

Supporting Information

First 18650-Format Na-ion Cells Aging Investigation: A Degradation Mechanism Study

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Table S1. Life-cycle ageing test conditions. $\times 2$ means that two different cells were launched simultaneously to confirm the reproducibility of the results.

	C/5	1C	2C
25°C	$\times 2$	$\times 2$	$\times 2$
45°C	$\times 2$	$\times 2$	$\times 2$

Table S2. Calendar test conditions at different SoC and temperatures. $\times 2$ means that two different cells were launched simultaneously to confirm the reproducibility of the results.

	30%	50%	100%	Number of cells
5°C			$\times 2$	2
25°C	$\times 2$	$\times 2$	$\times 2$	6
45°C		$\times 2$	$\times 2$	4

Table S3. Initial properties of thirty-six 18650-format cells.

Unit ID	Discharged capacity at C/10 (mAh)	Discharged capacity at C/5 (mAh)	Specific energy at C/10 (Wh·kg ⁻¹)	Specific energy at C/5 (Wh·kg ⁻¹)	Irreversible capacity at 1 st cycle	1C Resistance 75% SoC (Ohm·cm ²)	1st ch Q (mAh·g ⁻¹)
PR01	757	717	84	79	21.6%	N/A	131
PR02	761	724	84	80	19.8%	N/A	129
PR03	758	709	86	80	19.6%	N/A	128
PR04	756	718	83	79	20.3%	N/A	129
PR05	761	725	84	80	19.6%	N/A	128
PR06	755	718	84	80	19.7%	N/A	128
PR07	746	705	82	78	20.9%	50	128
PR08	750	710	83	79	20.8%	50	129
PR09	746	710	83	79	22.3%	50	130
PR10	751	709	83	79	20.8%	50	129
PR11	754	711	83	79	20.6%	51	129
PR12	753	711	84	79	20.4%	52	129
PR13	749	712	82	78	20.7%	52	128
PR14	749	704	83	78	21.0%	54	129
PR16	743	699	82	77	21.1%	53	128
PR17	747	706	83	78	20.5%	51	128
PR18	751	711	83	79	20.6%	50	128
PR19	746	701	83	78	20.8%	54	128
PR20	746	702	82	77	20.6%	52	128
PR21	754	713	83	79	20.2%	51	129
PR22	755	716	84	80	20.0%	48	129
PR23	750	713	83	79	21.0%	50	129
PR24	752	713	84	80	20.2%	52	128
PR25	751	713	83	79	20.9%	51	129
PR26	754	713	83	79	20.5%	52	129
PR27	757	718	84	80	20.3%	50	129
PR28	758	715	84	80	20.2%	54	129
PR29	744	700	83	78	20.8%	51	127
PR30	751	713	82	79	20.9%	49	129
PR31	752	712	83	79	20.7%	49	129
PR33	751	711	83	78	20.6%	53	129
PR34	753	713	83	79	20.5%	52	129
PR35	753	714	83	79	20.6%	49	129
PR36	750	714	83	79	22.0%	50	130
Min	743	699	81.6	76.9	19.6%	47.7	127.2
Max	761	725	85.6	80.5	22.3%	54.2	131.1
Average	752	712	83.2	78.9	20.6%	51.1	128.7

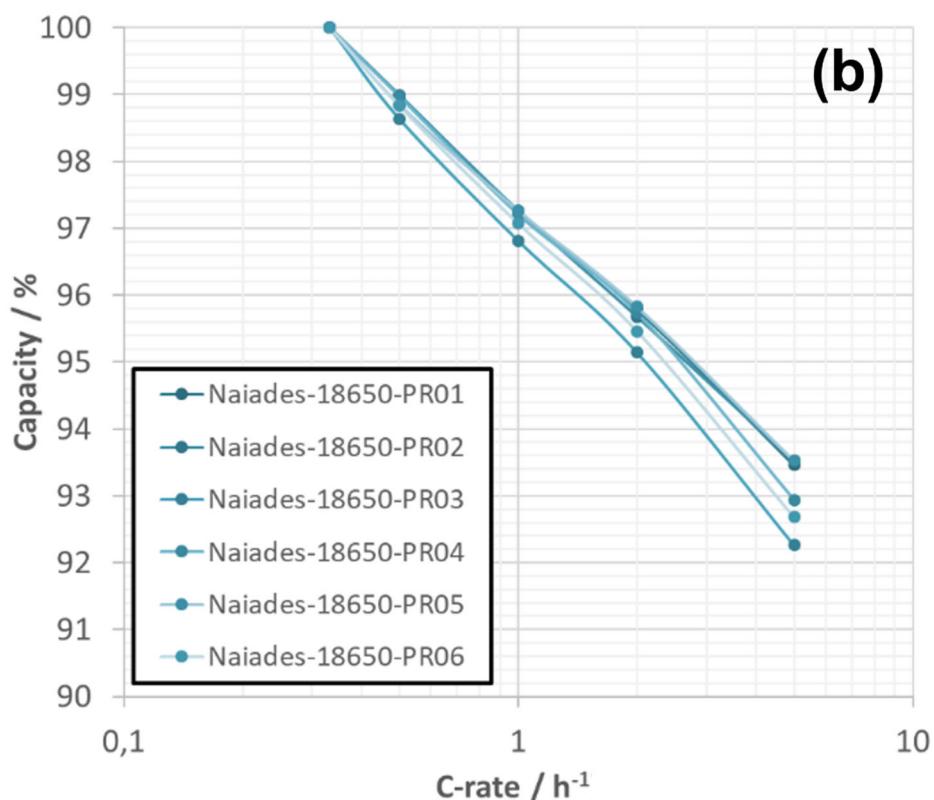
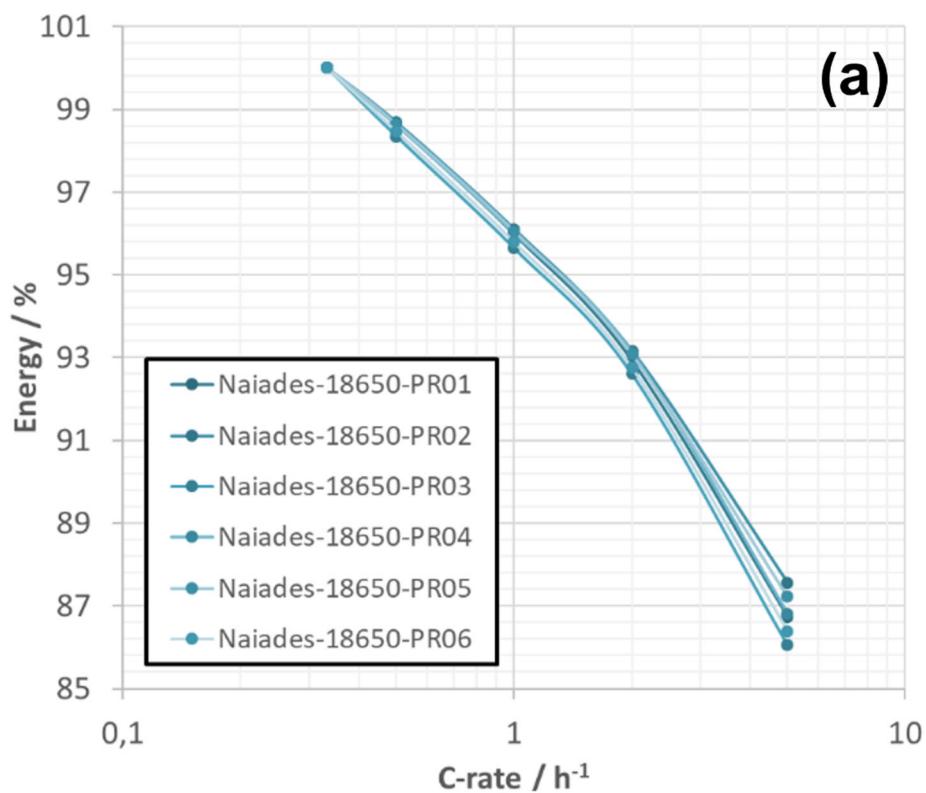


