Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Modulating the Cathode Interface in a Sodium-Beta Alumina-based Semi-Solid-State Sodium Cell Using Liquid-Organic Electrolytes

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Table S 1. Characteristic performance parameters for the cell systems mentioned in the text.

		Cell			
Parameter	Unit	1	2	3	4
Electrodes		2	3	3	2
Cycles		50	100	250 (100+50+100)	250 (150 + 100)
I	mA g_{AM}^{-1}	35.4	118	35.4	59 / 118
t_{BASE}	µm	500	500	500	300
V_{LOE}	µl	15	3	15	3
δ	°C	80	80	80	30
A_{PE}	cm²	2.54	2.54	2.54	2.54
m_{PE}	mg	3.4	4.2	4.0	4.7
$q_{sp,\ cycle\ 2}$	mAh g^{-1}	101.0	92.1	100.6	87.3 / 60.2
q_{ret}	%	97.2	92.1	80.1	89.0 / 99.8
U_{avg}	V	3.34	3.28	3.29	3.24
W_{AM}	Wh kg^{-1}	328	278	265	195
P_{AM}	W kg^{-1}	118	383	109	385
W_{PE}	Wh kg^{-1}	233	199	185	137
P_{PE}	W kg^{-1}	84	273	76	270

Electrodes: Two-electrode cell (2) or three-electrode cell (3)
Cycles: Number of charge and discharge cycles
I: Applied current of the galvanostatic charge and discharge
t_{BASE}: Thickness of the sodium-beta alumina solid electrolyte
V_{LOE}: Volume of the liquid organic electrolyte applied to the cathode before cell assembly
δ : Temperature of cell operation
A_{PE}: Area of the positive electrode
m_{PE}: Mass of the positive electrode after drying
$q_{sp,\ cycle\ 2}$: Specific discharge capacity in the second cycle, *i.e.*, in the first cycle after full charge
q_{ret}: Capacity retention in the last cycle (see “Cycles”), calculated with $q_{Cycles}/q_{sp,\ cycle\ 2}$
U_{avg}: Average discharge voltage of the last cycle
W_{AM}: Specific energy regarding the active mass of the cathode
P_{AM}: Specific power regarding the active mass of the cathode
W_{PE}: Specific energy regarding cathode mass
P_{PE}: Specific power regarding cathode mass

Table S 2. Elemental composition (at%) of the surface of the pristine and cycled NaC cathode.

	C	O	Na	Cl	F	P	V
Pristine cathode	78.4	7.8	0.9	-	10.4	1.6	0.9
NaC cathode	72.5	15.2	2.3	1.3	6.0	1.7	1.0

Table S 3. XPS binding energies with attributed species of the pristine and cycled NaC cathode.

		Pristine cathode	NaC cathode
Spectra details	Attributed species	Binding energy / eV	Binding energy / eV
Na 1s		1071.7	1072.0
C 1s	C-C/C-H	284.6	284.6
	C-O / C=O	286.1	286.0
	COOH / CO_3^{2-}	288.3	288.1
	C-F	290.7	290.5
F 1s	Na-F	-	684.8
	C-F	687.8-690.1	687.7-689.8
P $2p_{3/2}$	PO_x	133.3	133.3
Cl $2p_{3/2}$	NaCl	-	198.6
	C-Cl_x	-	200.3
	ClO_3^-	-	206.5
	ClO_4^-	-	208.3

Table S 4. Elemental composition (at%) of the surface of the pristine BASE sample (BASE), the surface of the electrolyte facing the cathode, which had been soaked with liquid organic electrolyte (1M $NaClO_4$ in PC) (NaC-BASE), and the same sample after sputtering (Sputtered NaC-BASE).

	C	O	Na	Al	Cl	F	Li	P
BASE	7.8	53.2	6.6	29.3	0.2	1.4	1.5	-
NaC-BASE	12.4	56.7	4.4	23.2	1.6	0.9	0.3	0.5
Sputtered NaC-BASE	2.0	59.0	2.5	34.4	1.1	0.4	0.6	-

