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Capacity fade of lithium-ion batteries upon mixed calendar/cycling aging protocol

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François Duclaud^{1,5}

Monday June 20th 2016 Session 2B





Outline

01 Introduction

02 Experimentation

03 Aging Results and Analysis

04 Conclusion and Perspectives



01 Introduction

02 Experimentation

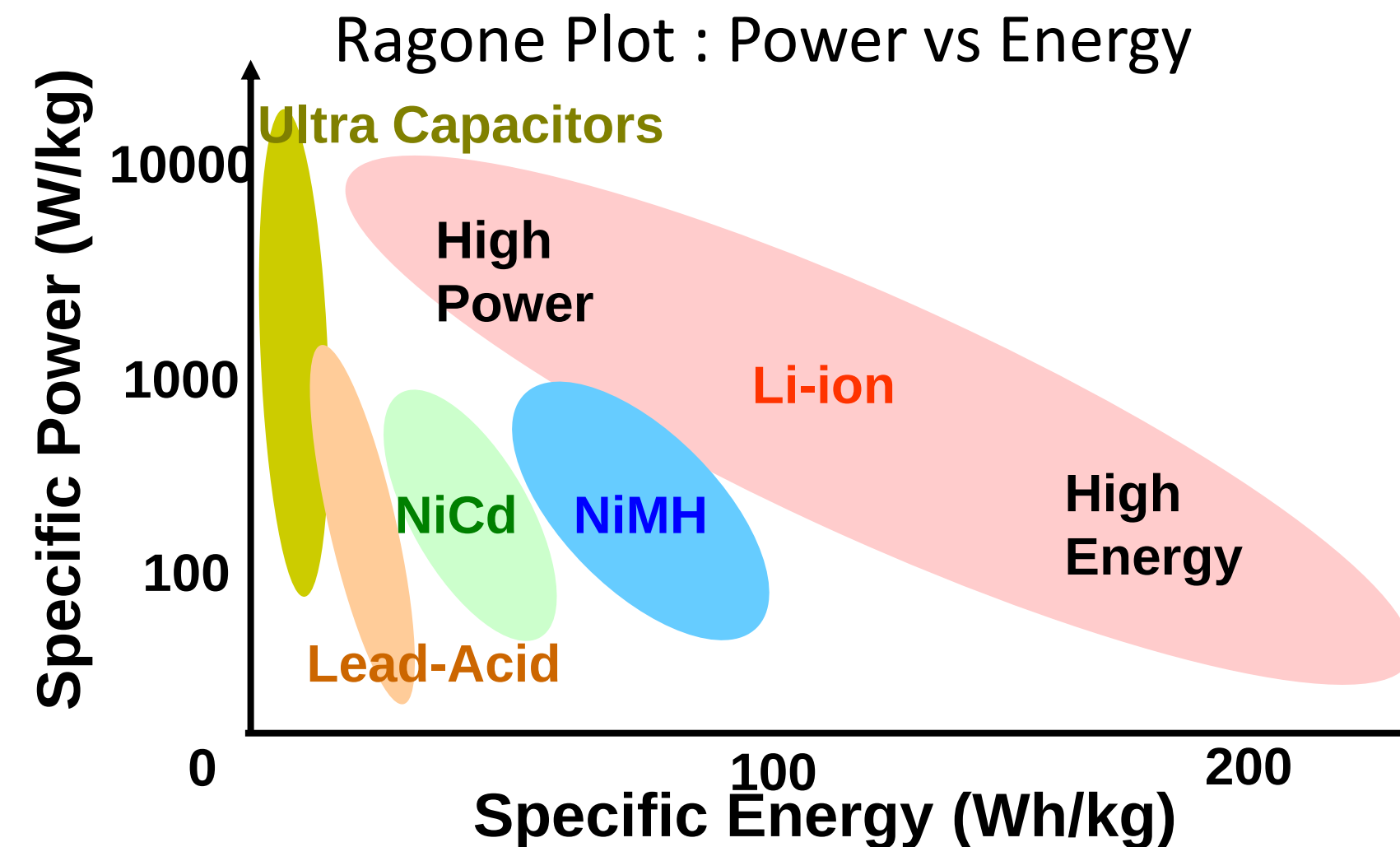
03 Aging Results and Analysis

04 Conclusion and Perspectives

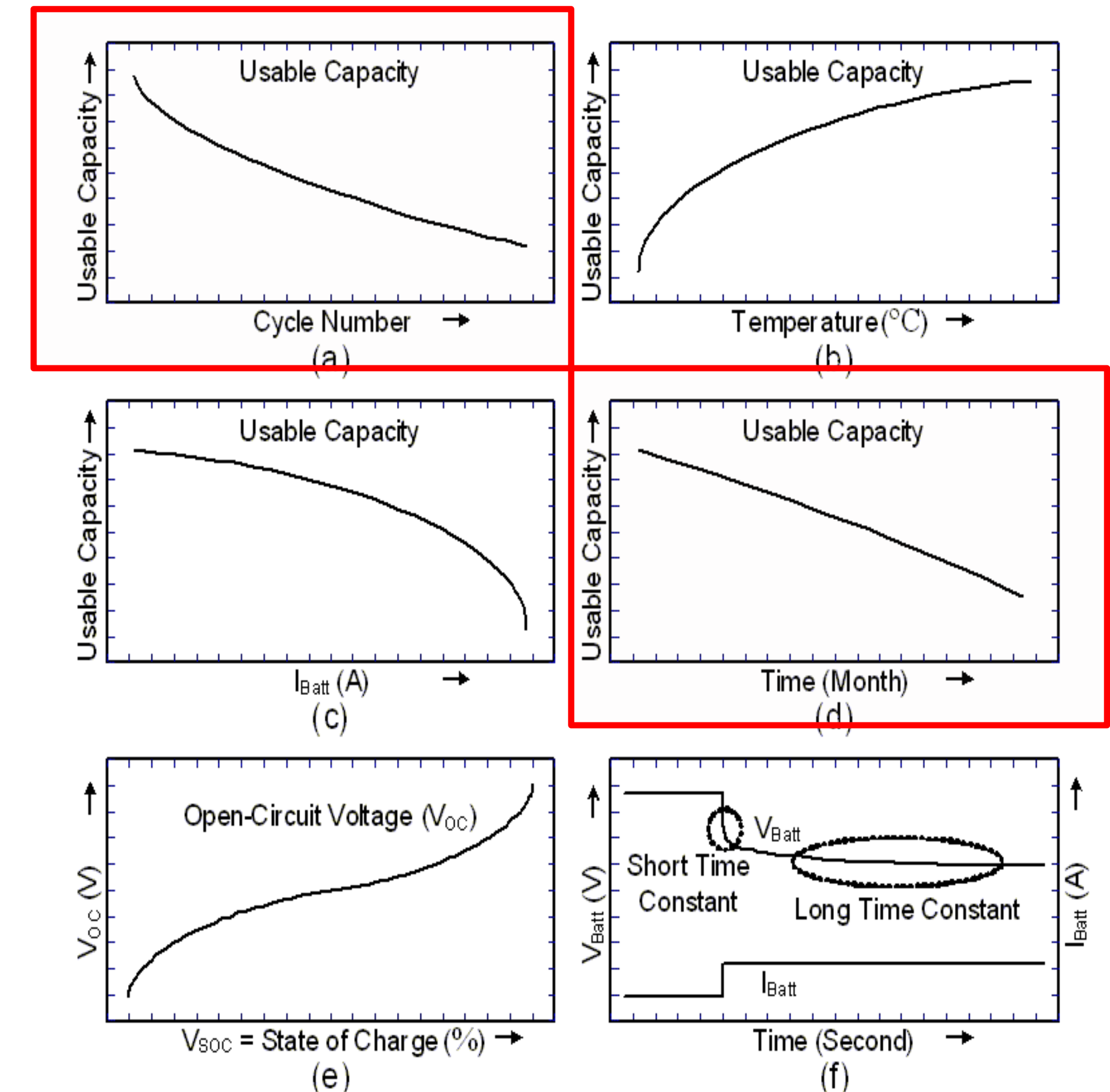


Context of lithium-ion batteries

- Li-ion batteries :
 - Promising candidates for electric transportation
 - Capacity Fade over time



- Ageing research
 - Extensive during cycling
 - Scarce during rest (calendar ageing)



