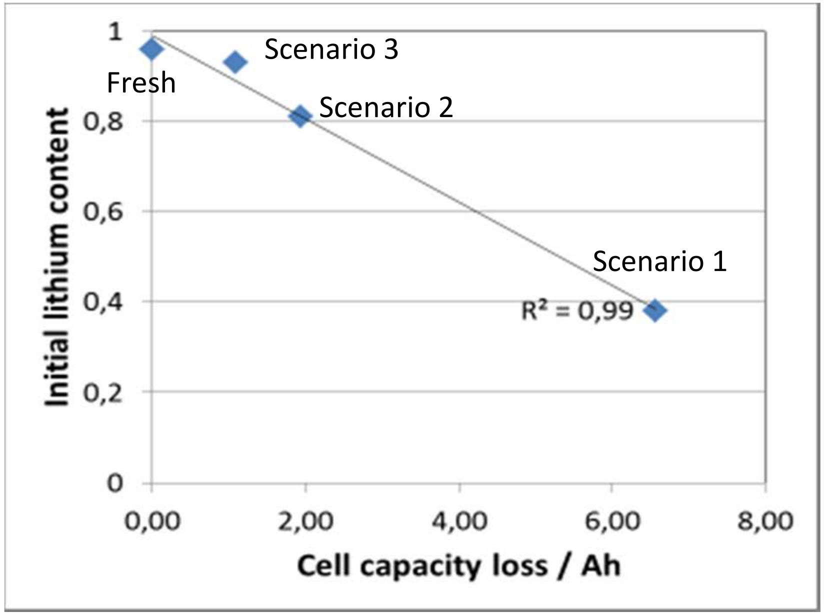


- Loss of electrode capacities is rather limited: cannot explain cell capacity loss
- Confirmed by XRD analyses on negative electrode

Post-mortem characterization

- Initial content of lithium in <u>positive</u> decreases with aging





→ *increase of the cell imbalance…*

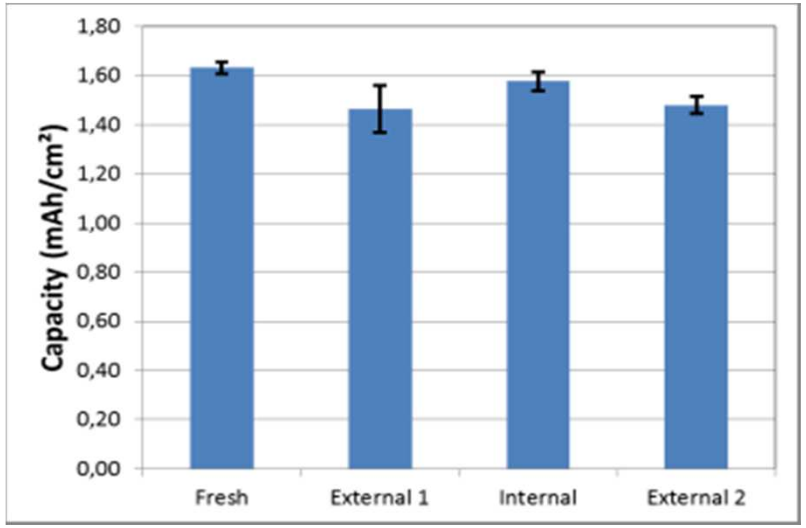
whitch is well correlated with cell capacity

