## Article

## A Post-Mortem Study of Stacked 16 Ah Graphite//LiFePO4 Pouch Cells Cycled at 5 °C

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## **Supplementary Material**



**Figure S1.** Results of 16 Ah soft prismatic cells cycled between the voltage limits of 2.5 V and 3.6 V at different temperatures: 5 °C (blue), 25 °C (green) and 45 °C (red) at 1 C discharge rate and 0.3 C (circle), and 2 C (square) in charge.

Electrode			Electrode					
Number in	Area 1	Area 2	Number in	Area 1	Area 2			
the Stack			the Stack					
Fresh Cell								
1	XPS	XPS	17	XPS	XPS			
2	SEM	Electrochem.	17–33	/	/			
3	Adhesion	Adhesion	34	Adhesion	Adhesion			
4–14	/	/	35	SEM	Electrochem.			
15	SEM (cathode rinsed with ACN)	Electrochem. (cathode rinsed with ACN)	36	Electrochem.	XPS			
16	Adhesion	Adhesion						
Aged Cells (Cell A and Cell B)								
1	XPS	XPS	17	XPS	XPS			
2	SEM	Electrochem.	17–33	/	/			
3	Adhesion	Adhesion	34	Adhesion	Adhesion			
4–14	/	/	35	SEM	Electrochem.			
15	SEM	Electrochem.	36	XPS	XPS			
16	Adhesion	Adhesion						

**Table S1.** Summary of measurements performed in different stack's positions. The samples for XPS analysis were not subjected to any rinsing with solvent. The other samples were all washed with Dimethylcarbonate (DMC) solvent excluding the cathode number 15 of the fresh cell for which Acetonitrile (ACN) was employed.



**Figure S2.** SEM images of LFP electrode extracted from different parts of the stack of Cell A: (**a**) beginning, (**b**) middle and (**c**) end of stack.



**Figure S3.** SEM images of LFP samples extracted from the middle of the stack of Cell B and sampled (**a**) in the center and (**b**) at the edge of the electrode tape.



**Figure S4.** EDX spectra of aged cathode from (**a**) cell A and (**b**) cell B. Note: In some EDX analysis (not shown here), small additional fluorine peak was observed, probably corresponding to remaining traces of LiPF<sub>6</sub> salt, randomly distributed on the surface of the electrode.



**Figure S5.** EDX analysis of the fresh graphite electrode. The main peak corresponds to carbon, as expected. Furthermore, small amounts of F, P and Na are detected. F and P can be ascribed to unremoved salt or SEI compounds. Na traces, most probably from CMC binder. Cu is also observed as it corresponds to the current collector.



**Figure S6.** EDX spectra of negative electrode extracted from Cell B and sampled at the (**a**) edge and (**b**) center of the electrode tape.



Figure S7. SEM of separators from Fresh Cell (a), Cell A (b) and Cell B (c).



**Figure S8.** Voltage profile of the first cycle of a pristine cathode obtained at 0.15 mA cm<sup>-2</sup> (0.065 C) in half-cell. (Electrode area  $\approx$  1.13 cm<sup>2</sup>).



Figure S9. Comparison of first de-lithiation of aged cathode in freshly re-assembled half-cells (samples taken from the center (c) of the electrode tapes harvested from different position of the stack).

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Test	Step	Conditions	Cycles	
1st arrala	Ch	$0.065\mathrm{C} \rightarrow 3.65~\mathrm{V/CV}$ <0.03 C & 2 h	1	
1 <sup>st</sup> cycle	Dis	0.065C→2.5V		
	Ch	$0.2C \rightarrow 3.65$ V/CV <0.03 C & 1 h	3	
	Dis	0.3C→2.5V		
	Ch	$0.2C \rightarrow 3.65 \text{ V/CV} < 0.03 \text{ C} \& 1 \text{ h}$	3	
	Dis	$0.65 \text{ C} \rightarrow 2.5 \text{V}$		
	Ch	$0.2 \text{ C} \rightarrow 3.65 \text{ V/ CV} < 0.03 \text{ C} \& 1 \text{ h}$	1	
	Dis	$0.2 \text{ C} \rightarrow 2.5 \text{ V}$	1	
	Ch	0.2 C→3.65 V/CV <0.03 C & 1 h	2	
	Dis	1.3C→2.5V	3	
	Ch	$0.2 \text{ C} \rightarrow 3.65 \text{ V/CV} < 0.03 \text{ C} \& 1 \text{ h}$	1	
C rate comebility	Dis	$0.2 \text{ C} \rightarrow 2.5 \text{ V}$	1	
C-rate capability	Ch	$0.2 \text{ C} \rightarrow 3.65 \text{ V/ CV} <\!\! 0.03 \text{ C} \& 1 \text{ h}$	3	
	Dis	2C→2.5V		
	Ch	0.2 C→3.65 V/CV <0.03 C & 1 h	1	
	Dis	0.2C→2.5V	1	
	Ch	$0.2 \text{ C} \rightarrow 3.65 \text{ V/CV} < 0.03 \text{ C} \& 1 \text{ h}$	2	
	Dis	6.5C→2.5V	3	
	Ch	$0.2 \text{ C} \rightarrow 3.65 \text{ V/CV} < 0.03 \text{ C} \& 1 \text{ h}$	1	
	Dis	$0.2 \text{ C} \rightarrow 2.5 \text{ V}$		
	Ch	0.2 C→3.65 V/CV <0.03 C & 1 h	3	
	Dis	13C→2.5V		
Carala life	Ch	$0.2C \rightarrow 3.65 \text{ V/CV} < 0.03 \text{ C} \& 1 \text{ h}$	100	
Cycle life	Dis	$0.65 \text{ C} \rightarrow 2.5 \text{ V}$		

**Table S2.** C-rate test protocol for half-cells with aged cathodes (1 C = 2.3 mAcm<sup>-2</sup>).



**Figure S10.** Examples of Rietveld refinement of XRD patterns of aged cathodes from the beginning of the stack (Sample 3) and the center of the electrode of Cell A (**a**) and Cell B (**b**). The indicated Bragg positions (in green) refer to LiFePO4 (top) and FePO4 (bottom).



Figure S11. XRD patterns (focus on 00l peak at 26.8°) of pristine, fresh and aged anodes.