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Influence of Formation Temperature on Cycling Stability of Sodium-Ion Cells: A Case Study of Na₃V₂(PO₄)₂F₃ |HC Cells

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Supporting Information

Influence of formation temperature on cycling stability of sodium-ion cells: A case study of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ | HC cells.

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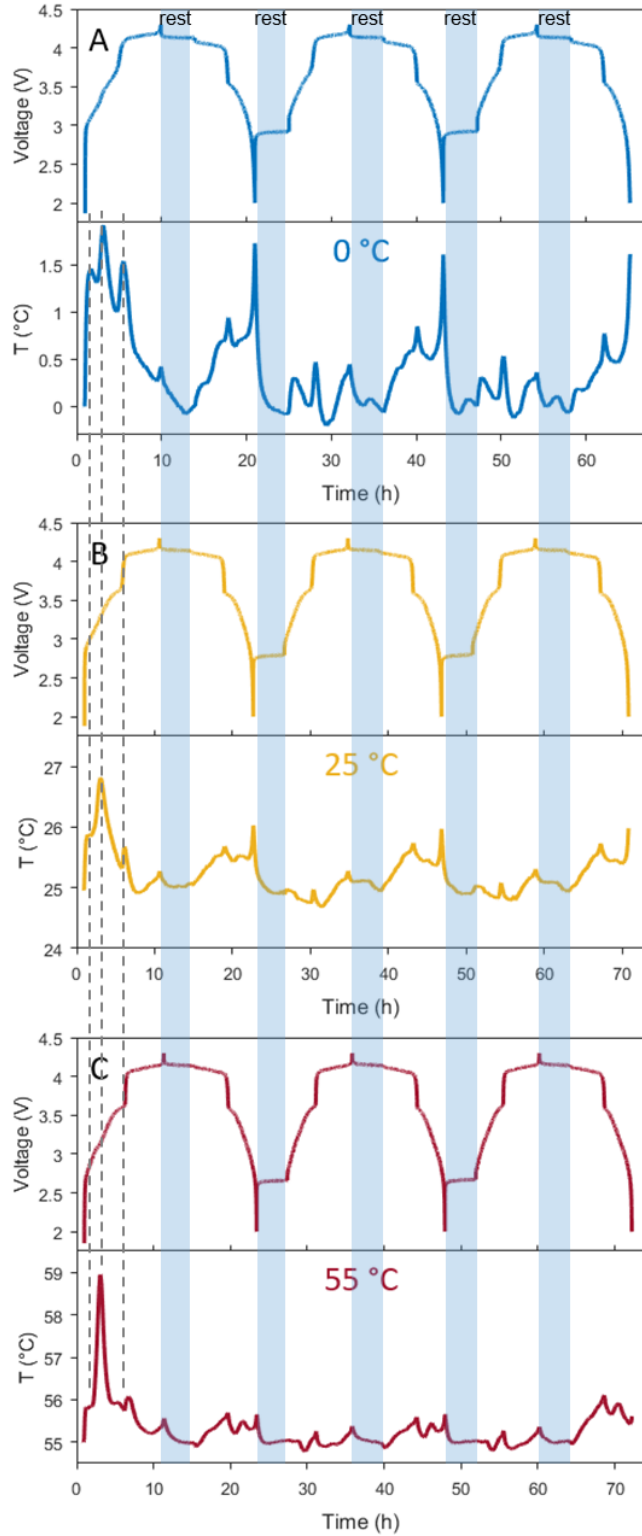


Figure S1. Recorded temperature inside 18650 cells during the three formation cycles, depending on the temperature employed during formation. A) 0 °C, B) 25 °C, and C) 55 °C. The peaks associated to heat release events in the first charge are marked with dashed lines, and the resting regions between charge and discharge are highlighted in light blue.