Post-mortem characterization

- Inhomogeneous deterioration inside the cell was observed

External 2
Internal
External 1

Deposit observed on negative electrode plate located near the edge

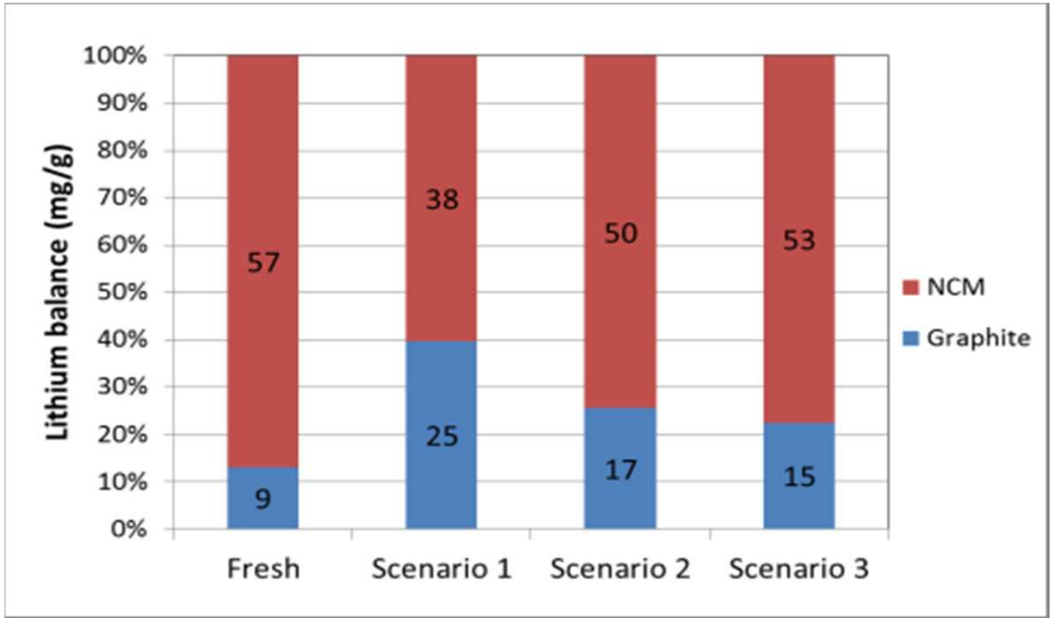


Cell from scenario 2

- Samples located on negative electrode plate near the edge exhibited **less capacity**

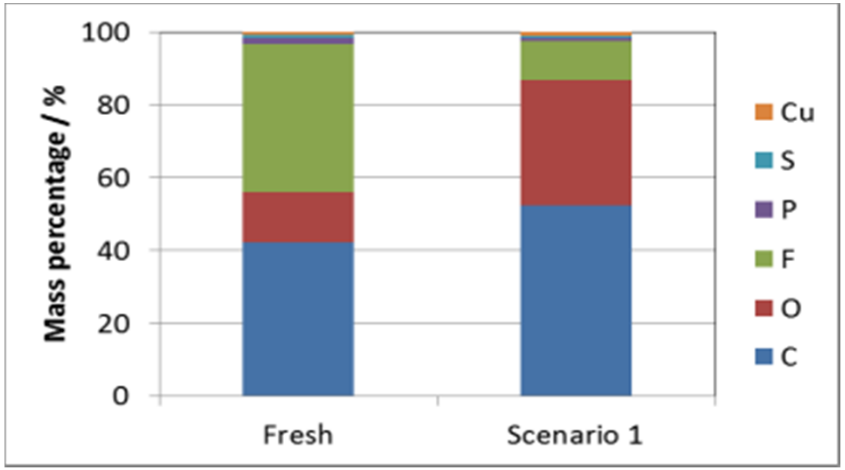
Post-mortem characterization

- ICP-MS analysis



- ICP confirms loss of lithium in positive electrode
- Lithium content in negative electrode increases but is trapped into the SEI

- Energy dispersive analysis on nega electrode surface



- Increase of carbon and oxygen content

→ **SEI growth on anode**

Conclusion

- Compared to aging upon storage, a daily cycle representative of an EV usage increases substantially the aging rate
- **Charging only when necessary** or/and by **limiting charge voltage** can extend substantially cell lifetime
- For all tested aging conditions, analyses of individual electrodes conclude that loss of lithium cyclable is the main aging mechanism (**SEI continuous growth)**
- **Next step is to understand why SEI growth is accelerated by a daily use**

Acknowledgments

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  … for post-mortem analyses and physical characterization

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