Vehicle applications

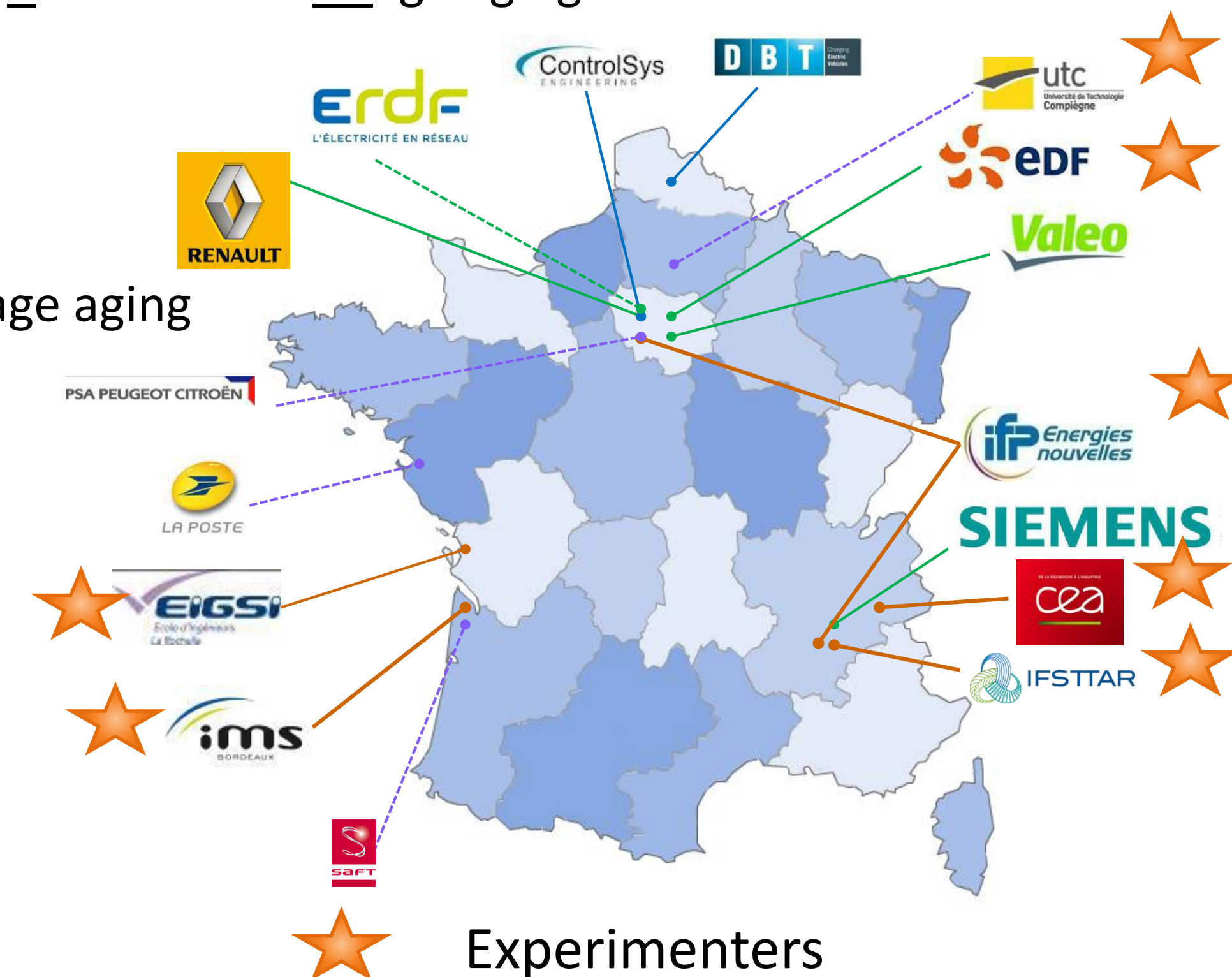
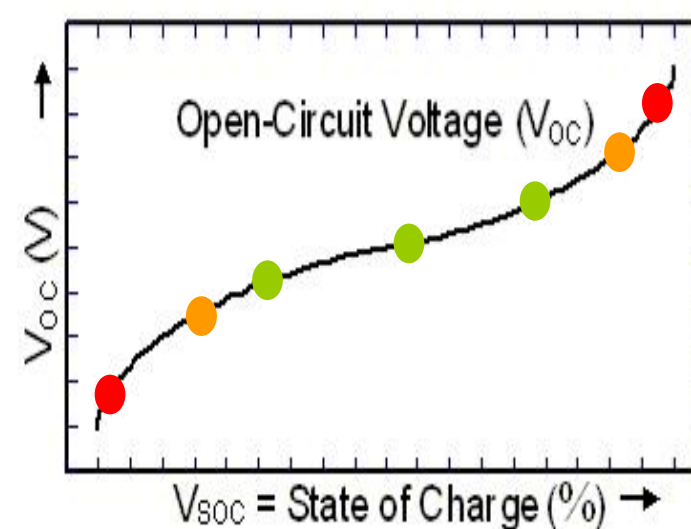
- Vehicle usage:
 - Calendar Mode (Parking)
 - Up to 95 % of real time
 - Usage Mode (Driving, Charging)
 - From 5% to 25 % of real time



- Battery tests
 - Mostly accelerated cycling or calendar aging
 - Need for improved representation of vehicle usage

Research Project on battery aging

- MOBICUS Project
 - French Collaborative project on battery aging
 - MOdeling of Batteries Including the coupling between Calendar and USage aging
 - Duration 36 months 2014-2017, Budget 4.3 M€
- Main objectives of the collaborative project :
 - To understand the coupling between Calendar and Usage aging
 - To develop a battery model representing Calendar and Usage aging
 - To design and validate strategies enabling to extend battery life according to real vehicle usage



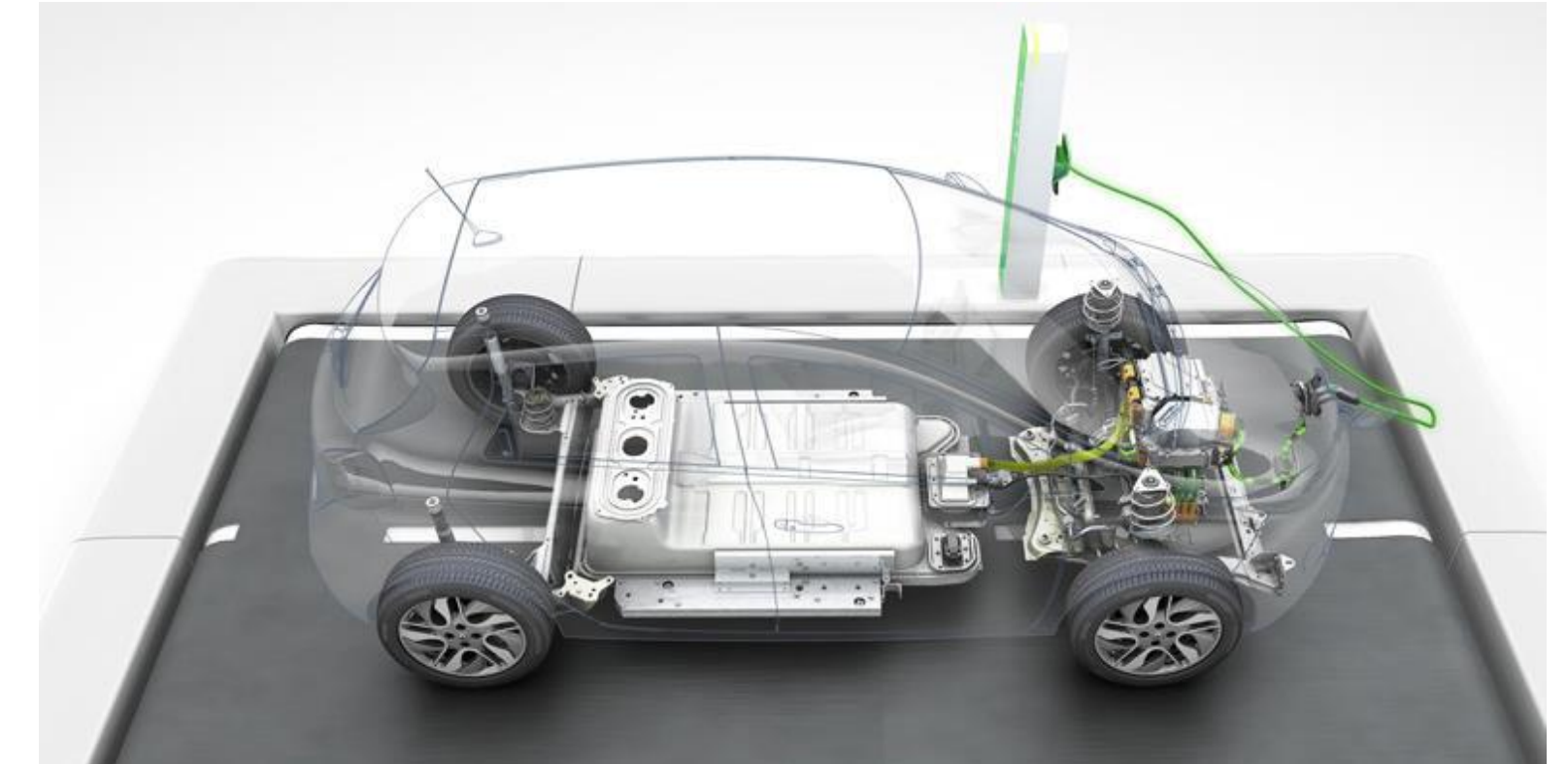


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Batteries Tested in MOBICUS Project

