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LFP battery aging behavior: diagnosis of cell materials for second life applications

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1. INTRODUCTION

- ✓ The battery sorting process is essential in achieving & ensuring reliability of batteries in **2nd life**
- ✓ Batteries from **electric vehicles** : different ageing due to design, use and environment
- ✓ 2nd life batteries must be **guaranteed** for a specified time and use
- ✓ **Sudden shift in cell ageing** may appear: capacity loss, resistance increase [1-3]
- ✓ **Prognosis** of the remaining useful life requires a diagnosis of aging modes to understand changes [4]
- ✓ This poster proposes a method to characterize graphite / lithium iron phosphate (C/LFP) cells
- ✓ Loss of Lithium Inventory (LLI)
- ✓ Loss of Active Material at the negative electrode (LAM_{NE})

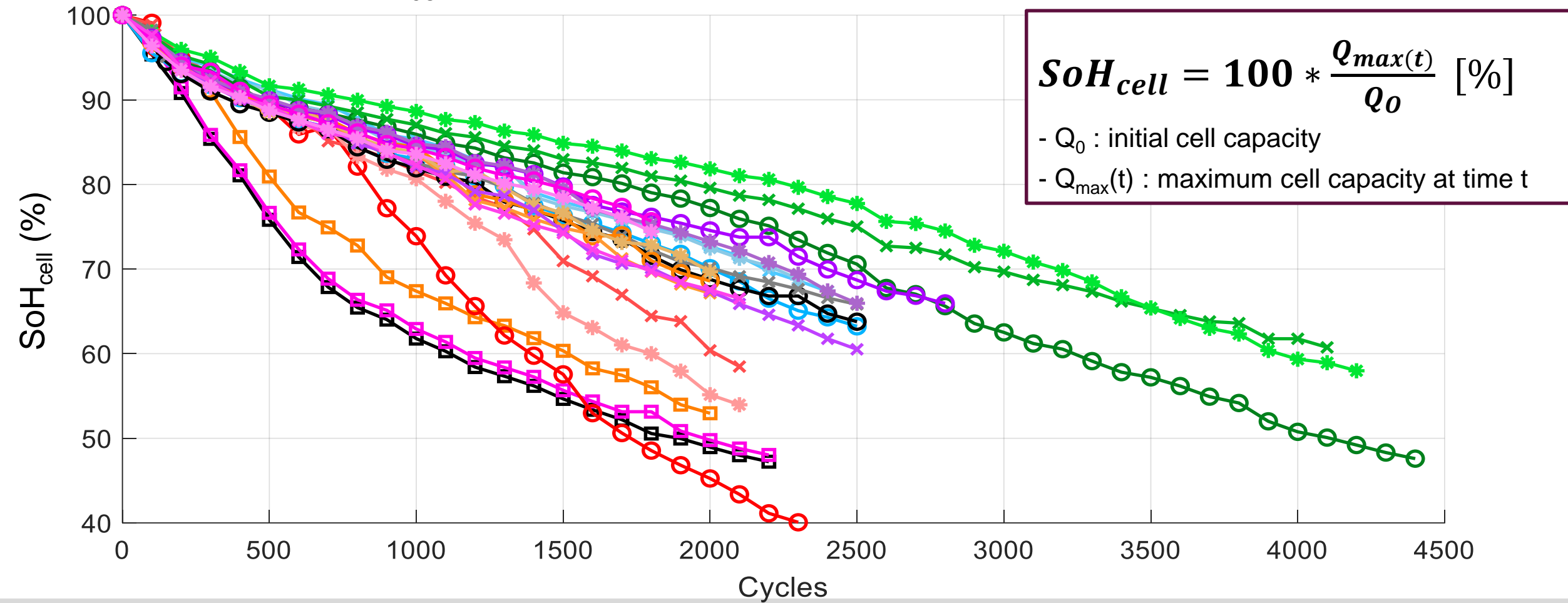
2. EXPERIMENTS

Cell reference	Charge type	Charge Cut-off voltage	Charge C-rate	Discharge type	Discharge C-rate	DoD
Prismatic cell 1 ■	CC	3.65 V	C/3	WLTP	C/3	70 %
Prismatic cell 2 ■	CC-CV	3.65 V	C/3	WLTP	C/3	70 %
Prismatic cell 3 ■	CC-CV	3.55 V	C/3	WLTP	C/3	70 %
18650 cell 4 ○, 5 ×	CC	3.65 V	C/3	WLTP	C/3	70 %
18650 cell 6 ○, 7 ×, 8 *	CC	3.65 V	C/3	WLTP	C/3	100 %
18650 cell 9 ○, 10 ×, 11 *	CC-CV	3.55 V	C/3	WLTP	C/3	70 %
18650 cell 12 ○, 13 ×, 14 *	CC-CV	3.65 V	2C	WLTP	C/3	70 %
18650 cell 15 ○, 16 ×, 17 *	CC-CV	3.55 V	2C	WLTP	C/3	70 %
18650 cell 18 ○, 19 ×, 20 *	CC-CV	3.65 V	2C	CC	2C	70 %
18650 cell 20 ○, 21 ×, 23 *	CC-CV	3.65 V	C/3	WLTP	C/3	70 %

CC: Constant Current CV: constant Voltage WLTP: Worldwide Harmonised Light Vehicles Test Procedure

3. SOH_{CELL} FOLLOW-UP

- ✓ **Cell State of Health (SoH_{cell})**
- ✓ Fast SoH_{cell} decrease for all the cells in the first hundred cycles
- ✓ Fast decrease of SoH_{cell} for cells 7,8 & 9 after 700-1000 cycles