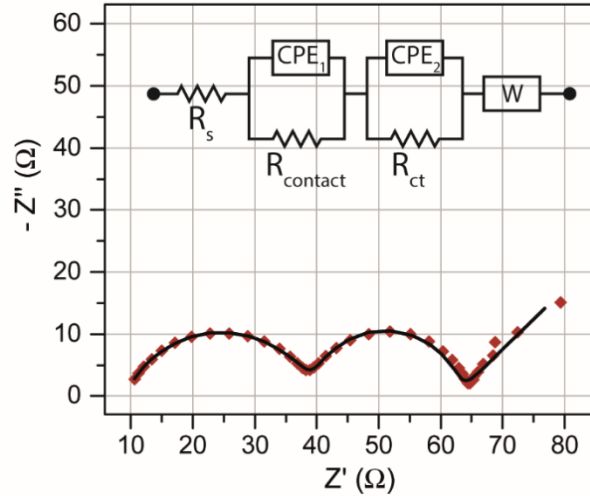


Figure S2. Fitting of the obtained PEIS spectrum right after formation (measured at 100 % SOC and 10 °C). Points represent the obtained experimental data and the black line is the fitted spectrum using the equivalent circuit shown as inset.

Table S1. Parameters obtained for the PEIS fitting procedure, as shown in Figure S2, for the three different formation protocols.

Formation protocol	R_s (Ω)	R_{contact} (Ω)	CPE_1 ($F \cdot s^{a-1}$)	a_1	R_{ct} (Ω)	CPE_2 ($F \cdot s^{a-1}$)	a_2
55x3	9.08	30.49	13.5×10^{-6}	0.748	23.02	0.77×10^{-3}	0.909
25x3	8.43	17.48	4.90×10^{-6}	0.861	15.76	0.97×10^{-3}	0.833
0x3	11.17	14.35	10.5×10^{-6}	0.831	15.45	1.02×10^{-3}	0.884

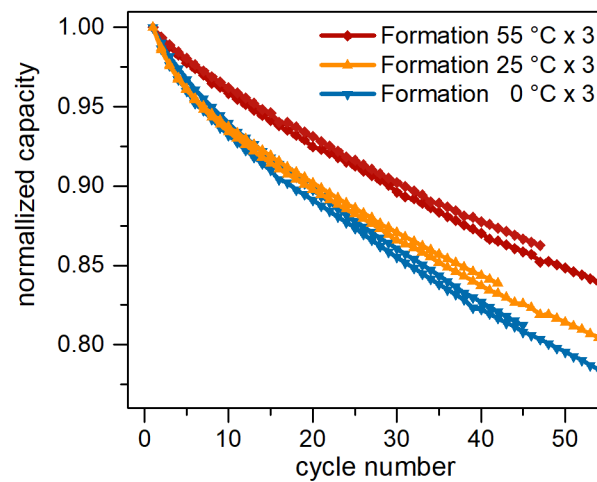


Figure S3. Capacity retention of the NVPF|HC cells depending on the formation protocol used, normalized by the initial discharge capacity of the cell after formation. Two twin cells are presented for each formation.