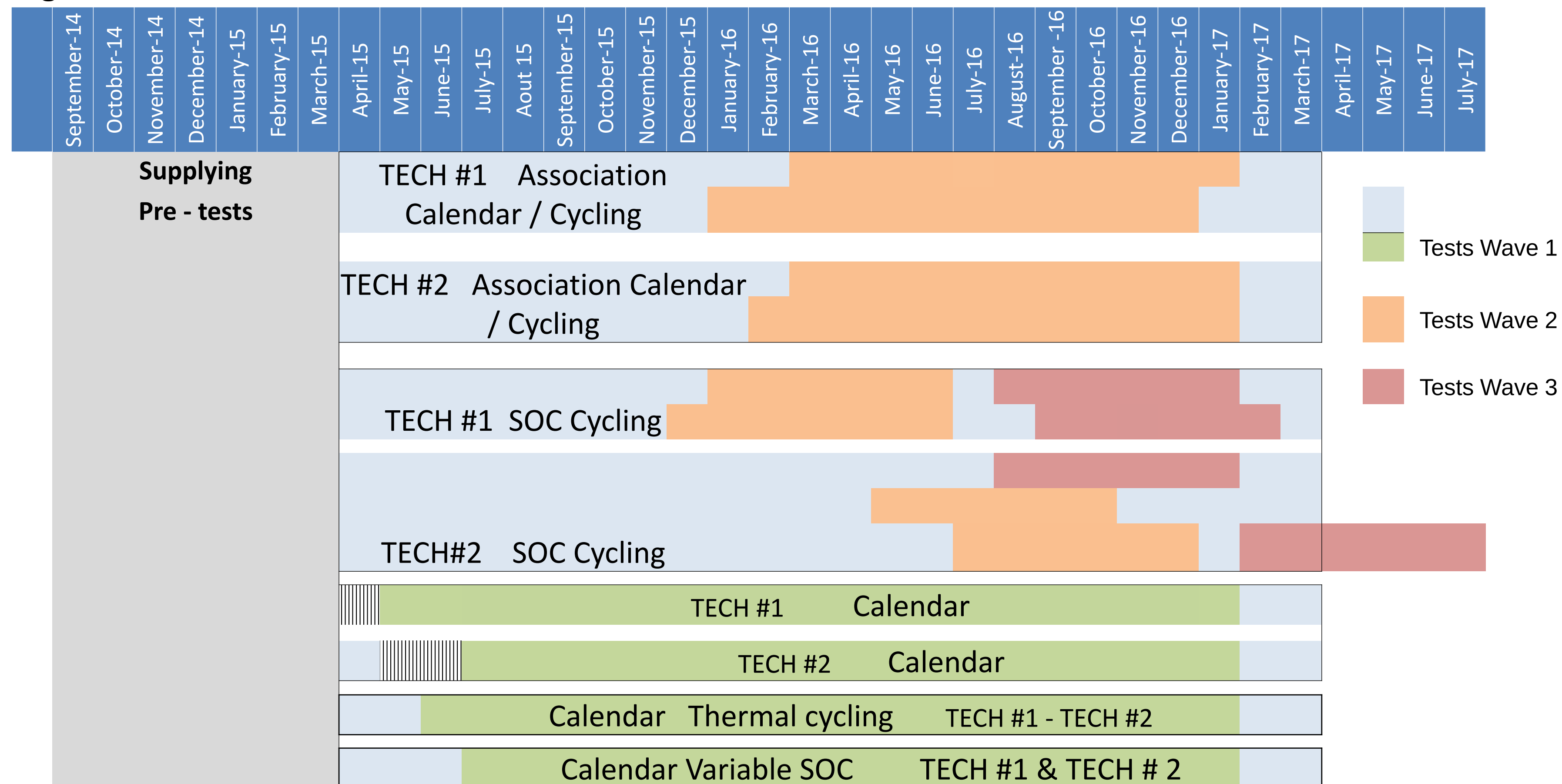
- Commercial Lithium –Ion Batteries



Characteristics at 25 °C		TECH #1	TECH # 2
Nominal capacity	Ah	43	26
Format		Pouch	Prismatic
Electrochemistry		NMC-LMO	NMC / Ni Rich
End of discharge voltage	V	3.00	2.80
End of charge voltage	V	4.20	4.15
End of charge current under floating voltage	A	2.2 (~C/20)	1.5 (~C/20)

Overview of experimental plan

- Testing Conditions



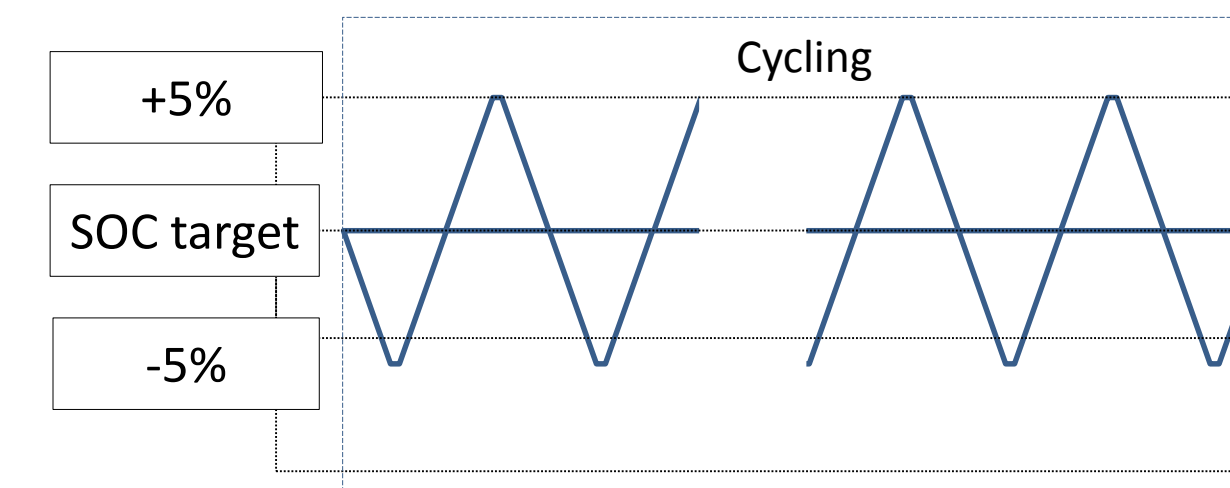
Design of Experiment for Calendar Aging

- Testing Conditions : Calendar Aging
 - 5 different SOC levels (0% - 100 %)
 - 4 different Temperatures (0°C to 60°C)

	SoC=0%	SoC=30%	SoC=65%	SoC=80%	SoC=100%
Temp. 60°C		#2	#2	#1, #2	#2
Temp. 45°C	#1, #2	#1, #2	#1, #2	#1, #2	#1, #2
Temp. 25°C		#2	#2	#1, #2	#2
Temp. 0°C		#1, #2		#1, #2	#2

Design of Experiment for Cycling Aging

- Cycling : variation of +/- 5% SOC around the reference SOC Value
- Table of cycling conditions
 - 3 temperatures (0°C, 25°C, 45 °C)
 - 4 SOC (30 %, 65 %, 80 %, 90 %)
 - 2 current levels charge and discharge ($I_{\min}$, $I_{\max}$)



Test wave 1 (finished)				
Test	Temperature	SoC	I charge	I discharge
1	0	30	MAX	min
2	0	80	min	MAX
3	0	80	MAX	MAX
4	25	30	min	MAX
5	25	30	MAX	min
6	25	80	MAX	min
7	45	30	min	min
8	45	30	MAX	MAX
9	45	80	min	MAX

Test wave 2 (on-going)				
Test	Temperature	SoC	I charge	I discharge
10	0	90	min	min
11	25	65	min	min
12	25	65	MAX	MAX
13	45	65	MAX	MAX

Test wave 3 (planned)				
Test	Temperature	SoC	I charge	I discharge
14	0	65	min	MAX
15	25	90	min	MAX
16	45	90	MAX	MAX
17	45	90	min	MAX