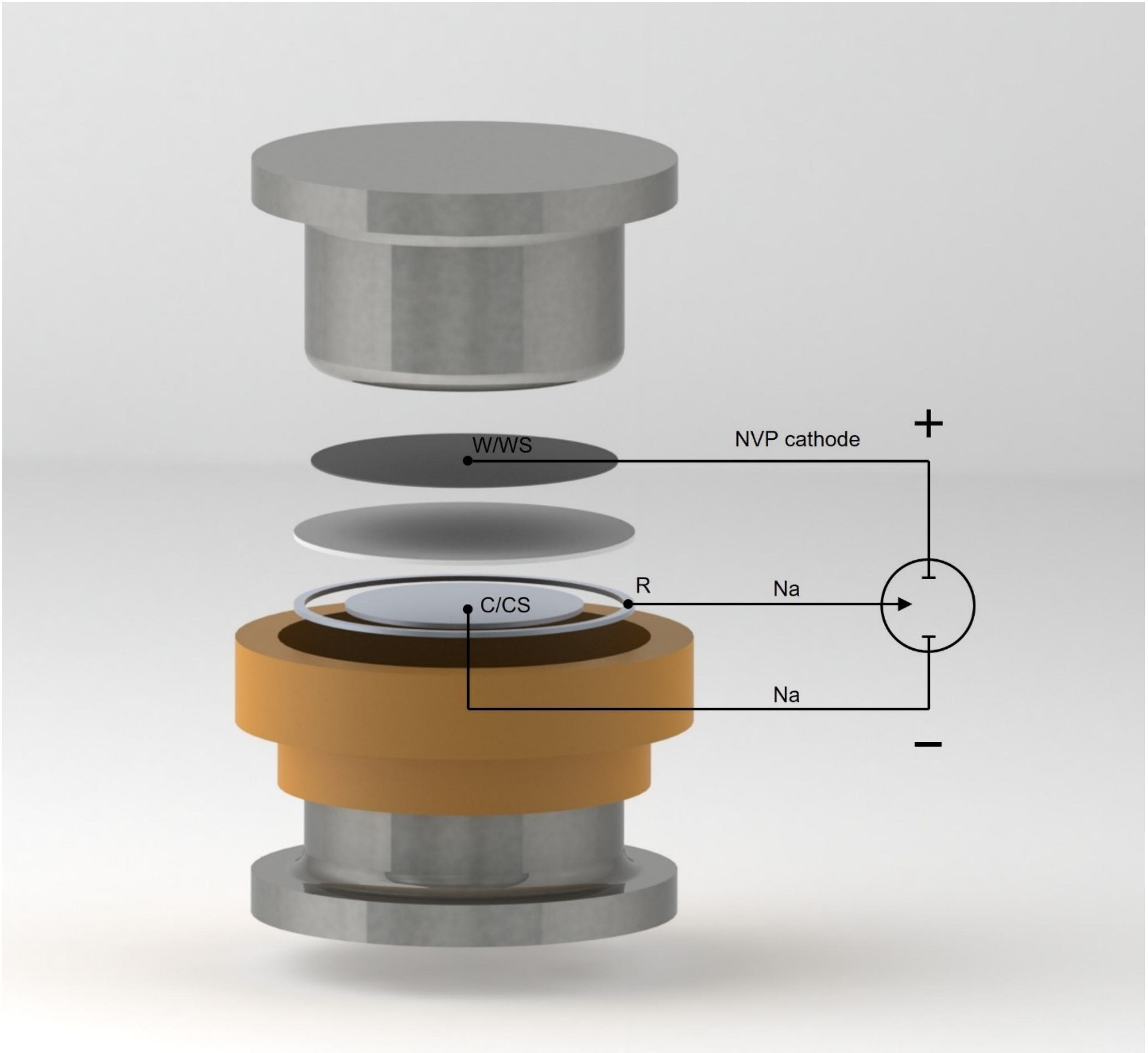

Figure S 1. Cell scheme of the four probe three-electrode measurement using a ring-shaped sodium reference electrode and a sodium counter electrode.