Figure S1. Energy retention (a) and Capacity retention (b) at different rate capabilities of six representative cells measured at 25°C.

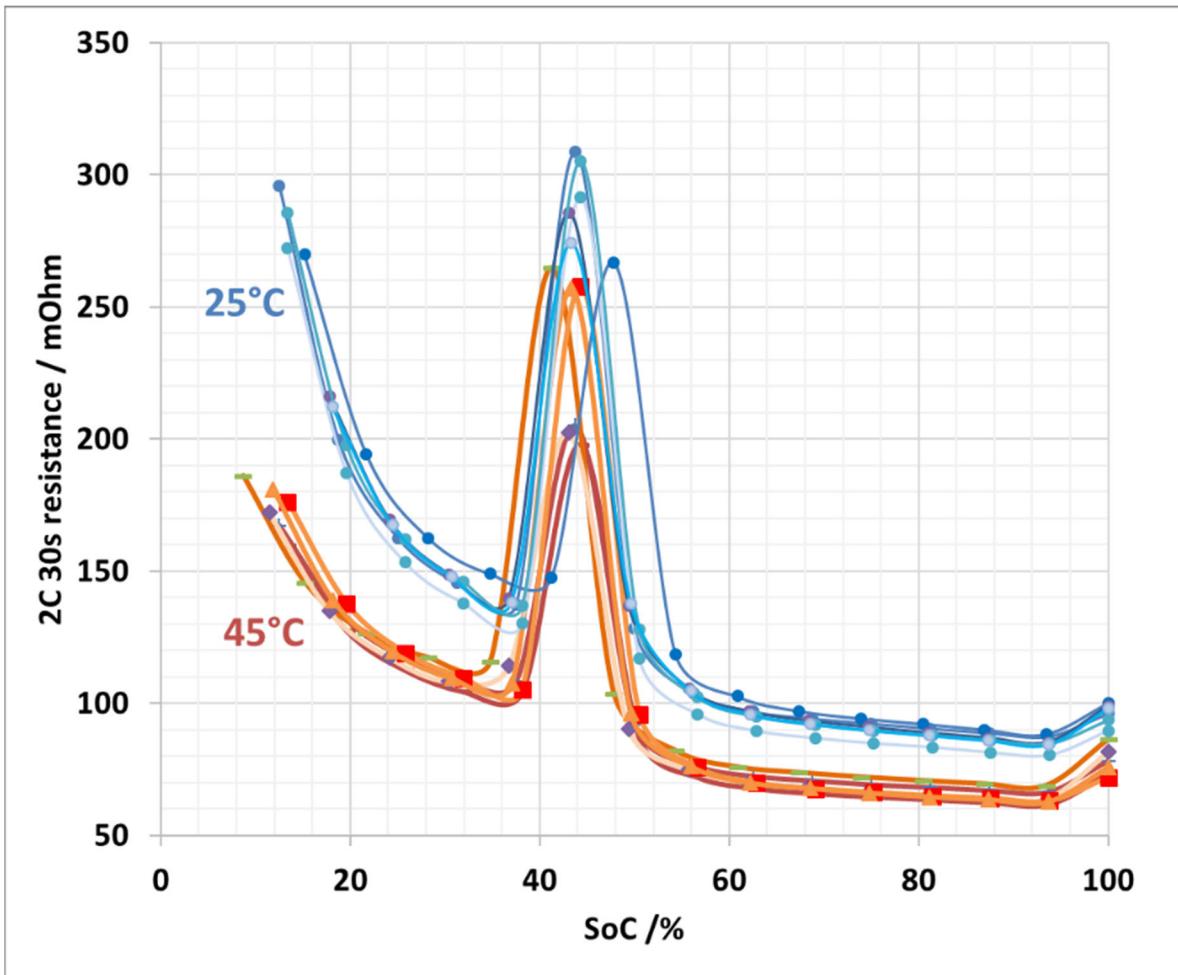


Figure S2. Discharge resistance measured as a function of SoC of six representative cells at 25°C and 45°C by using a pulse length of 30 s at 2C current.