01 Introduction

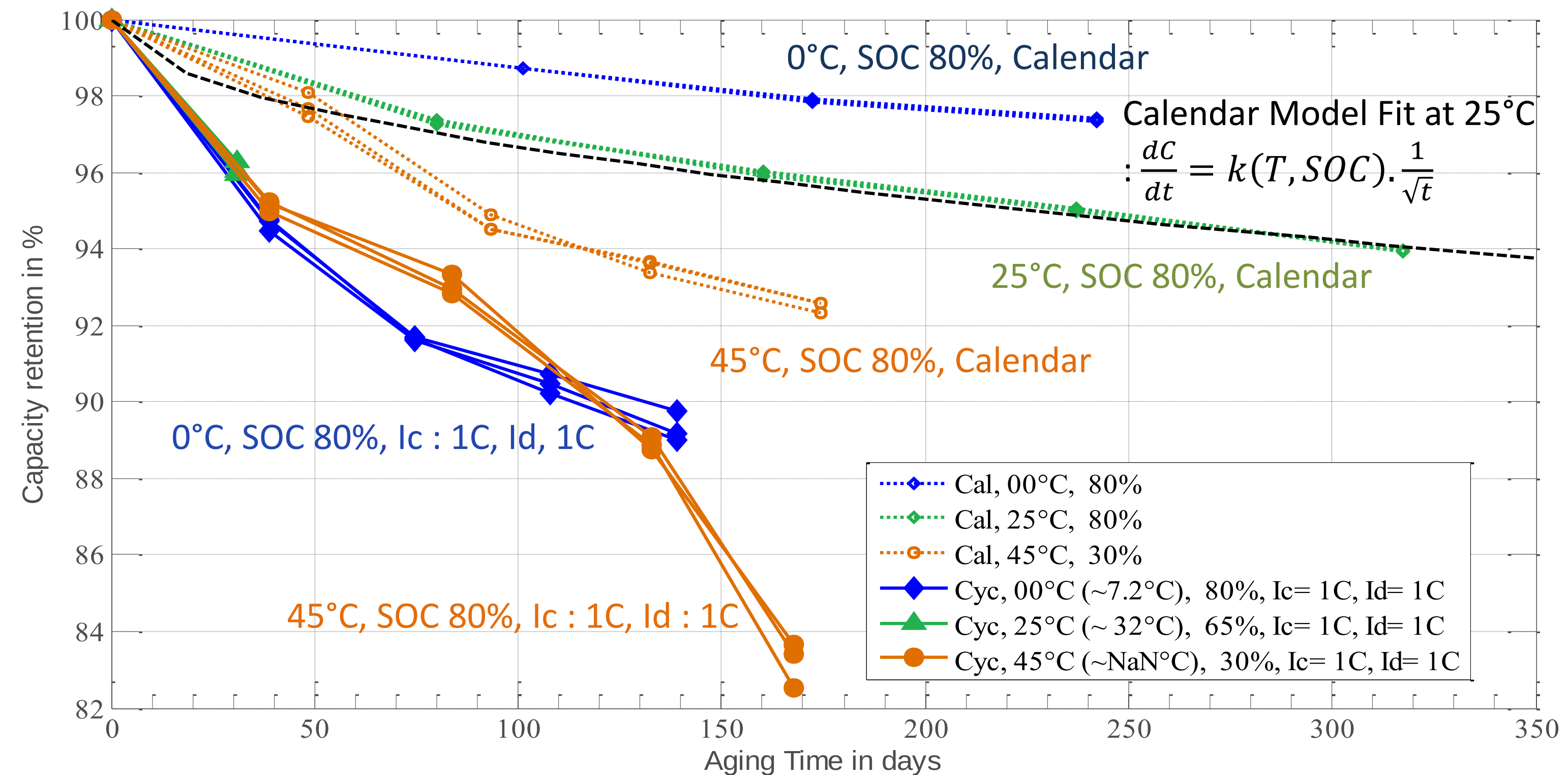
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Calendar and Cycling aging results

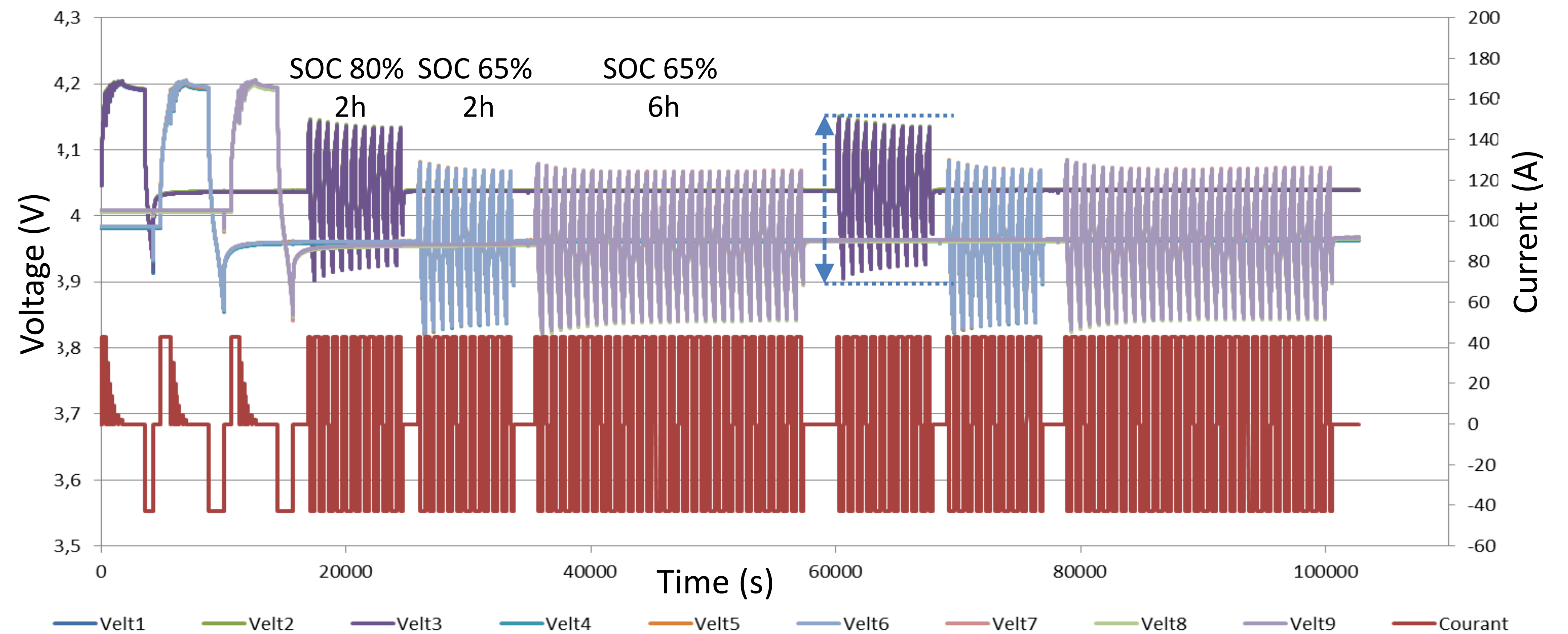
- Calendar and continuous cycling aging tests **TECH #1**



Capacity loss accelerated with cycling, especially in cold conditions

Mixed cycling aging results

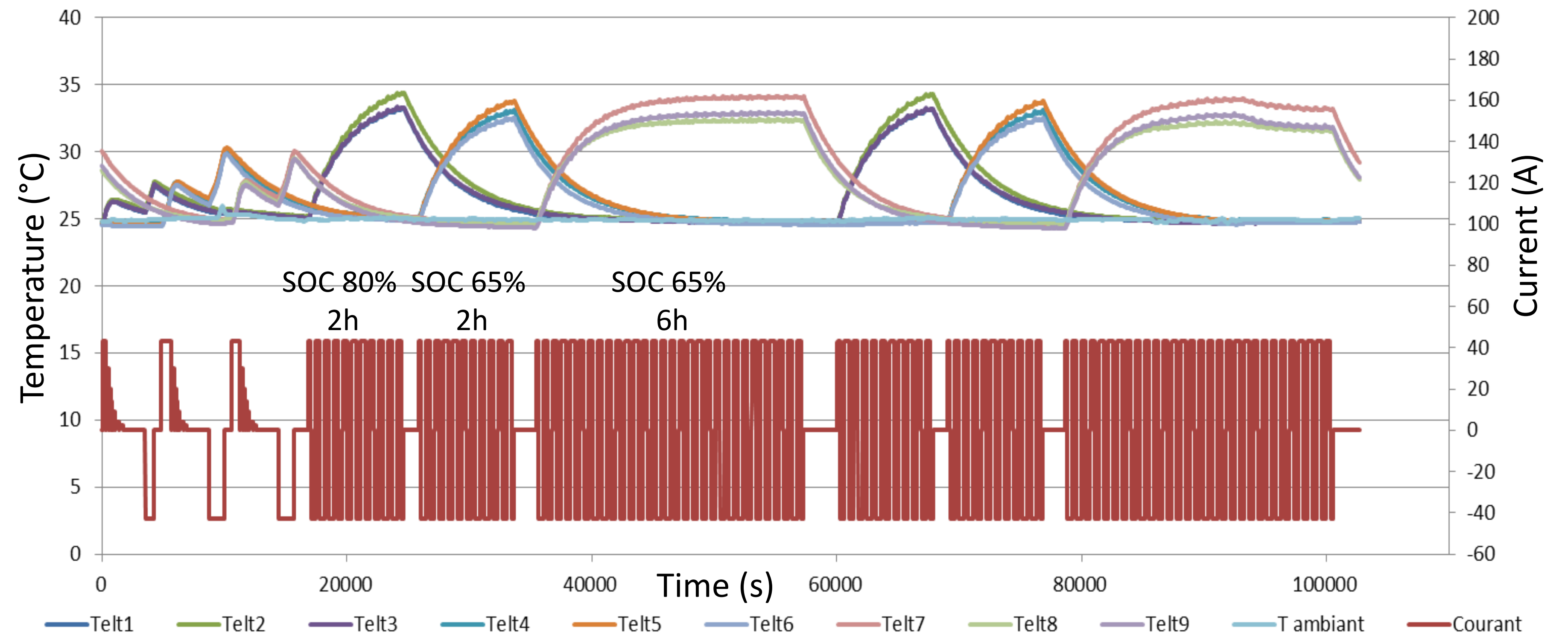
- Current and Voltage during mixed cycling aging test **TECH #1**