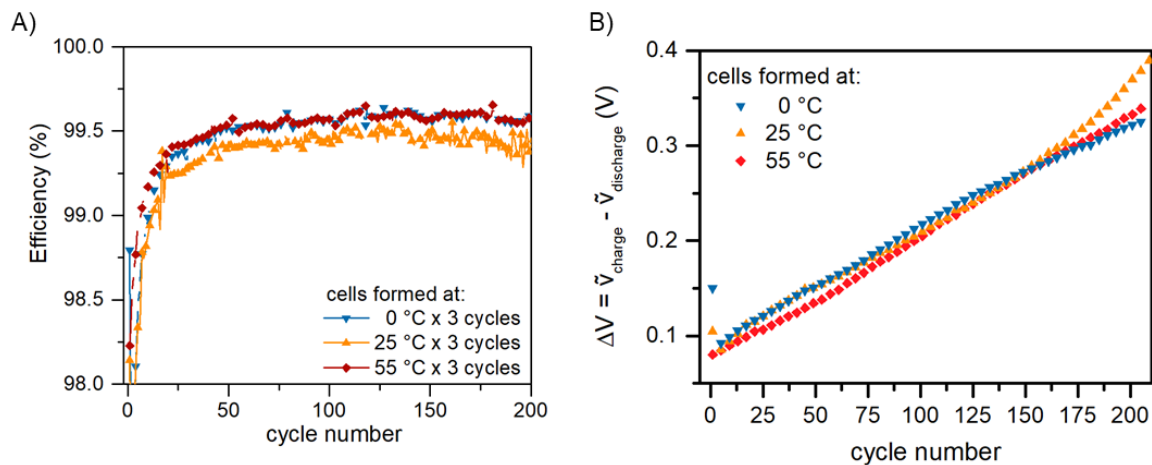


Figure S4. Performance metrics of the NVPF|HC cells as depending on the formation protocol used. A) Coulombic efficiency evolution upon cycling, and B) Evolution of polarization (calculated as the difference between the average voltage during charge and the average voltage during discharge)