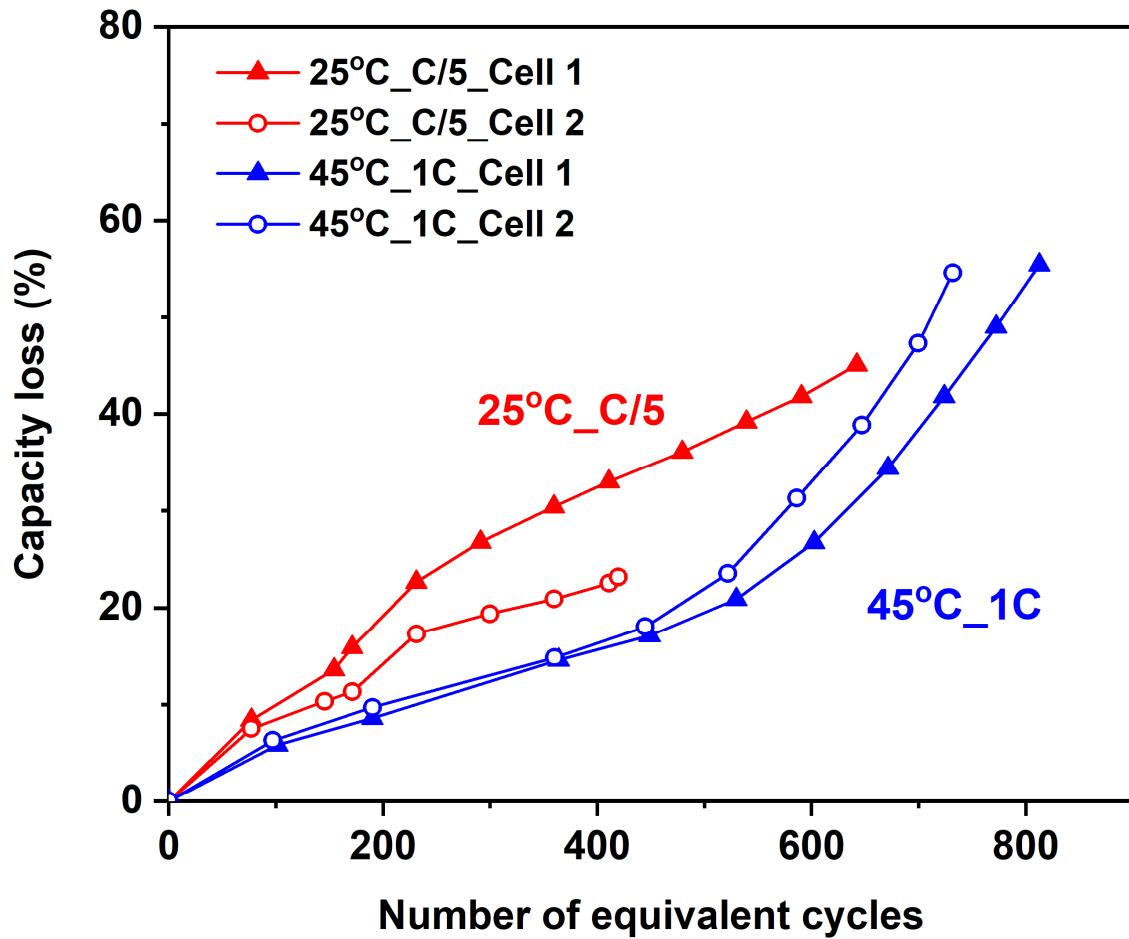


Figure S3. Comparison between the capacity loss of the cells cycled at 25°C with the C/5 current rate and those cycled at 45°C with the 1C current rate.

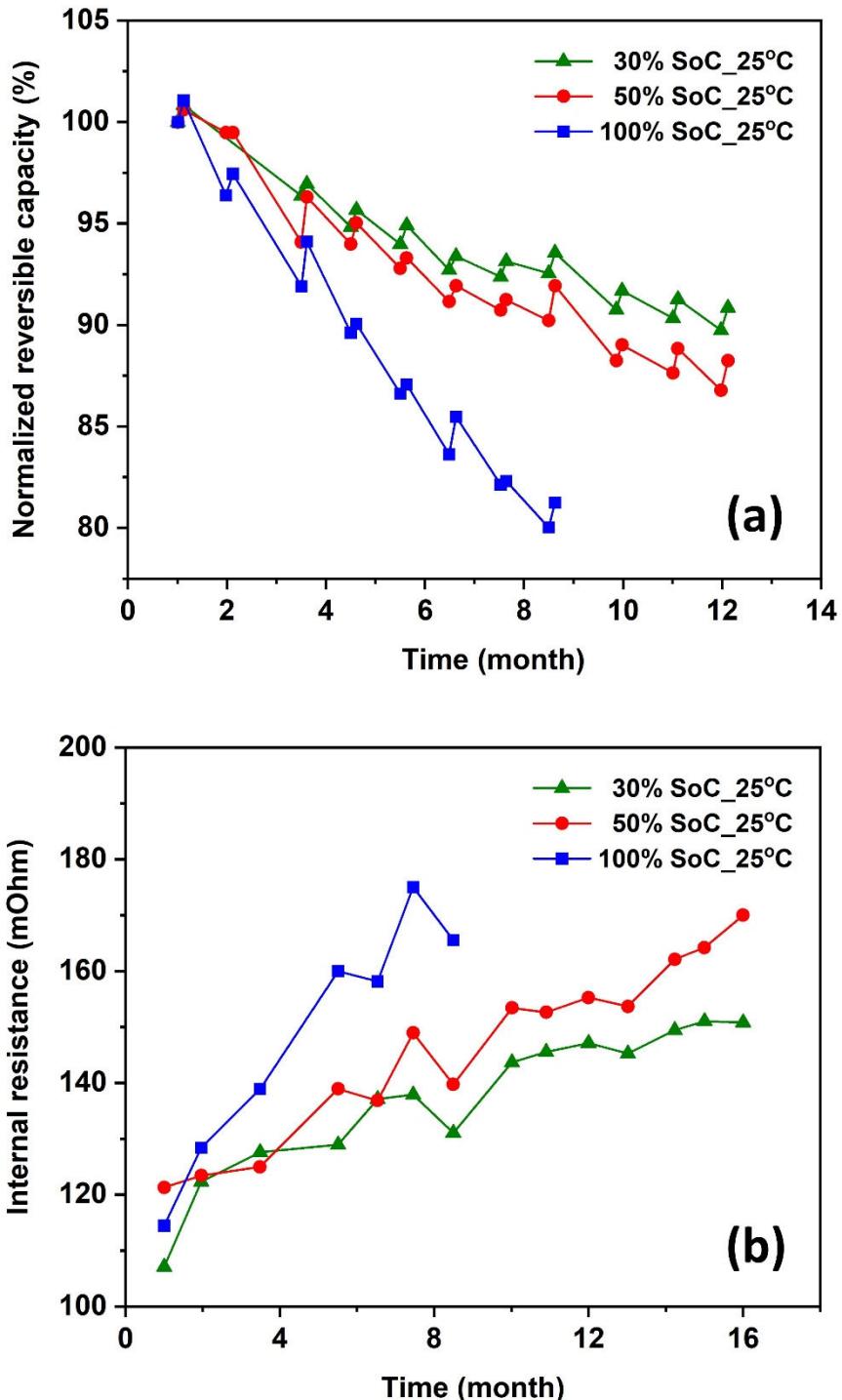
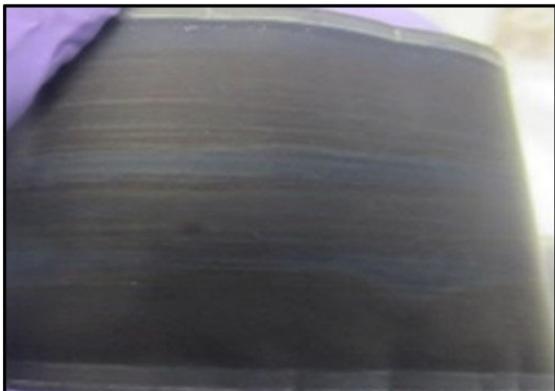
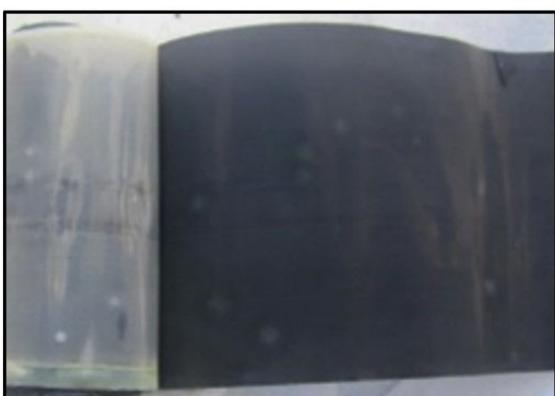
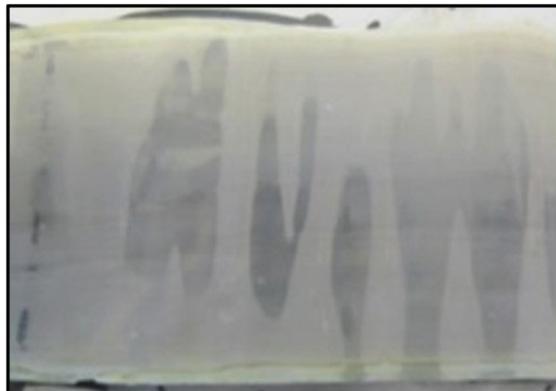