Voltage amplitude variation due to temperature rise during cycling

Mixed cycling aging results

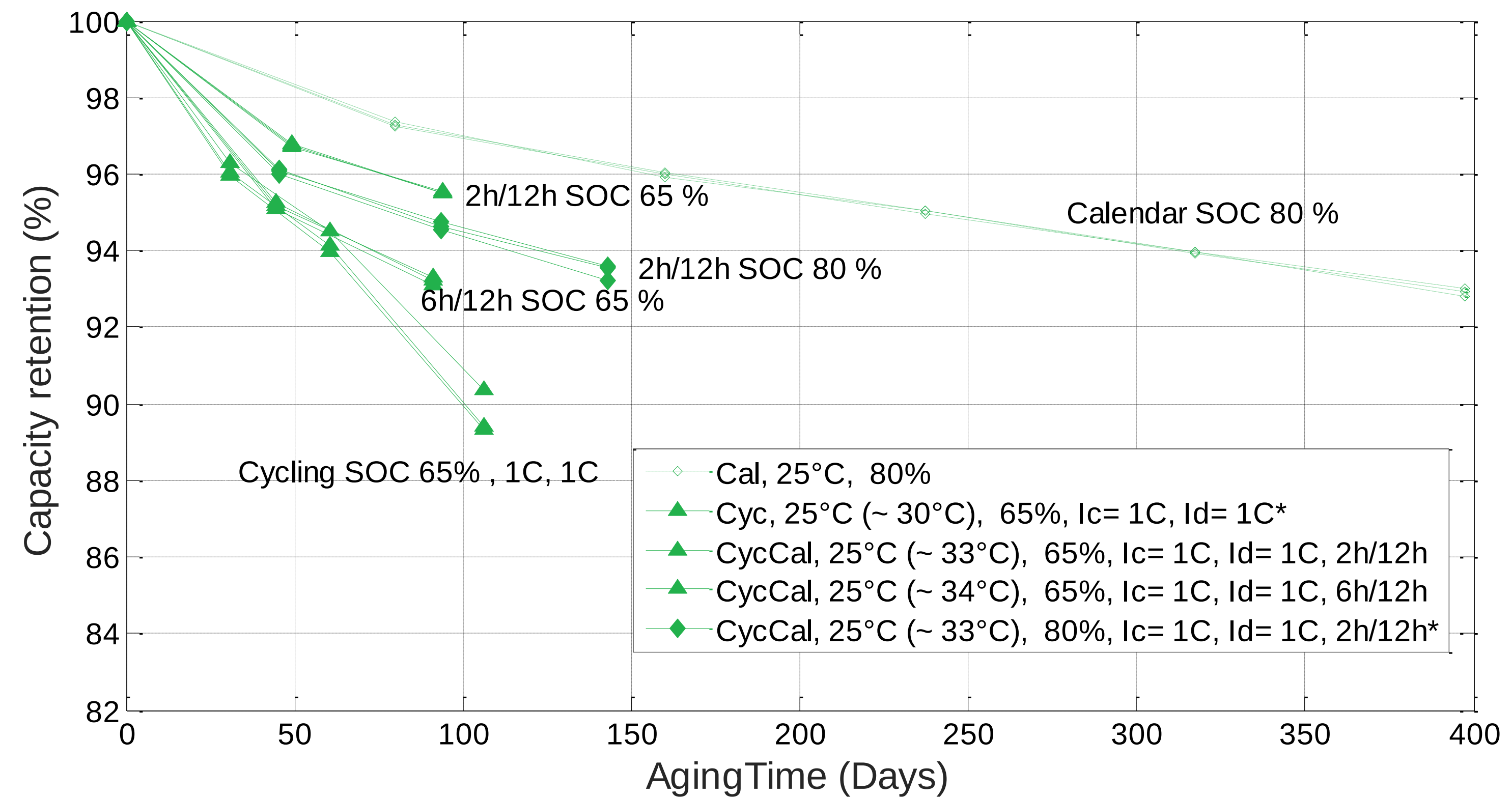
- Current and Temperature during mixed cycling aging test **TECH #1**