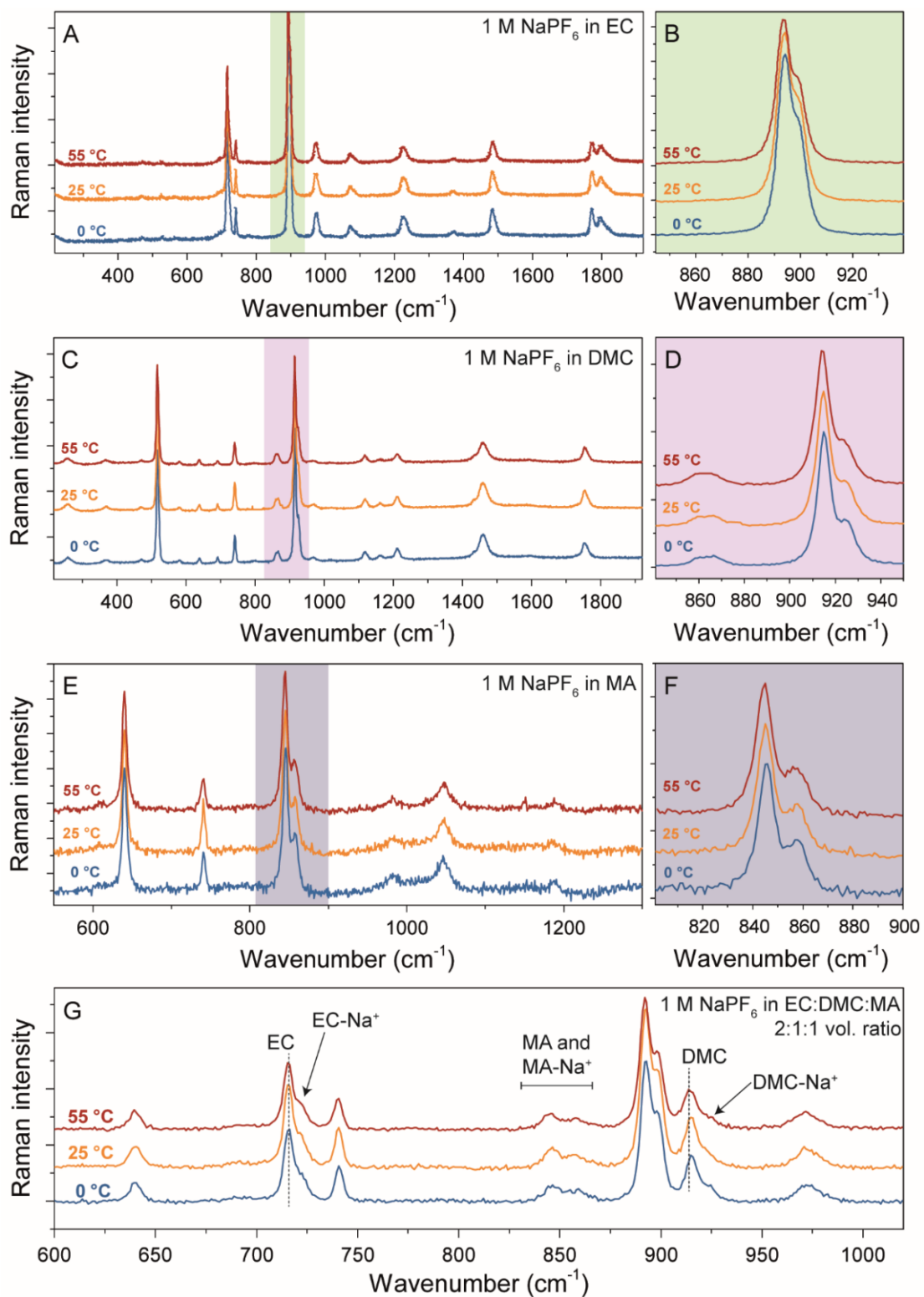


Figure S5. Raman spectra of NaPF_6 electrolytes in different solvent blends, as function of temperature. The solvents in each case EC (panels A and B), DMC (panels C and D), MA (panels E and F), and EC:DMC:MA (panel G). Panels on the right are a zoom in the colored region of the spectra on the left.

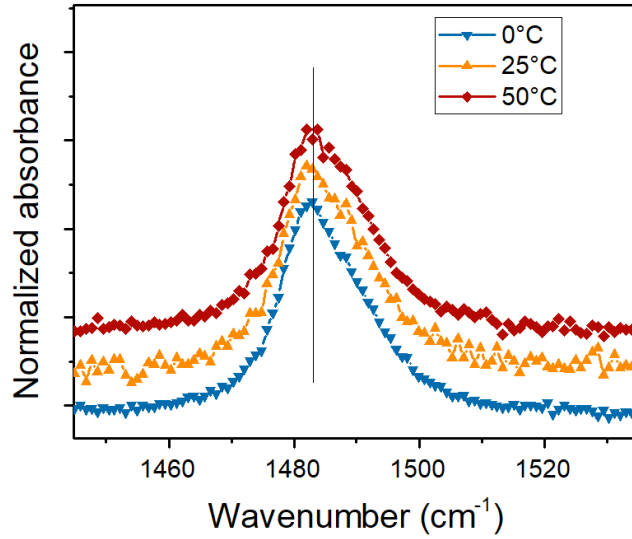


Figure S6. Effect of the temperature on a Raman band of EC. No significant displacement is observed in a solvent upon changes in temperature.