Figure S4. (a) Capacity loss of the cells stored at 25°C, at 30%, 50%, and 100% SoC. The discharge capacity was measured at C/5 current rate and the calendar test terminated when the cell's SoH reached 80%. (b) Impact of SoC on the internal resistance measured at 50% of discharge after 1 month storage at 25°C.

Negative electrode



Separator 1



Positive electrode

Separator 2

Figure S5. Visual aspect of the electrodes and the separators recovered from a Hard carbon// $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ full-cell stored at 100% SoC at 45°C during four months. The cell was discharged to 2.0 V at a current rate of 1C before it was dismantled.

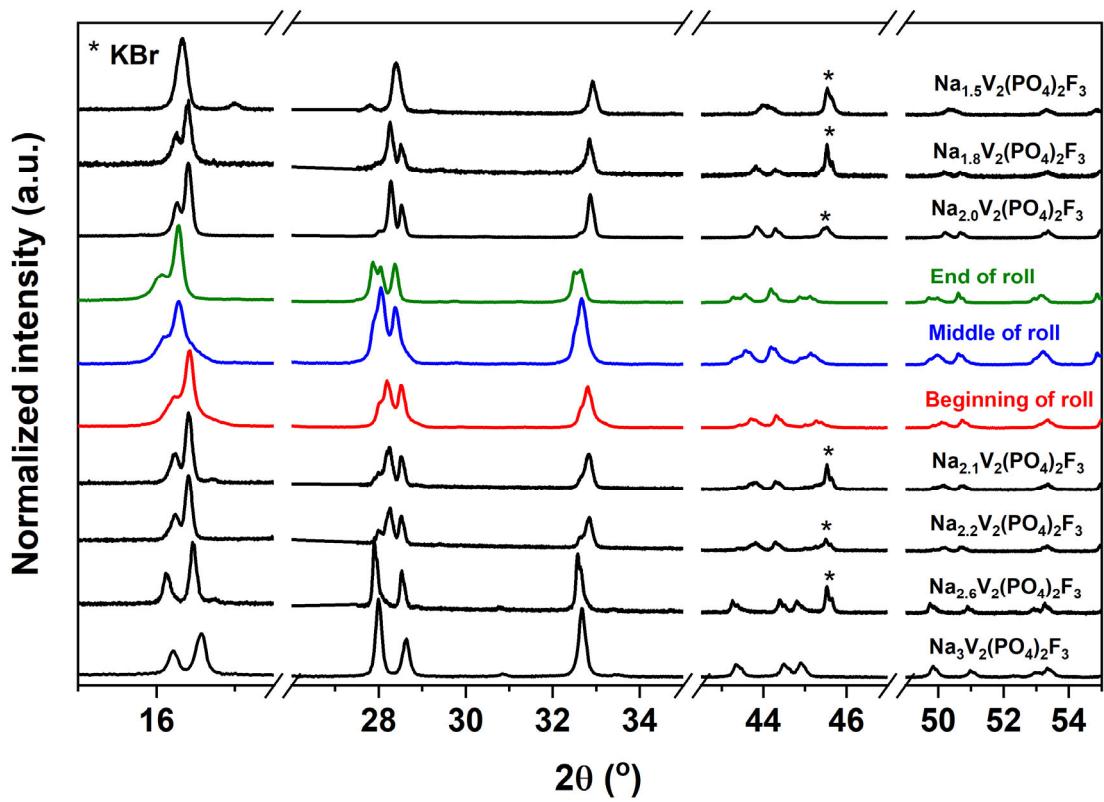


Figure S6. XRD patterns recorded at the beginning, the middle and the end of the positive electrode recovered from the long-term cycling test at 1C cycling rate at 45°C as compared to those of “ $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ ” reference.

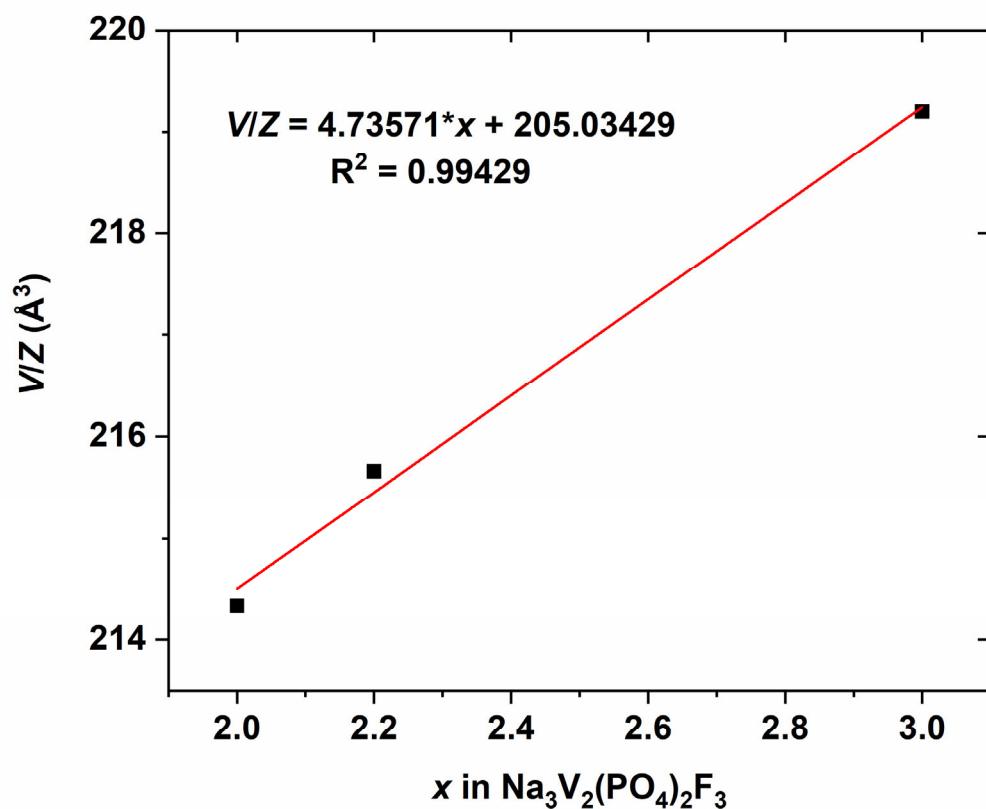


Figure S7. Standard line constructed from the known cell parameters of $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ ($x = 3, 2.2, 2.0$). This line is used to determine the composition of $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ electrodes recovered from the aging tests.