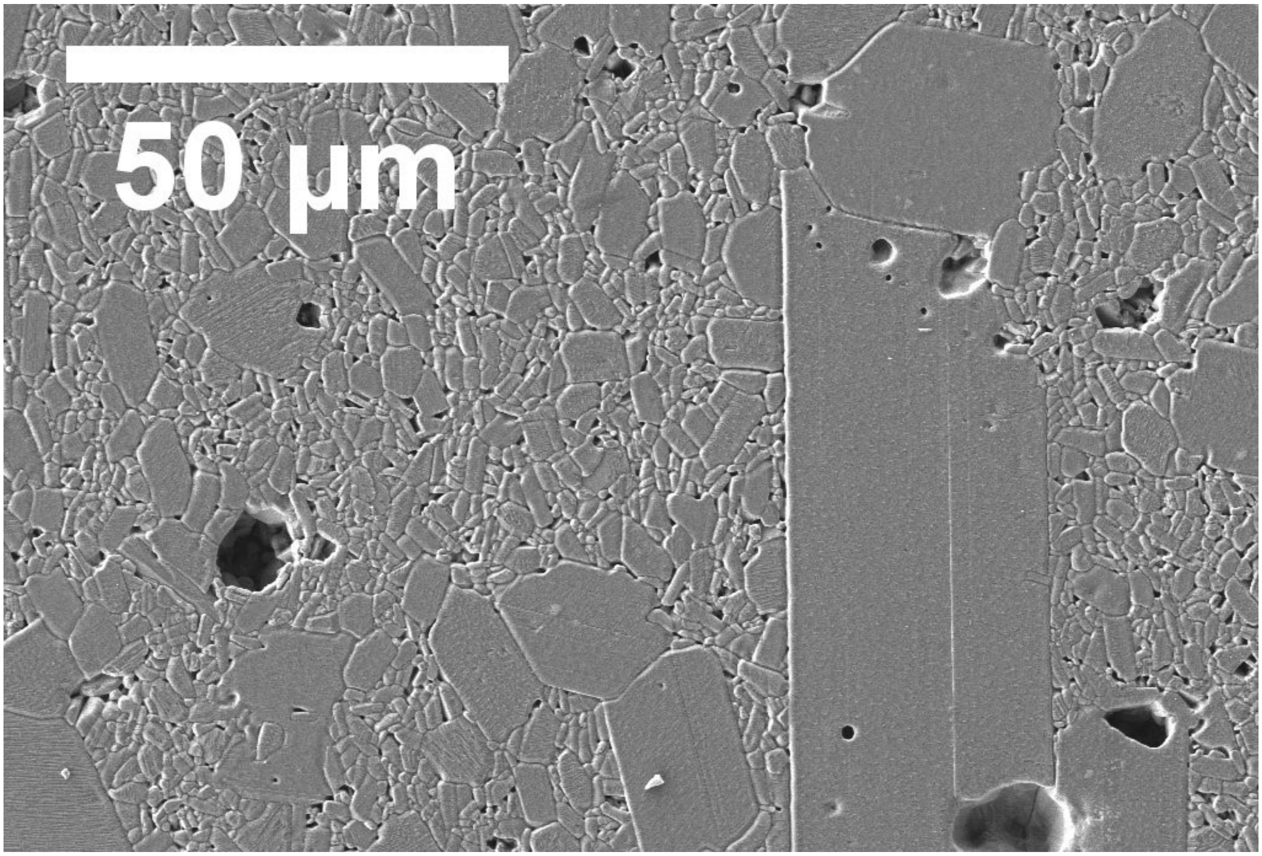

Figure S 2. SEM image of the microstructure of the thermally-etched sodium-beta alumina solid electrolyte (BASE) specimen. The microstructure shows larger crystallites embedded in smaller crystallites and pores at 10 µm.

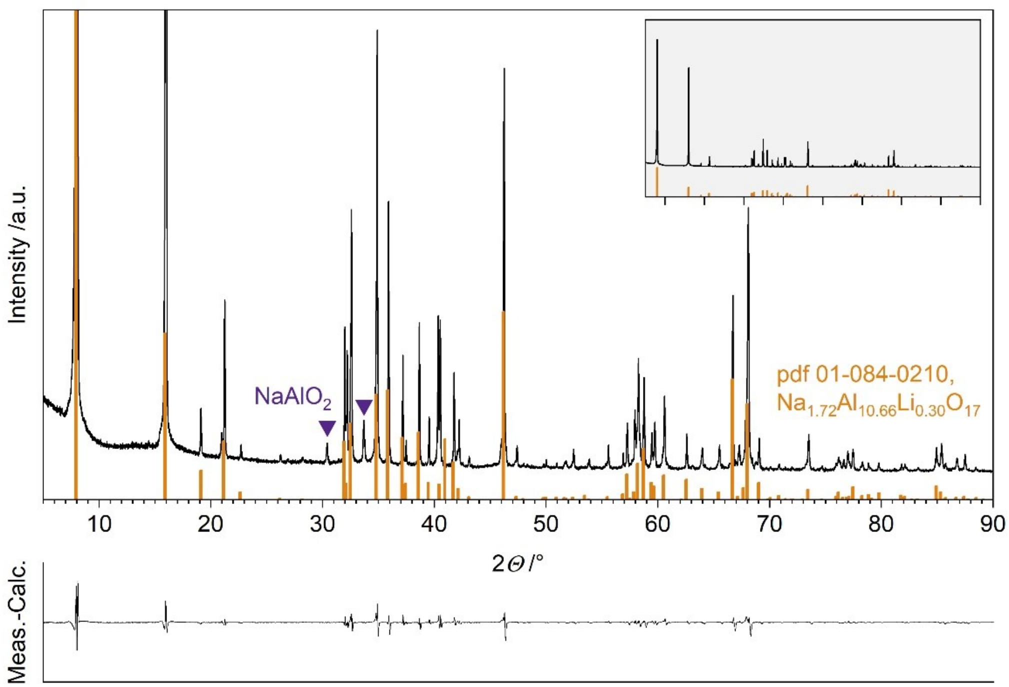

Figure S 3. Diffractogram of the sodium-beta alumina solid electrolytes (BASE). The peaks show good agreement with the literature peaks for $Na_{1.72}Al_{10.66}Li_{0.30}O_{17}$ (pdf 01-084-0210), indicated by the slight difference between measured and calculated peaks. The purple triangles indicate $NaAlO_2$, a common impurity for BASE due to the solid-state synthesis.