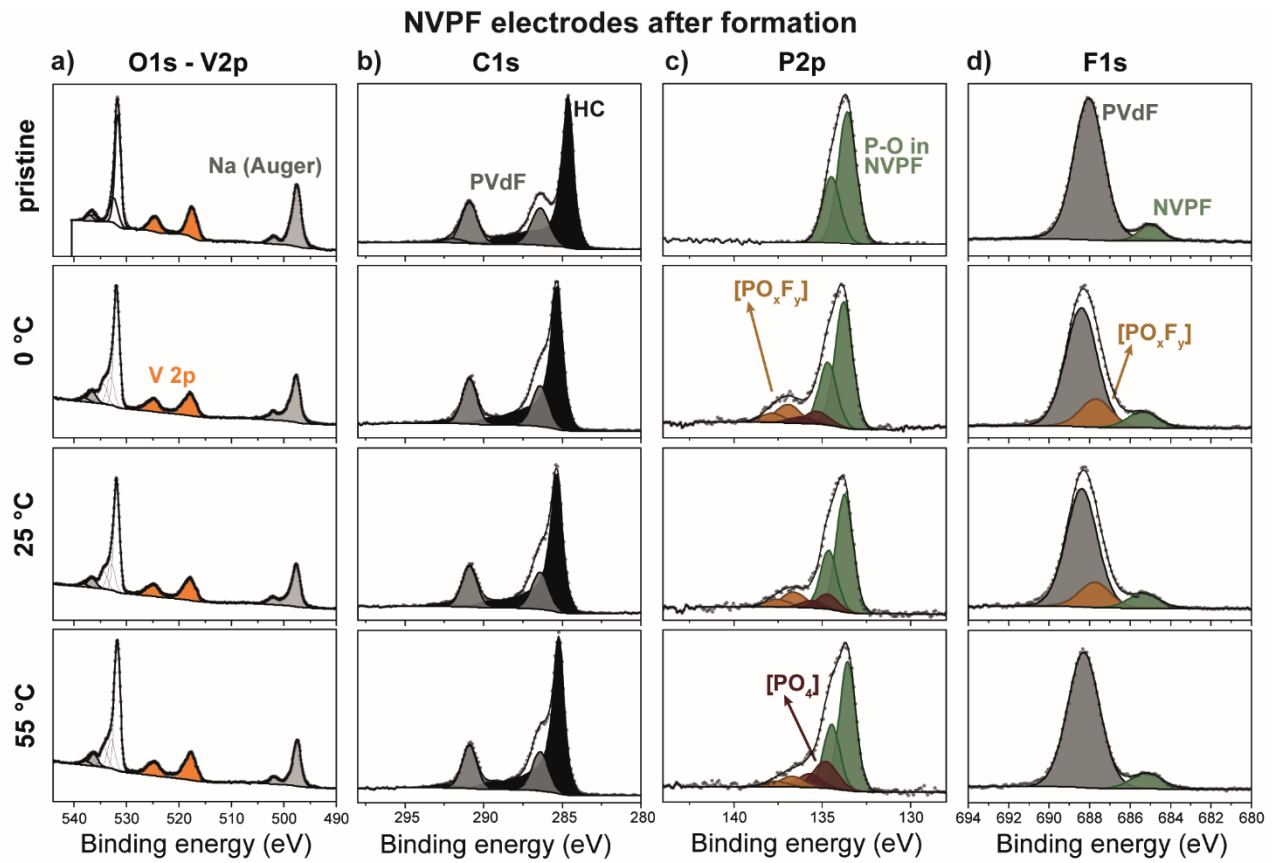


Figure S7. XPS spectra of NVPF electrodes' surface after formation.

Table S2. Integrated intensity of the deconvoluted XPS spectra showed on Figure 5 and Supplementary Figure S6

	C 1s			F 1s		Na 1s	P 2p			V 2p	
	HC	PVdF	Deposited C	PVdF + PO _x F _y	NaF	Na	134,0 eV	135,3 eV	137,8 eV	V	
HC electrodes	Pristine	51	24	-	20	3,4	-	-	-	-	
	0 °C	5	6,7	5,1	11,3	25,1	37,6	0,7	0,5	0,8	
	25 °C	9,3	10	8,4	13,6	20,3	29,6	0,6	0,3	0,6	
	55 °C Pt1	0,2	0,6	8,2	8,3	25,8	28	4,3	-	0,9	4,7
	55 °C Pt2	1,1	1,4	5,5	9,5	25	37,9	0,9	1,7	1,2	0,8
NVPF electrodes	C black	PVdF	Deposited C	PVdF + PO _x F _y	NaF and NVPF	NVPF	133,8 eV	135,3 eV	136,9 eV	V NVPF	
	Pristine	38	22	-	23	1,9	2,7	2,9	-	-	1,5
	0 °C	36,4	19	-	23,2	2,7	2,6	2,7	0,4	0,5	1,4
	25 °C	37,1	19,1	-	23,1	2,5	2,5	2,7	0,3	0,4	1,6
	55 °C	38,1	18,6	-	21,5	2,4	2,3	2,8	0,7	-	1,6