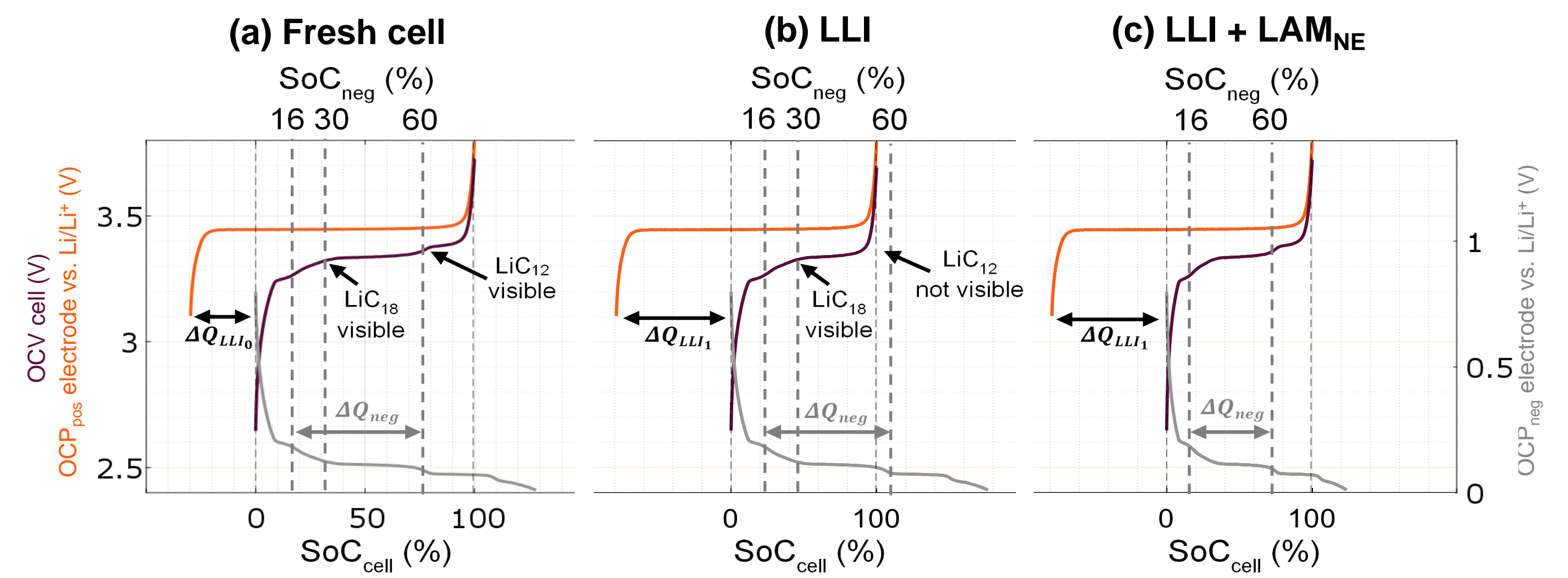
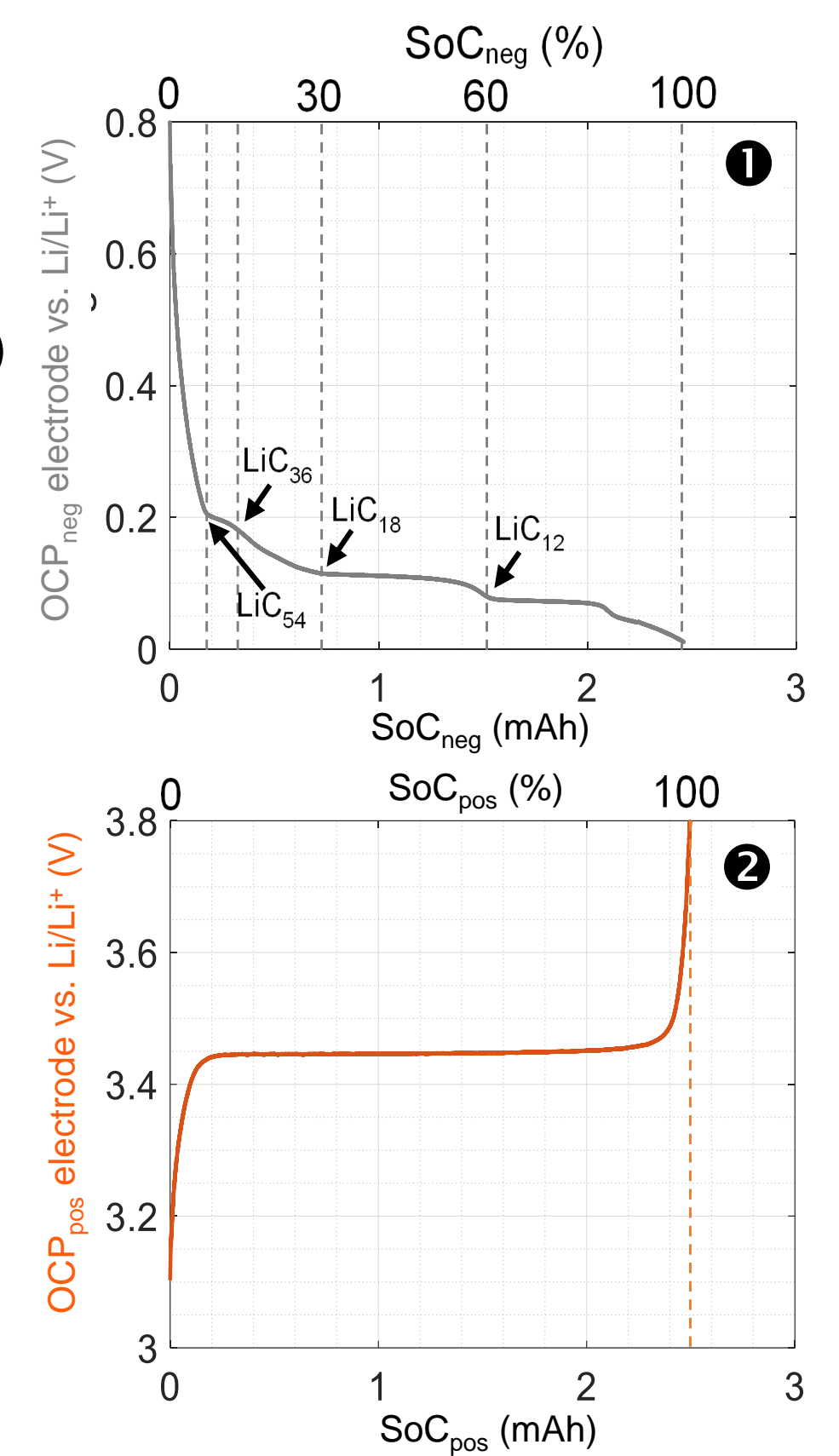


4. ELECTRODE CHARACTERISATION

- ✓ **Electrode material characterisation**
- ✓ 18650 fresh cylindrical cells (18650) dismantling in glove box
- ✓ Electrode characterisation in half cell vs. Li/Li⁺ (coin cell CR2032)
- ✓ Open Circuit Potential (OCP) of each electrode (figures 1 & 2)
- ✓ Negative electrode phase transition detection using ICA/DVA [5] (figure 1)