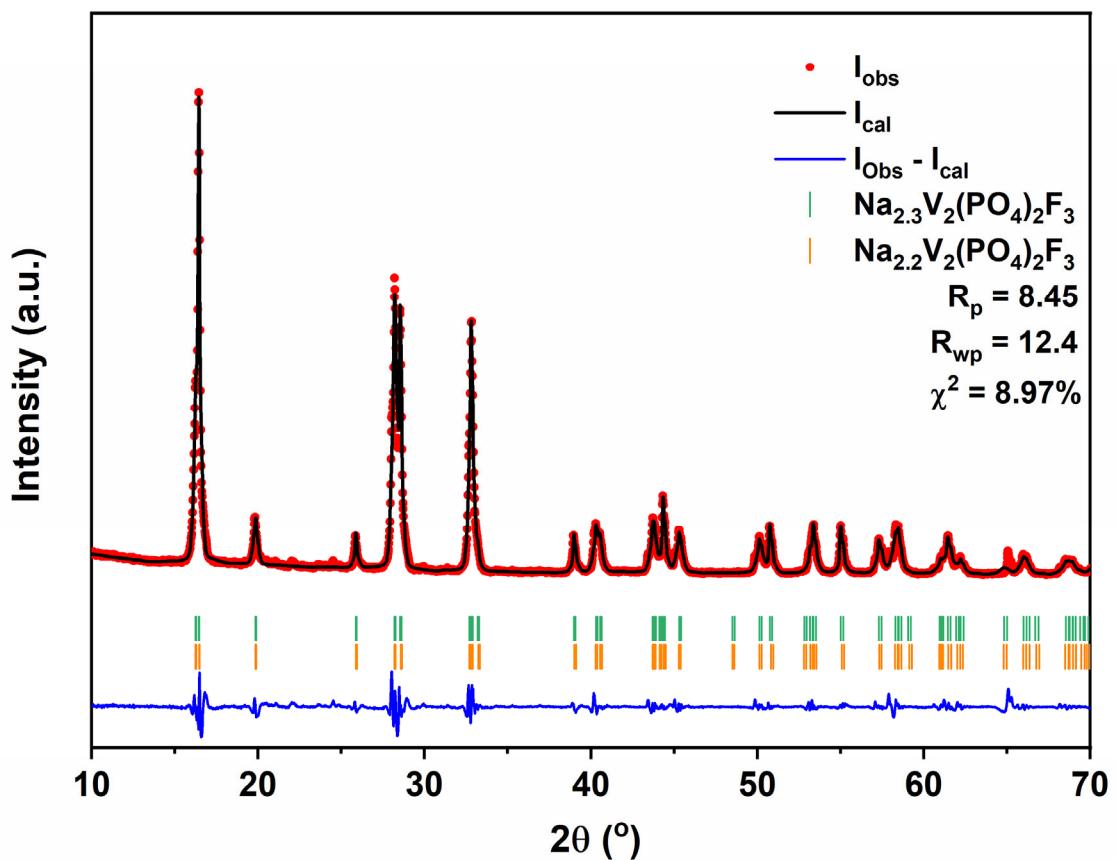


Figure S8. Le Bail fitting performed on the XRD pattern recorded at the beginning of the positive electrode recovered from a long-term cycling test at 1C cycling rate and 45°C.

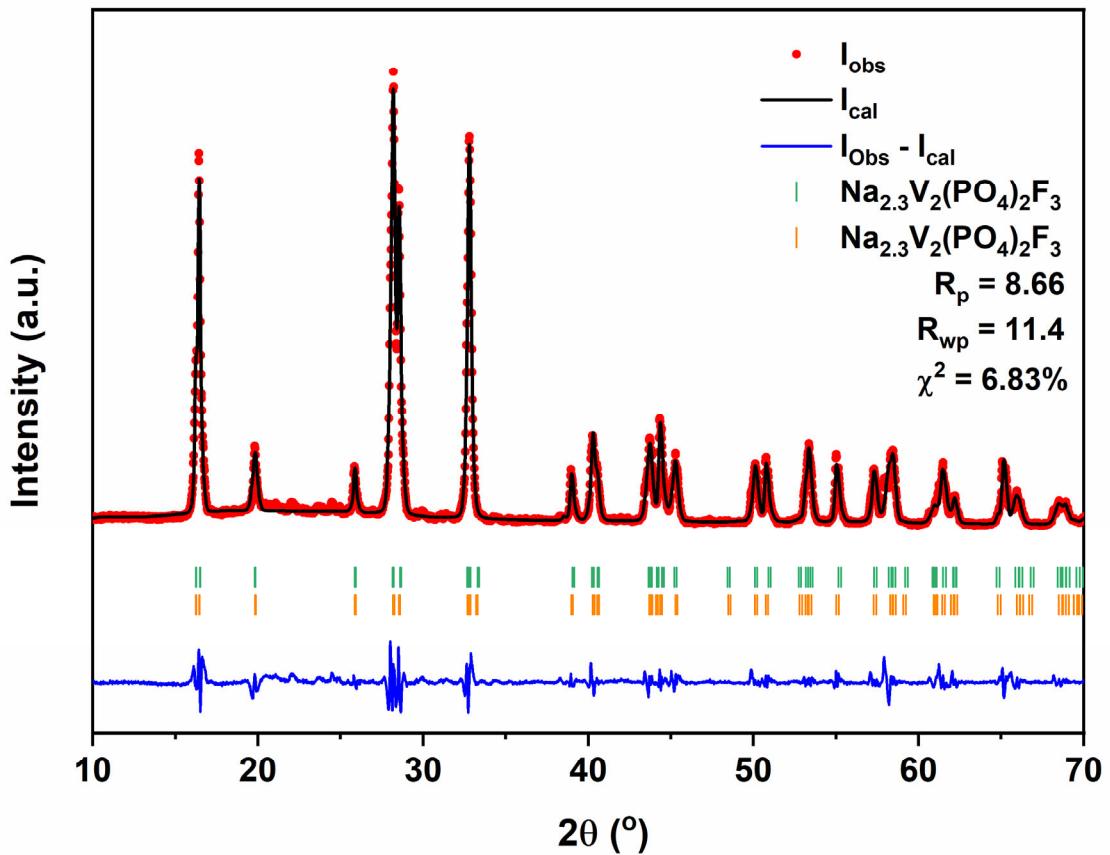


Figure S9. Le Bail fitting performed on the XRD pattern recorded at the middle of the positive electrode recovered from a long-term cycling test at 1C cycling rate and 45°C.