Temperature rise during cycling : between +7 to +9 °C

Mixed cycling aging results

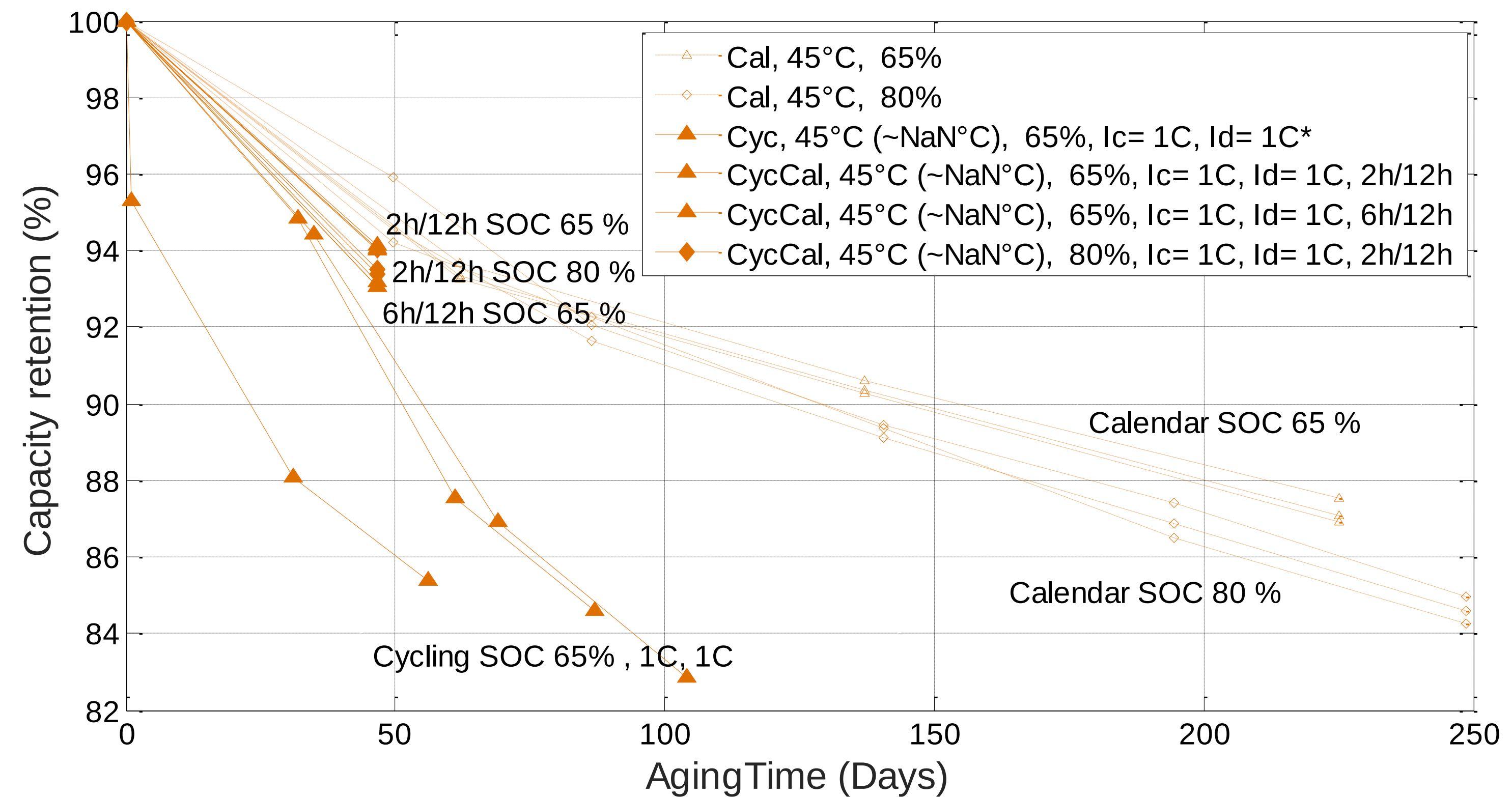
- Capacity retention 25°C **TECH #1**



Acceleration of degradation with cycling time proportion

Mixed cycling aging results

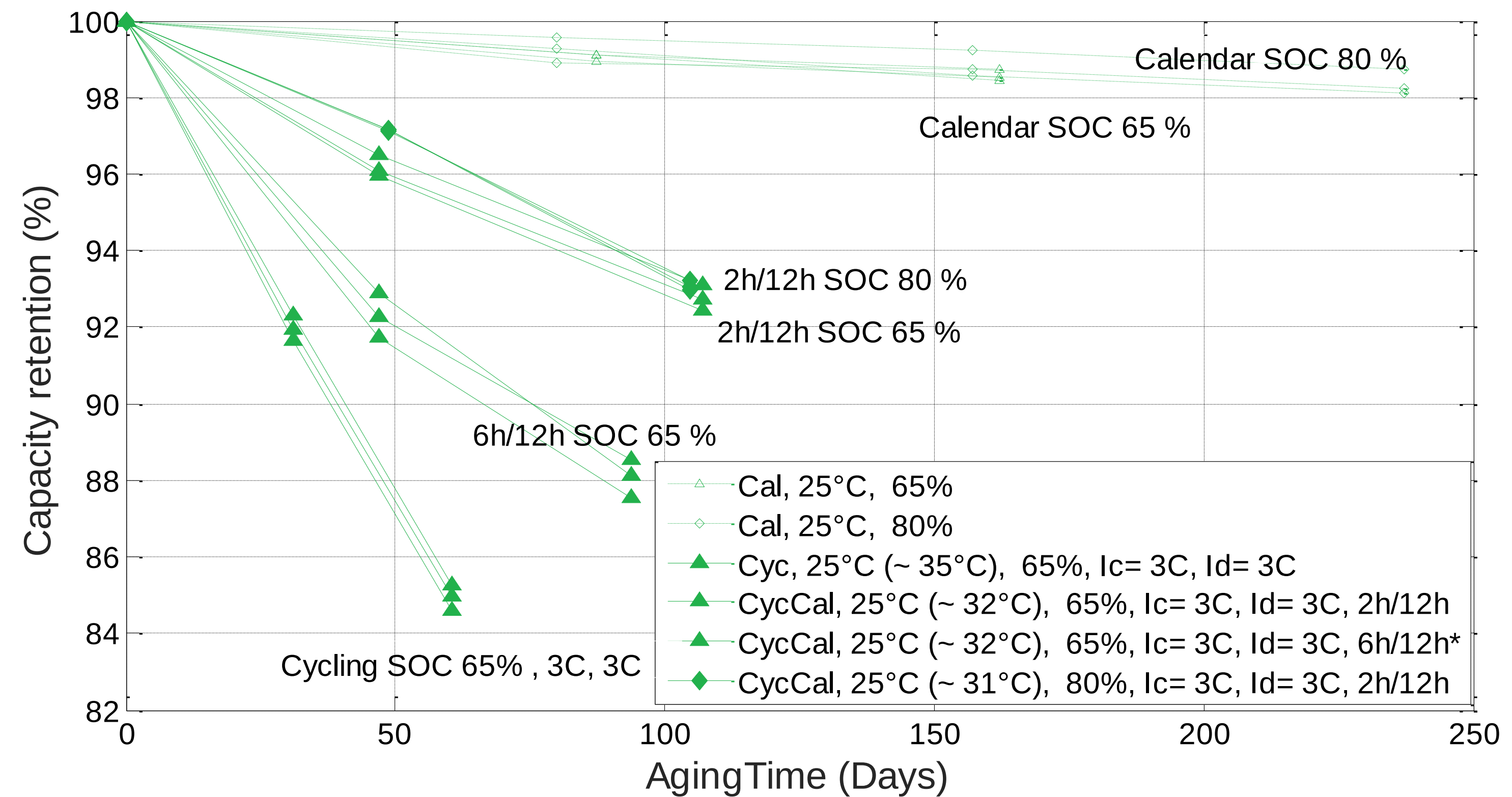
- Capacity retention 45°C **TECH #1**



Much smaller degradation differences between test conditions at higher temperature

