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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
- $\checkmark 2^{nd}$ 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)
 - \checkmark Loss of Active Material at the negative electrode (LAM_{\rm NE})

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 & ❷)
- \checkmark Negative electrode phase transition detection using ICA/DVA [5] (figure $oldsymbol{0}$)

Phase transition	С	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)



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 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: const	tant Voltage	WLTP: Wo	orldwide Harm	nonised Light Ve	hicles Test Prod	cedure

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



- **Possible ageing scenarios**
- ✓ LLI (Loss of Lithium Inventory) : offset ∆Q_{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
- Estimation SoH_{neg} LiC_a SoC_{neg a} LiC_b SoC_{neg b}

• Step 1: $\Delta Q_{neg} = Q(LlC_a) - Q(LlC_b) $ [An]	
✓ Step 2 : $Q_{neg_{max}} = \frac{\Delta Q_{neg}}{SoC_b - SoC_a}$ [Ah]	
✓ Step 3 : $SoH_{neg} = \frac{Q_{neg_{max}}}{Q_{neg_0}}$ [%]	

Method 1	С	0	<i>LiC</i> 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".



between 1000 and 3500 depending on the cell LLI is too great \rightarrow LiC₁₂ phase transition disappears in cell voltage profile (figures (a) & (b)) Estimations methods 3 and 4 works on all lifecycl
 ✓ Lower accuracy due to the use of closer phase transition

✓ Fast SoH_{neg} decrease for cells with fast decrease of SoH_{cell} (cells 7, 8 & 9 with 100% DoD, in red)

7. CONCLUSION	8. FUTUR WORK	ACKNOWLEDGEMENT	REFERENCES
 The estimation method makes it possible to differentiate: Aging dynamics between cell and negative electrode Aging of the negative electrode accelerates during use 	 ✓ Link between the negative electrode aging acceleration and cell aging acceleration 	We acknowledge EVE SYSTEM for the funding of this research with the support of ANRT (Grant number: CIFRE 2018/1625).	 [1] S.F. Schuster, T. Bach, E. Fleder, J. Müller, M. Brand, G. Sextl, A. Jossen, Nonlinear aging characteristics of lithium-ion cells under different operational conditions, J. Energy Storage. 1 (2015) 44–53. doi:10.1016/j.est.2015.05.003. [2] M. Klett, R. Eriksson, J. Groot, P. Svens, K. Ciosek Högström, R.W. Lindström, H. Berg, T. Gustafson, G. Lindbergh, K. Edström, Non-uniform aging of cycled commercial LiFePO4//graphite cylindrical cells revealed by post-mortem analysis, J. Power Sources. 257 (2014) 126–137. doi:10.1016/j.ipowsour.2014.01.105.
✓ Correlation between cell and negative electrode for the	✓ Prognosis of the RUL in 2 nd life applications based	We thank IRN-FACES for their	[3] M. Safari, C. Delacourt, Aging of a Commercial Graphite/LiFePO4 Cell, J. Electrochem. Soc. 158 (2011) A1123. doi:10.1149/1.3614529.

aging acceleration

 \checkmark

✓ End of the experimental tests : planned for $SoH_{cell} = 30\%$

on the diagnosis of	
degradation modes	

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