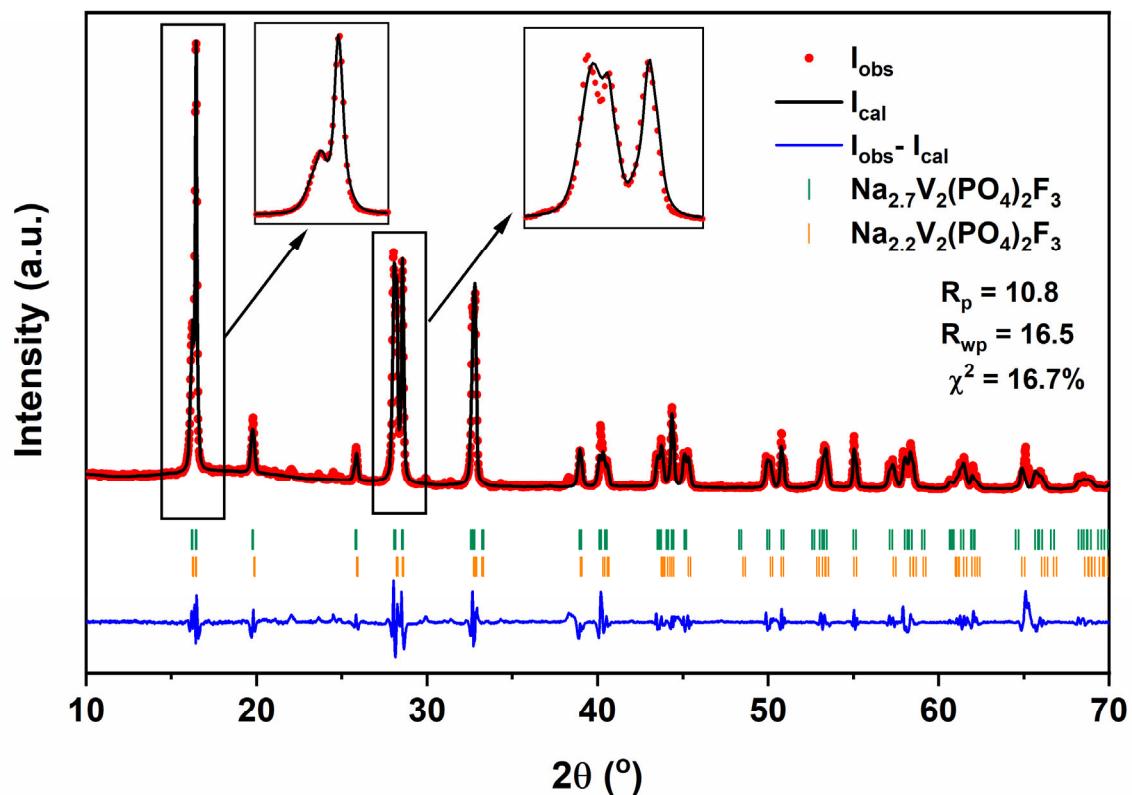


Figure S10. Le Bail fitting performed on the XRD pattern recorded at the end of the positive electrode recovered from a long-term cycling test at 1C cycling rate and 45°C.

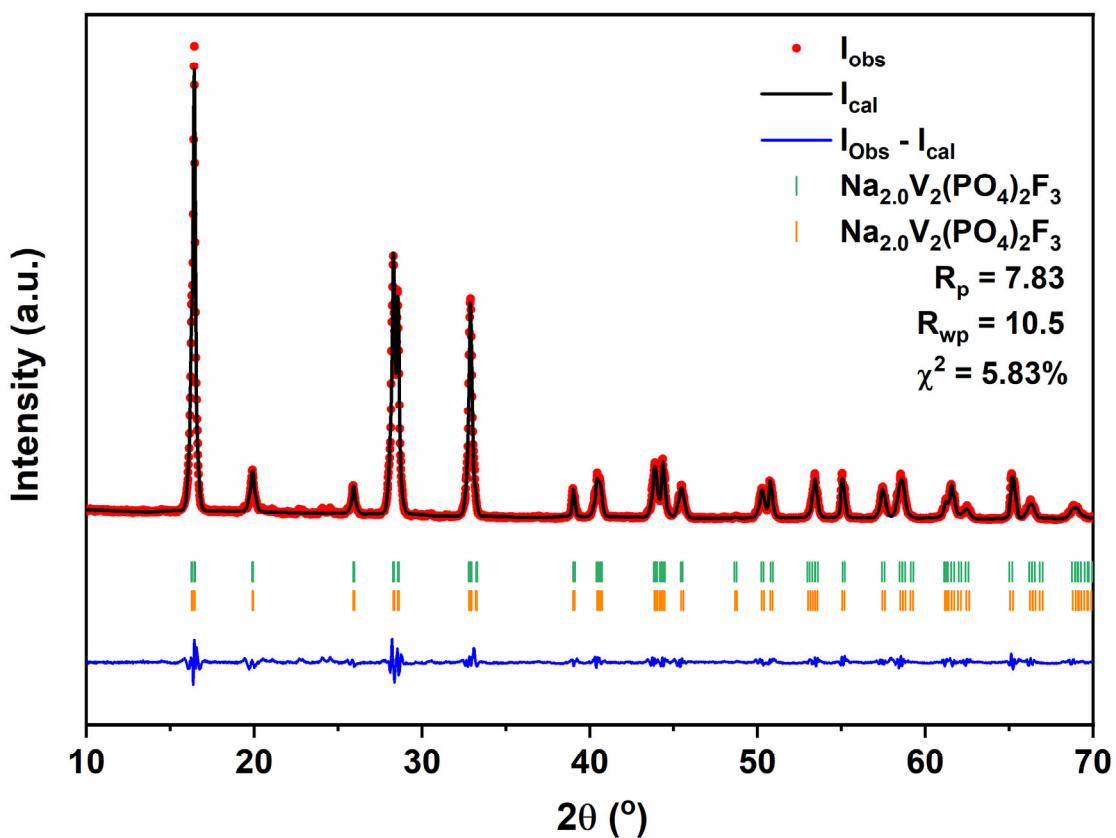


Figure S11. Le Bail fitting performed on the XRD pattern recorded at the middle of the positive electrode recovered from the calendar test at 45°C.

Table S4. Fermi contact shifts and the relative area of ^{23}Na NMR resonances observed in $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ ($x = 2.0\text{--}2.6$) references and the positive electrodes recovered from the long-term cycling test at 1C and 45°C and from the calendar test at 45°C.