Mixed cycling aging results

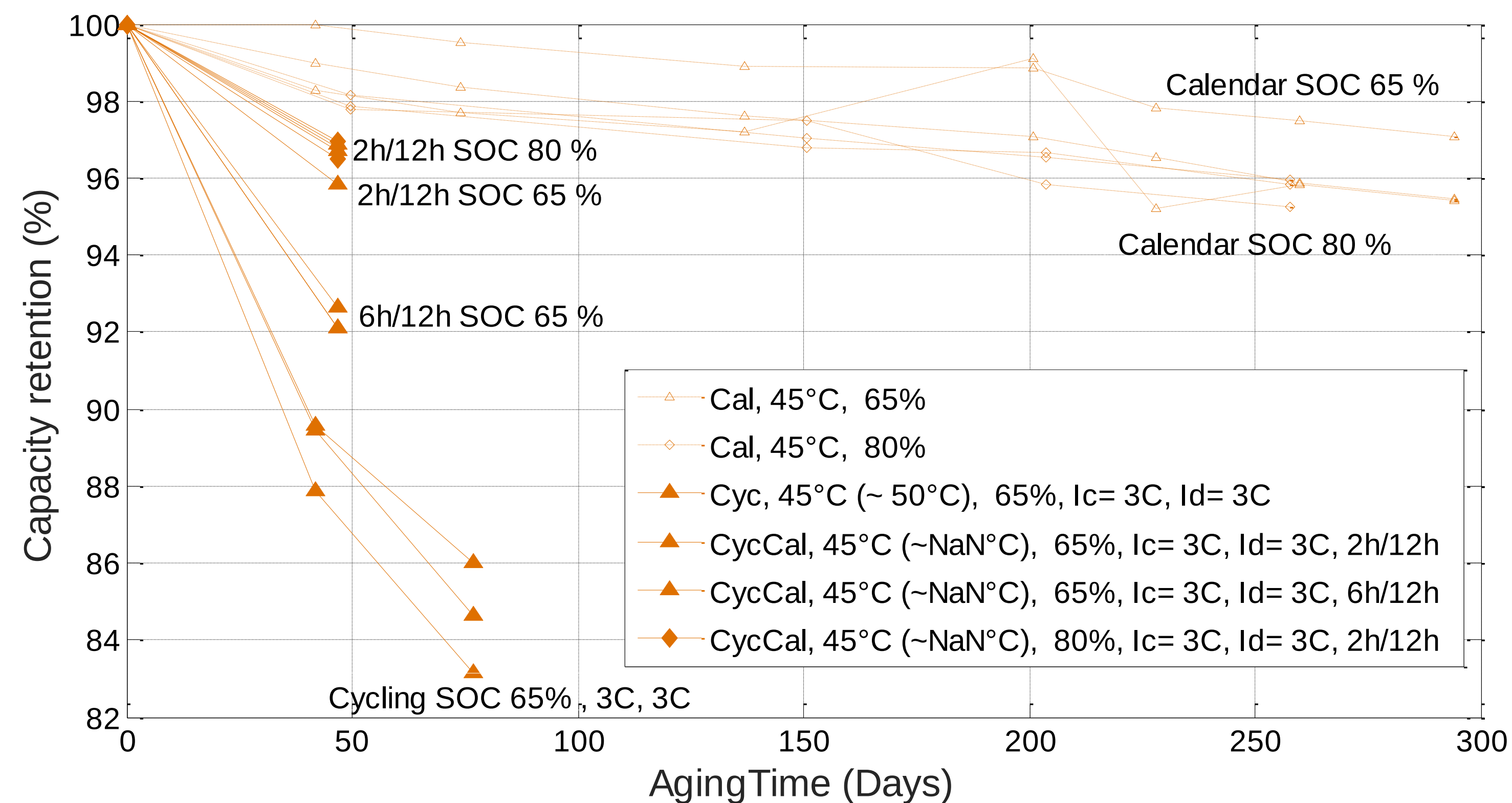
- Capacity retention 25°C TECH #2



In TECH #2, Strong effect of cycling time proportion, little effect of SOC

Mixed cycling aging results

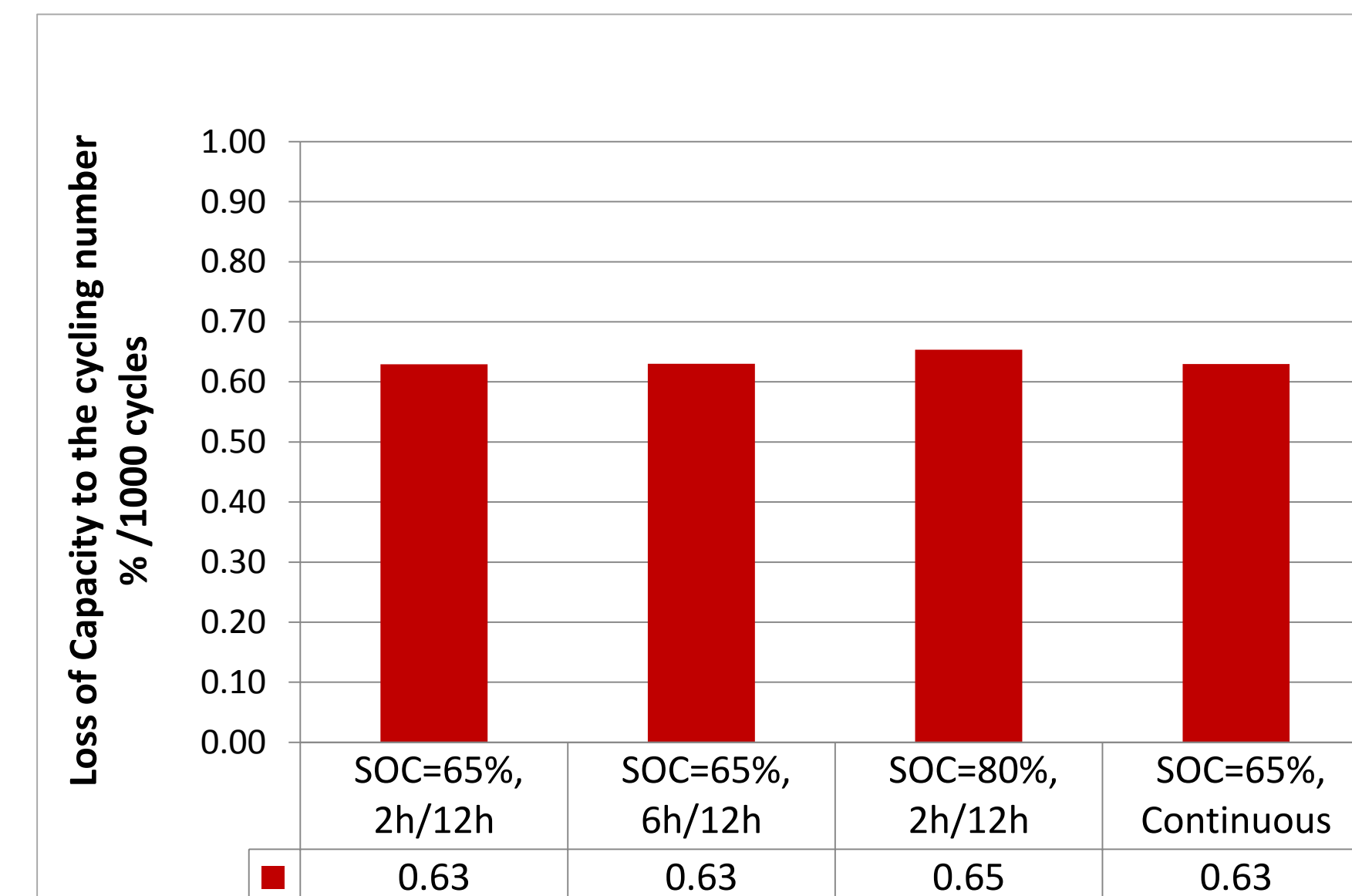
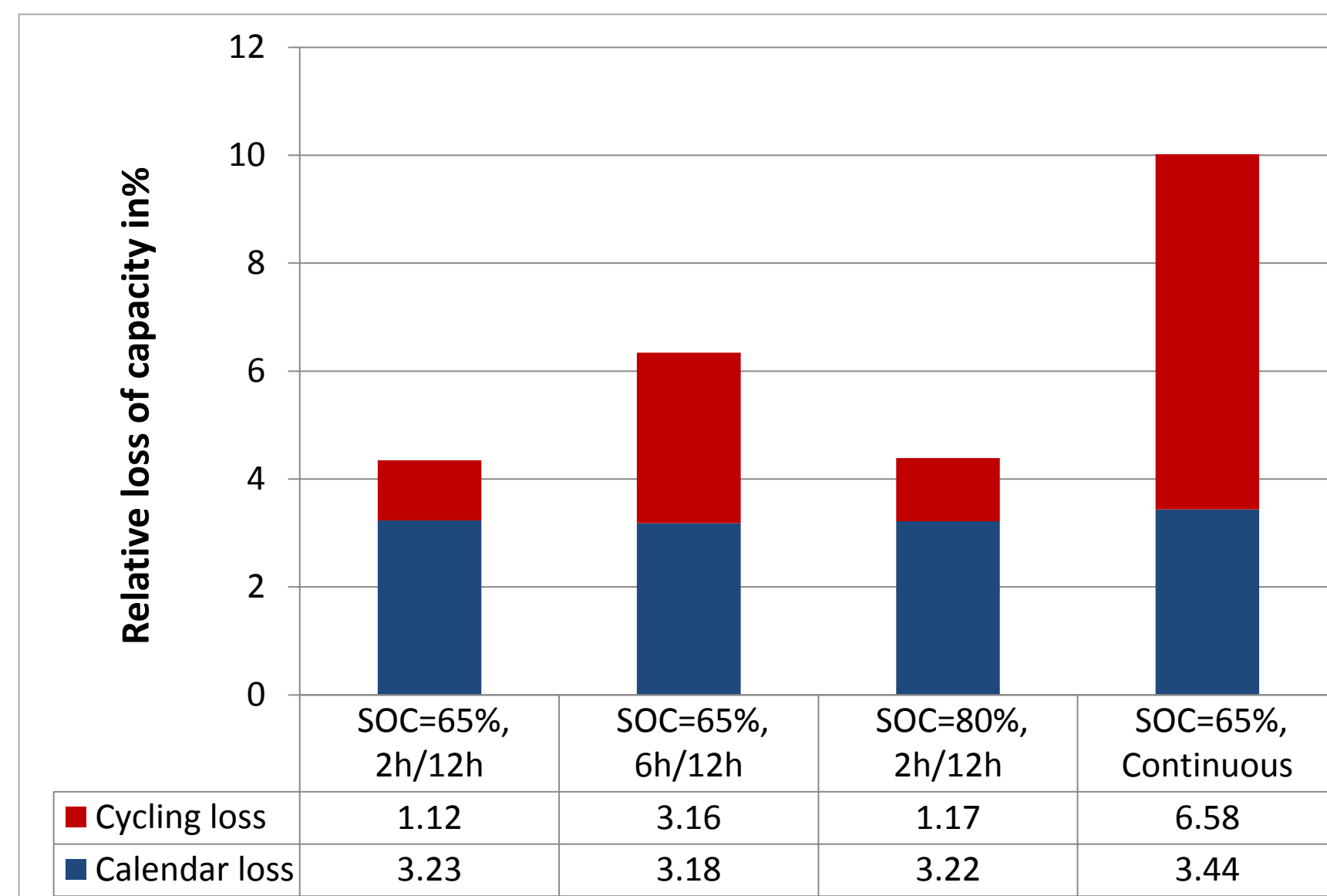
- Capacity retention 45°C TECH #2