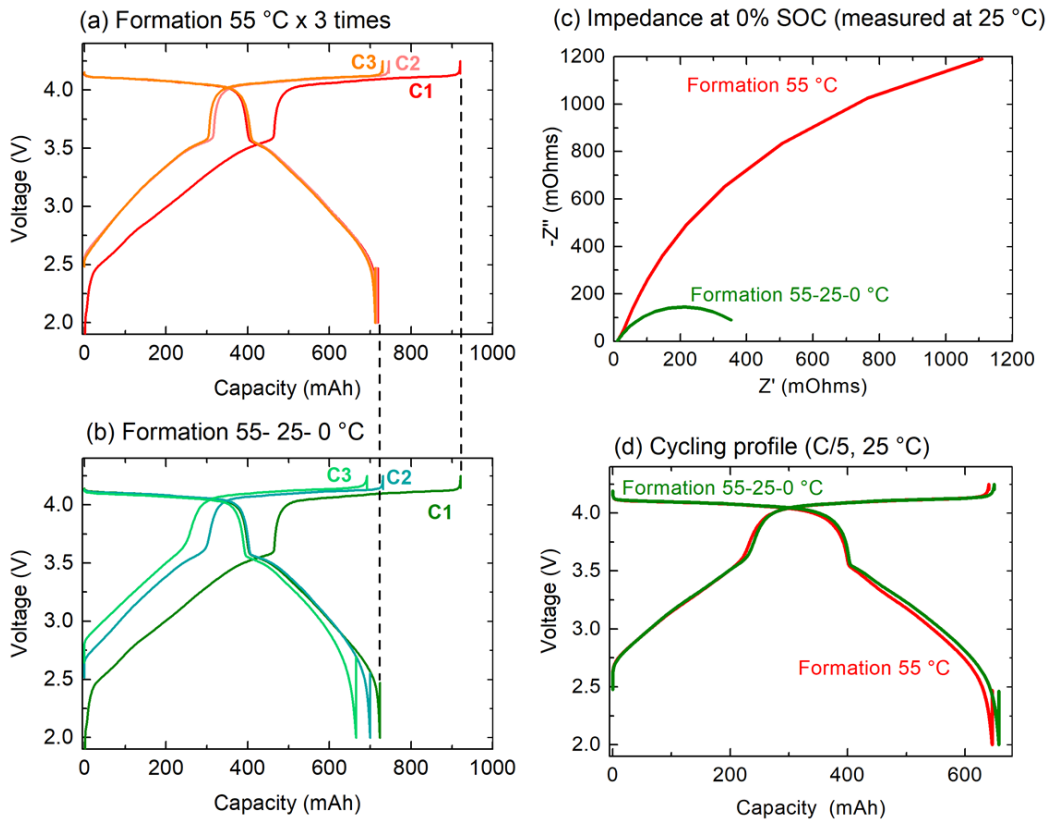


Figure S8. Formation of 18650 NVPF | HC cells. a) Cycling profiles during formation for the 55 °C x 3 formation protocol, b) Cycling profiles during the 55-25-0 °C formation protocol, c) Nyquist plot of the cell impedance measured right after formation, at 25 °C and 0 % state of charge (SOC), and d) First cycle of both cells right after formation.

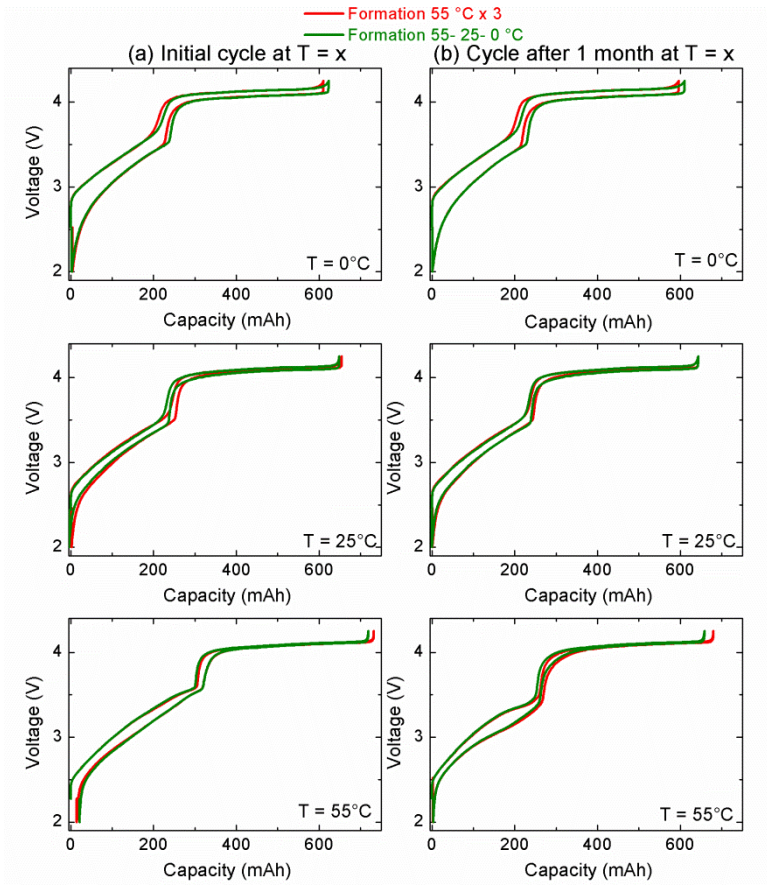


Figure S9. Evolution of the cycling curves of the cells during cycling at different temperatures.