	$\text{V}^{3+}/\text{V}^{4+}$ ratio	Resonance 1		Resonance 2		Resonance 3	
		δ (ppm)	Relative area	δ (ppm)	Relative area	δ (ppm)	Relative area
$x = 3.0$	100	139	97%			92	3%
$x = 2.6$	80/20	138	94%	121	5%	91	1%
$x = 2.2$	60/40	135	25%	108	42%	86	34%
$x = 2.1$	55/45	137	11%	107	65%	88	24%
$x = 2.0$	50/50			103	39%	88	61%
Long-term cycling test							
Beginning		138	32%	109	50%	86	18%
Middle		140	30%	112	36%	87	34%
End		137	49%	118	37%	95	14%
Calendar test				95	63%	84	37%

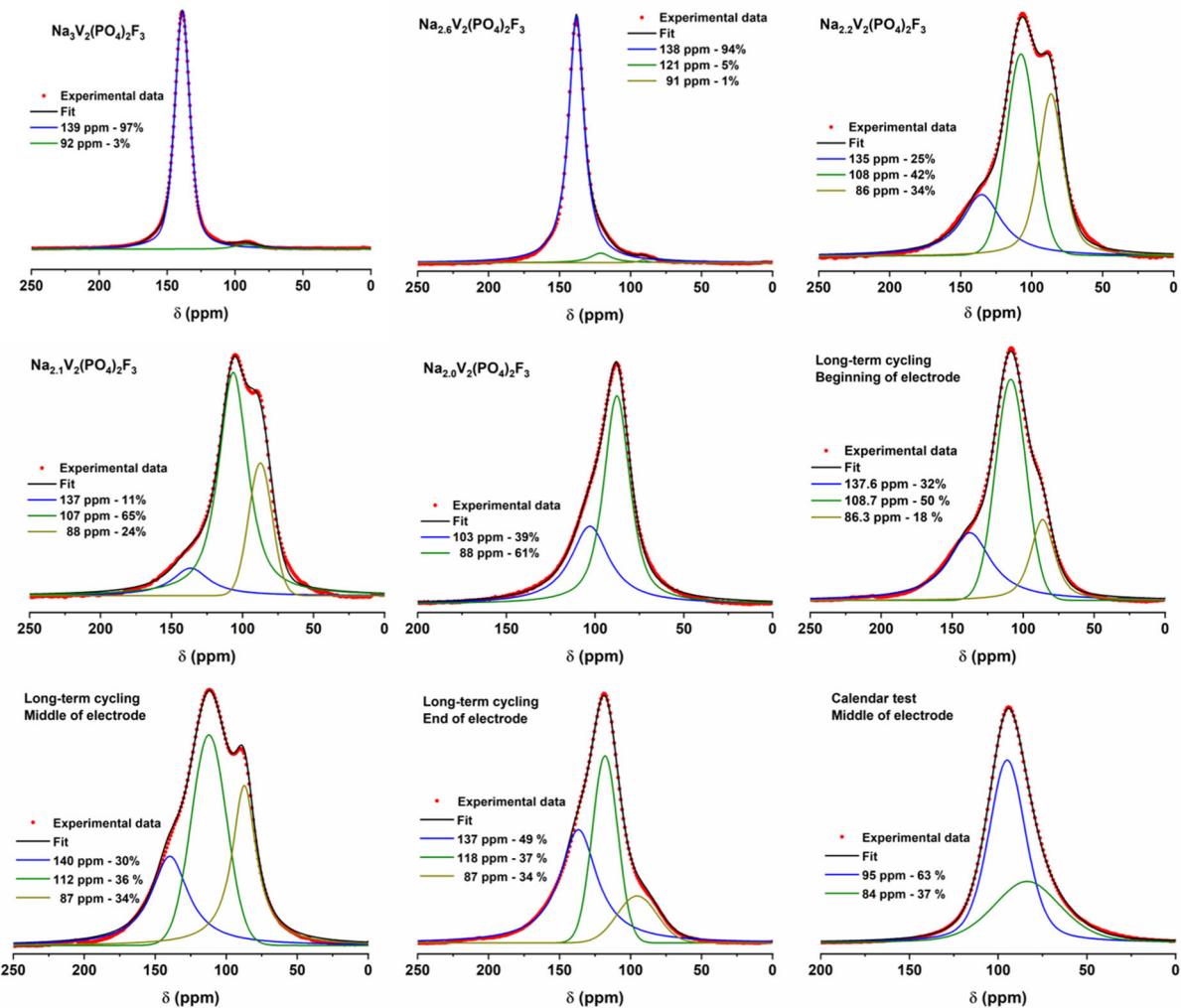


Figure S12. Deconvolution of ^{23}Na ss-NMR signals recorded on $\text{Na}_x\text{V}_2(\text{PO}_4)_2\text{F}_3$ ($x = 3.0, 2.6, 2.2, 2.1$, and 2.0) references, and different parts of the positive electrodes recovered from a long-term cycling test at 1C current rate and 45°C , and a calendar test at 45°C .