In TECH #2, small degradation differences between SOC 65% and SOC 80%

Mixed cycling aging results analysis

- Mixed and continuous cycling, 25 °C, **TECH #1**



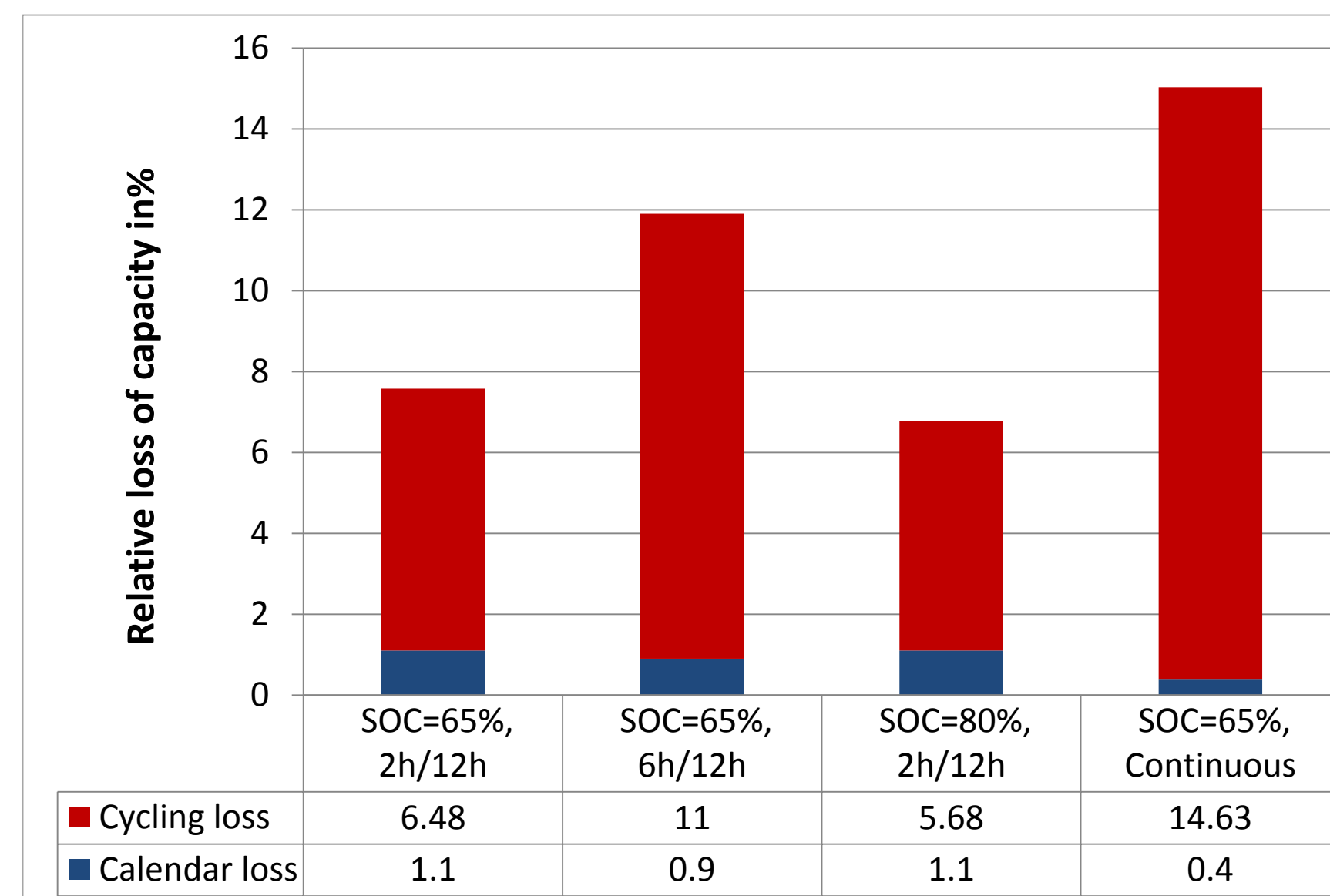
repartition between estimated calendar and cycling loss

derived degradation rates upon cycling

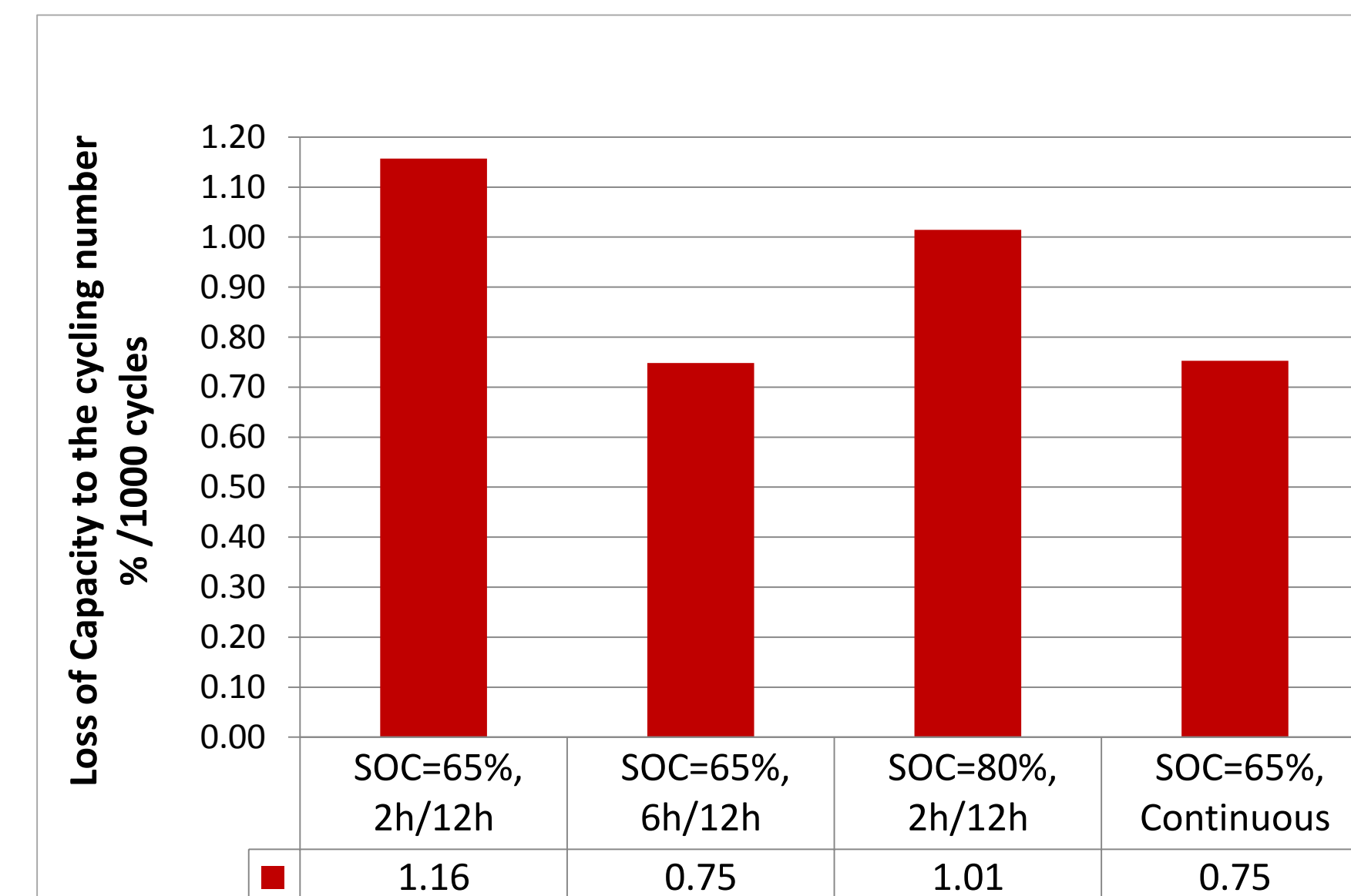
- Identification of the calendar degradation through a model
- Calculation of the cycling contribution, by difference with calendar model
- Identification of the cycling contribution per number of cycles

Mixed cycling aging results analysis

- Mixed and continuous cycling, 25 °C, TECH #2



repartition between estimated calendar and cycling loss



derived degradation rates upon cycling

- Cycling performed @ 3C for TECH #2
- Higher effect of cycling



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Conclusions

- Specific mixed calendar-cycling tests addressed within the French collaborative project MOBICUS
 - Large collection of Data, characterization and validation
- Development of a aging pattern combining calendar and cycling, considering
 - Duration of cycling
 - Temperature
 - Contribution of cycling decreases with temperature due to calendar aging
- Degradation during mixed cycling :
 - Higher than calendar conditions
 - Lower than full cycling conditions
 - Contribution of cycling decreases with temperature
- Influence of SOC depends on battery technology
 - Aging phenomena on batteries can be either chemical or mechanical and are interrelated
 - Calendar aging <-> chemical



Conclusions

- Time plays a crucial role and cycling separated by long pauses may be different than continuous accelerated cycling
- Mixed aging protocol permits to :
 - test batteries in more closer ways than the real automotive usage
 - unvalidate common assumption that calendar aging and cycling aging can be treated apart to make lifetime predictions
- Analysis of preliminary results on two cell technologies show that degradation by cycling does not depend on only cycling pattern



Perspectives

- Deeper analysis of results from both technologies
 - New experimental results from Test Wave 2
- Modeling of thermal behavior of cells during testing
 - Temperature increase during cycling
- Development of aging models representing the capacity loss and resistance increase of cells
- Improvement of aging prediction accuracy for batteries in real vehicle usage



Acknowledgments

- We acknowledge all members of the MOBICUS program (FUI15) for fruitful discussions and contributions. This program received financial support from BPI France, the Conseil Général des Yvelines and the Conseil Régional du Nord Pas De Calais.

- Active Partners



- Invited Partners



- Labeling Poles



- Financial Support



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THANK YOU FOR YOUR ATTENTION