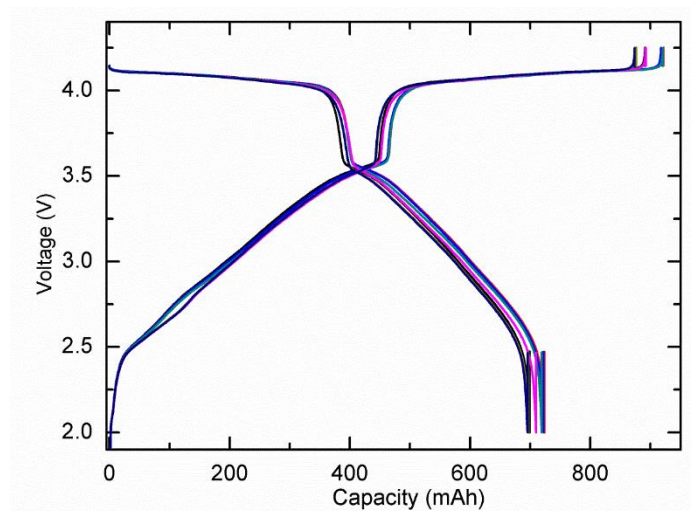


Figure S10. The first cycle profile of the eight 18650 cells used in this study

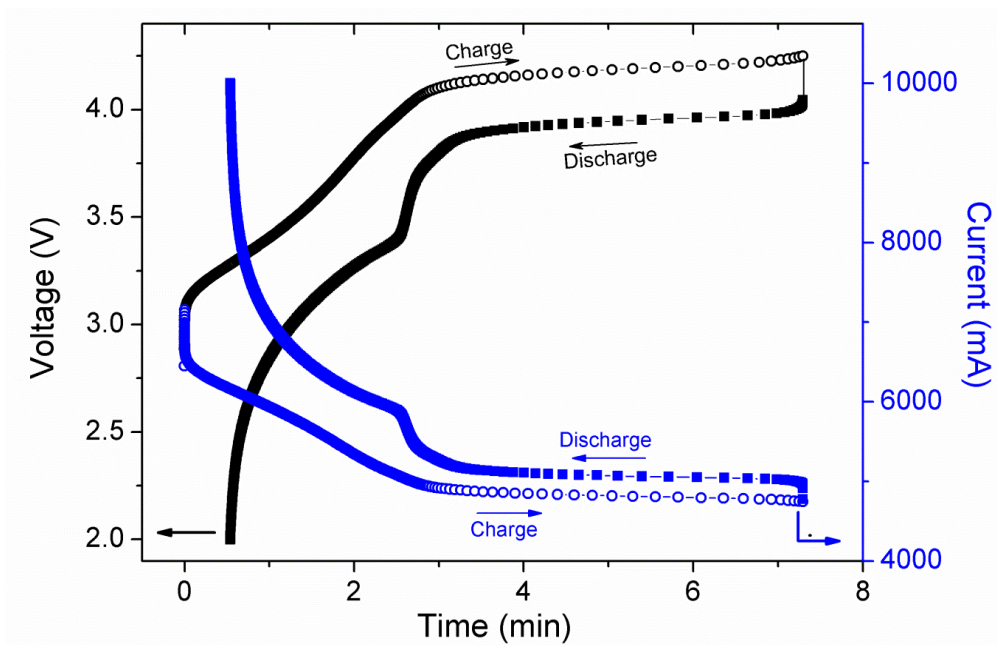


Figure S11. Charge (circles) and discharge (squares) cycling profile of NVPF-HC full cell under constant power protocol with the power of 20 W. The discharge current direction is opposite to that of charge current; however, the absolute number is used here for clarification purposes.