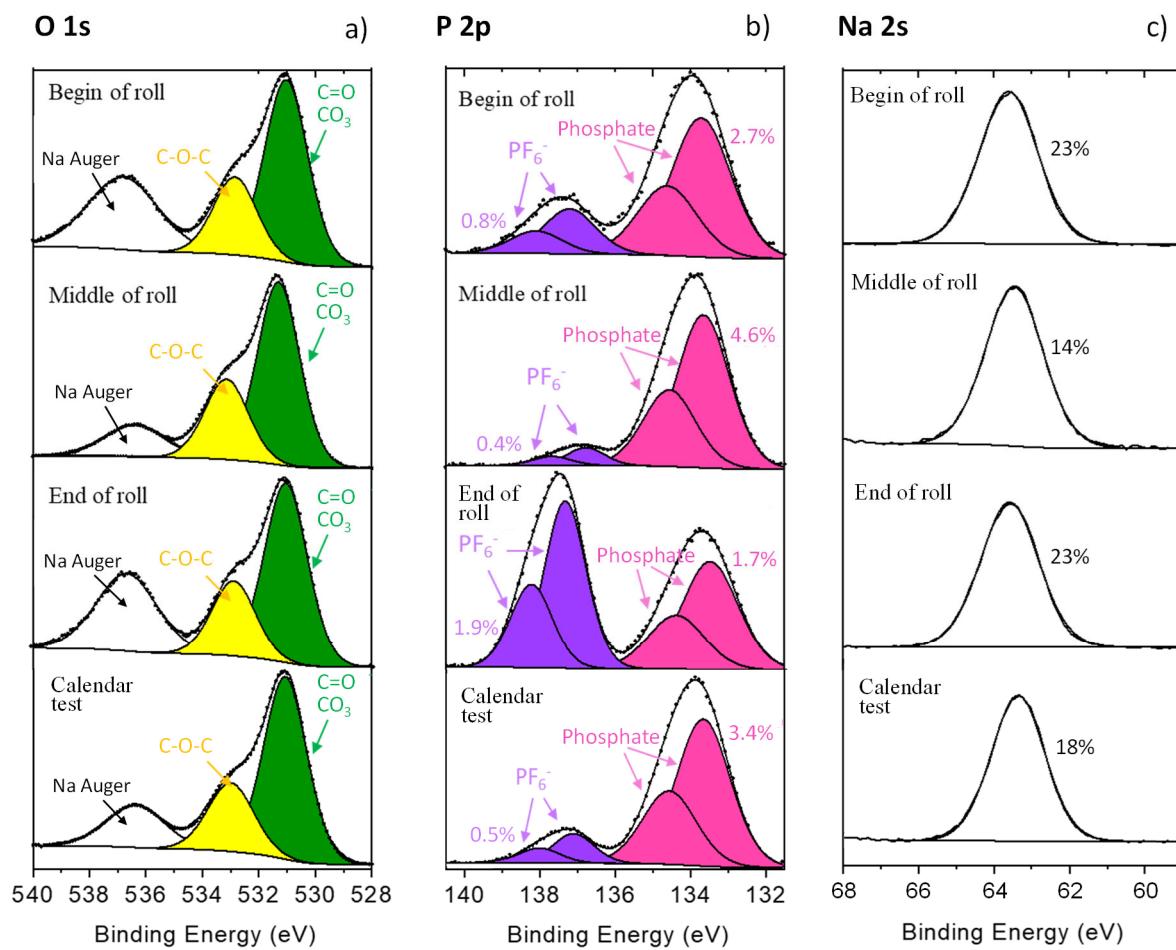


Figure S13. XPS (a) O 1s, (b) P 2p and (c) Na 2s of HC electrodes after a long-term cycling at 45°C at different locations of the roll and after the calendar aging test. Na Auger peaks overlapping with O 1s spectra correspond to the Na KL₁L_{2,3} (¹P₁) transition.

Table S5. Binding energy (eV) and atomic percentage (%) of the components observed in XPS spectra of HC negative electrodes after cycling at 1C (cell PR02) at different locations and calendar test (cell PR23).

Peak	Beginning of roll (cycling)		Middle of roll (cycling)		End of roll (cycling)		Calendar test		Chemical attribution
	BE (eV)	%	BE (eV)	%	BE (eV)	%	BE (eV)	%	
C 1s	285.0	10.1	285.0	14.1	285.0	11.4	285.0	12.6	CH _x
	286.1	0.4	286.1	1.0	286.1	0.5	286.2	0.7	CH ₂ (PVdF)
	286.7	8.8	286.8	13.1	286.6	8.1	286.8	10.1	C=O
	288.4	2.0	288.4	2.0	288.4	1.3	288.6	3.6	O=C=O
	289.4	2.0	289.4	3.0	289.6	2.3	289.6	1.2	CO ₃
	290.6	0.4	290.7	1.0	290.7	0.5	290.7	0.7	CF ₂ (PVdF)
V 2p_{3/2}	515.5	0.7	515.5	0.5	515.4	0.6	515.6	0.4	V ³⁺ (V ₂ O ₃)
	---	---	516.3	0.7	---	---	516.5	0.8	V ⁴⁺ (V ₂ O ₄)
	517.5	1.2	517.4	0.5	517.6	0.4	517.5	2.1	V ⁵⁺ (V ₂ O ₅)
O 1s	531.0	15.1	531.3	21.2	531.0	14.2	531.0	19.7	C=O, CO ₃
	532.8	6.5	533.1	9.5	532.9	6.0	533.0	7.8	C—O—C, phosphates
F 1s	684.1	19.8	684.3	7.8	684.0	15.3	684.2	13.3	NaF
	686.7	5.2	686.8	5.1	686.8	11.7	686.8	4.4	NaPF ₆ (+PVdF)
P 2p_{3/2}	137.2	0.8	136.8	0.4	137.3	1.9	136.8	0.5	NaPF ₆
	133.7	2.7	133.7	4.6	133.5	1.7	133.4	3.4	phosphates
Na 2s	63.6	23.2	63.4	14.1	63.5	23.3	63.3	17.7	all Na species
N 1s	400.1	0.1	400.2	0.3	399.9	0.2	400.0	0.4	impurity
Cl 2p_{3/2}	198.6	0.9	198.3	1.3	198.8	0.4	198.4	0.8	impurity

Table S6. Binding energy (eV) and atomic percentage (%) of the components observed in XPS spectra of NVPF positive electrodes after cycling at 1C (cell PR02) at different locations and calendar test (cell PR23).

Peak	Pristine NVPF		Beginning of roll (cycling)		Middle of roll (cycling)		End of roll (cycling)		Calendar test		Chemical attribution
	BE (eV)	%	BE (eV)	%	BE (eV)	%	BE (eV)	%	BE (eV)	%	
C 1s	284.5	37.1	284.6	20.6	284.5	21.8	284.6	22.0	284.5	18.6	SP carbon
	285.1	1.6	285.1	2.0	285.0	1.0	285.2	1.9	285.2	2.9	CH _x
	286.1	7.7	285.8	8.5	285.8	8.6	285.8	8.6	285.6	8.1	CH ₂ (PVdF)
	286.9	2.4	286.7	5.3	286.5	4.9	286.7	5.1	286.6	6.7	C-O
	---	---	287.6	2.1	287.4	1.7	287.6	2.2	287.7	2.8	O-C-O
	288.3	1.3	288.9	2.5	288.8	2.0	288.9	2.4	288.9	4.3	O=C-O
	---	---	289.5	0.5	---	---	289.5	0.5	---	---	CO ₃
V 2p_{3/2}	290.7	7.7	290.3	8.4	290.3	8.6	290.3	8.6	290.1	8.1	CF ₂ (PVdF)
	517.0	1.9	517.3	1.5	517.5	2.6	517.3	1.4	517.2	1.6	NVPF + others
O 1s	531.2	9.0	531.2	6.7	531.2	8.1	531.2	5.7	531.1	8.1	PO ₄ ³⁻ in NVPF
	532.1	2.6	532.3	7.0	532.0	8.8	532.2	7.1	532.2	8.3	Mixed oxygen species
	533.3	0.8	533.8	5.6	533.6	6.6	533.8	5.9	533.5	7.5	
F 1s	684.5	2.4	684.7	2.3	684.4	1.6	684.7	2.4	684.3	1.6	NVPF
	687.8	15.2	687.4	17.4	687.5	15.5	687.5	17.0	687.3	13.5	PVdF
P 2p_{3/2}	---	---	136.8	0.2	---	---	136.8	0.2	---	---	PF ₆ ⁻
	---	---	134.6	2.1	134.5	1.7	134.6	1.8	134.5	1.1	Phosph. + PO _x F _y
	133.2	4.2	133.1	2.9	133.3	4.2	133.2	2.9	133.2	3.4	PO ₄ ³⁻ in NVPF
Na 2s	63.5	5.6	63.2	4.3	63.0	1.8	63.2	3.8	63.1	2.9	NVPF (+NaF)
N 1s	400.5	0.5	400.9	0.4	400.8	0.6	400.9	0.5	400.4	0.5	impurity