Phase transition	C	LiC ₅₄	LiC ₃₆	LiC ₁₈	LiC ₁₂
SoC _{neg} [%]	0	10	16	30	60

- ✓ No characteristic transition for the positive electrode
- ✓ **Cell voltage profile (OCV) reconstruction**
- ✓ Enable negative electrode phase transition detection on full-cell measurement (figure (a)) & allow SoH_{neg} estimation (section 5)
- ✓ **Possible ageing scenarios**
- ✓ LLI (Loss of Lithium Inventory) : **offset** ΔQ_{LLI} increase between electrode OCP (figures (a) & (b))
- ✓ LAM_{NE} (Loss of Active Materials at the Negative Electrode) : **shrink of negative electrode OCP** (figure (b) & (c)). Lower charge/discharge capacity between phase transitions, ΔQ_{neg} decrease
- ✓ LLI + LAM_{NE} : combination of both effects: offset increase and negative electrode shrinking.



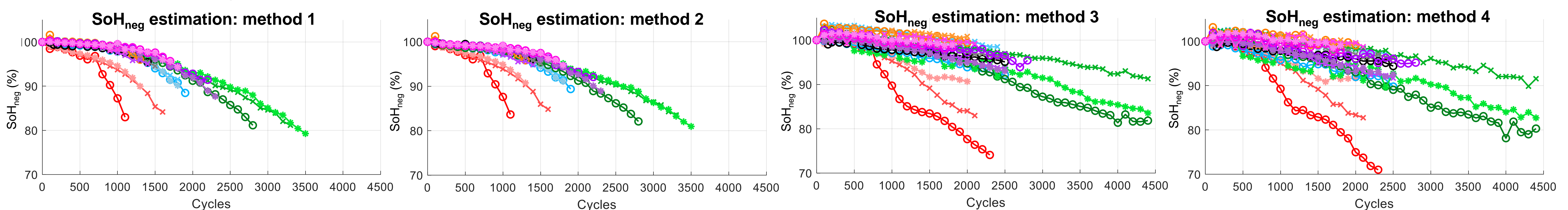
5. PROPOSED SOH_{NEG} ESTIMATION METHODS

- ✓ **SoH_{neg} negative electrode follow-up**
- ✓ Based on full-cell measurement and phase transition detection using ICA/DVA
- ✓ **SoH_{neg} negative electrode estimation**
- ✓ Step 1 : ΔQ_{neg} = |Q(LiC_a) - Q(LiC_b)| [Ah]
- ✓ Step 2 : Q_{neg,max} = ΔQ_{neg} / (SoC_b - SoC_a) [Ah]
- ✓ Step 3 : SoH_{neg} = Q_{neg,max} / Q_{neg,0} [%]

Estimation SoH _{neg}	LiC _a	SoC _{neg a}	LiC _b	SoC _{neg b}
Method 1	C	0	LiC ₁₂	0,6
Method 2	LiC ₅₄	0,1	LiC ₁₂	0,6
Method 3	LiC ₅₄	0,1	LiC ₁₈	0,3
Method 4	LiC ₃₆	0,16	LiC ₁₈	0,3

6. SOH_{NEG} ESTIMATION RESULTS

- ✓ The results of the four SoH_{neg} estimations are presented below. Colors correspond to cells in the table in section 2 "experiments".



- ✓ **Estimations methods 1 and 2 are rendered unusable after a certain number of cycles:** between 1000 and 3500 depending on the cell
- ✓ LLI is too great → LiC₁₂ phase transition disappears in cell voltage profile (figures (a) & (b))
- ✓ **Estimations methods 3 and 4 works on all lifecycle**
- ✓ Lower accuracy due to the use of closer phase transition
- ✓ **SoH_{neg} loss accelerates during use**
- ✓ Fast SoH_{neg} decrease for cells with fast decrease of SoH_{cell} (cells 7, 8 & 9 with 100% DoD, in red)

7. CONCLUSION

- ✓ The estimation method makes it possible to differentiate:
- ✓ **Aging dynamics between cell and negative electrode**
- ✓ Aging of the negative electrode **accelerates** during use
- ✓ Correlation between cell and negative electrode for the aging acceleration
- ✓ End of the experimental tests : planned for SoH_{cell} = 30%

8. FUTUR WORK

- ✓ Link between the negative electrode aging acceleration and cell aging acceleration
- ✓ **Prognosis** of the RUL in 2nd life applications based on the diagnosis of degradation modes

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