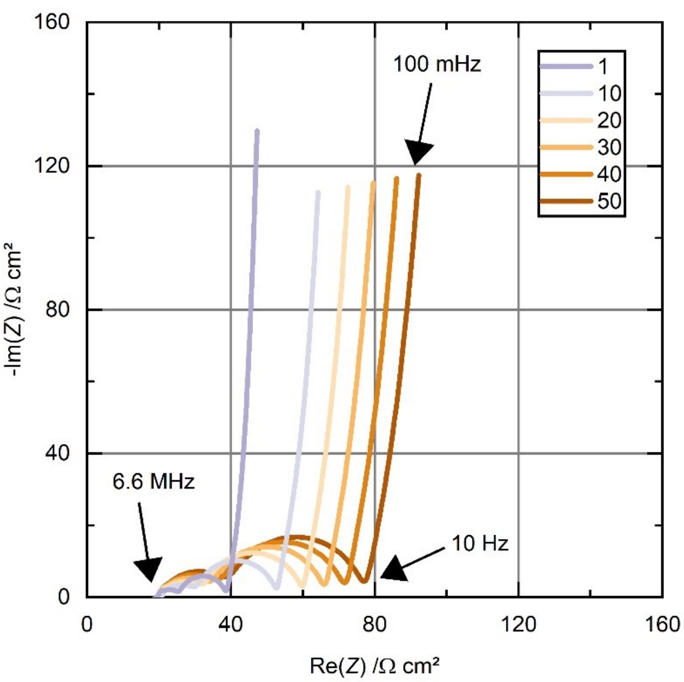

Figure S 4. Nyquist plot of the two-electrode cell with NaC operated at 80 °C and 0.3C for 50 cycles. The increase in internal resistance is discussed for the three-electrode measurements.

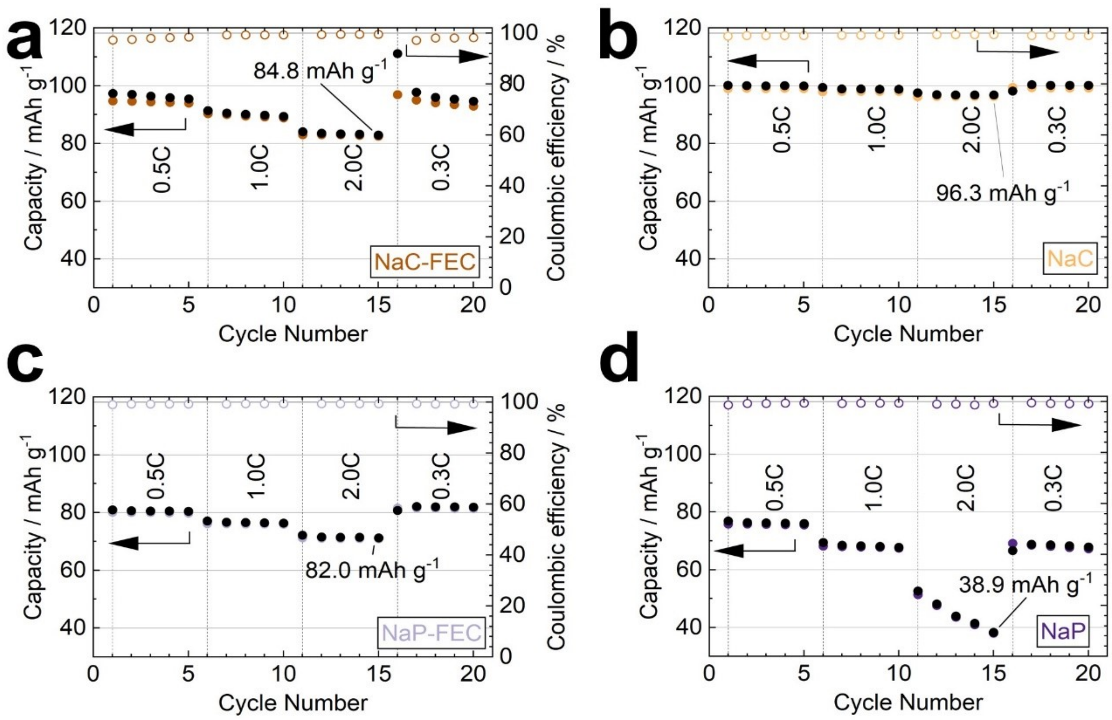

Figure S 5. Rate capability measurements of the four cells cycled with 0.5C, 1.0C, 2.0C, and 0.3C for five cycles each with a) NaC-FEC. b) NaC. c) NaP-FEC. d) NaP.

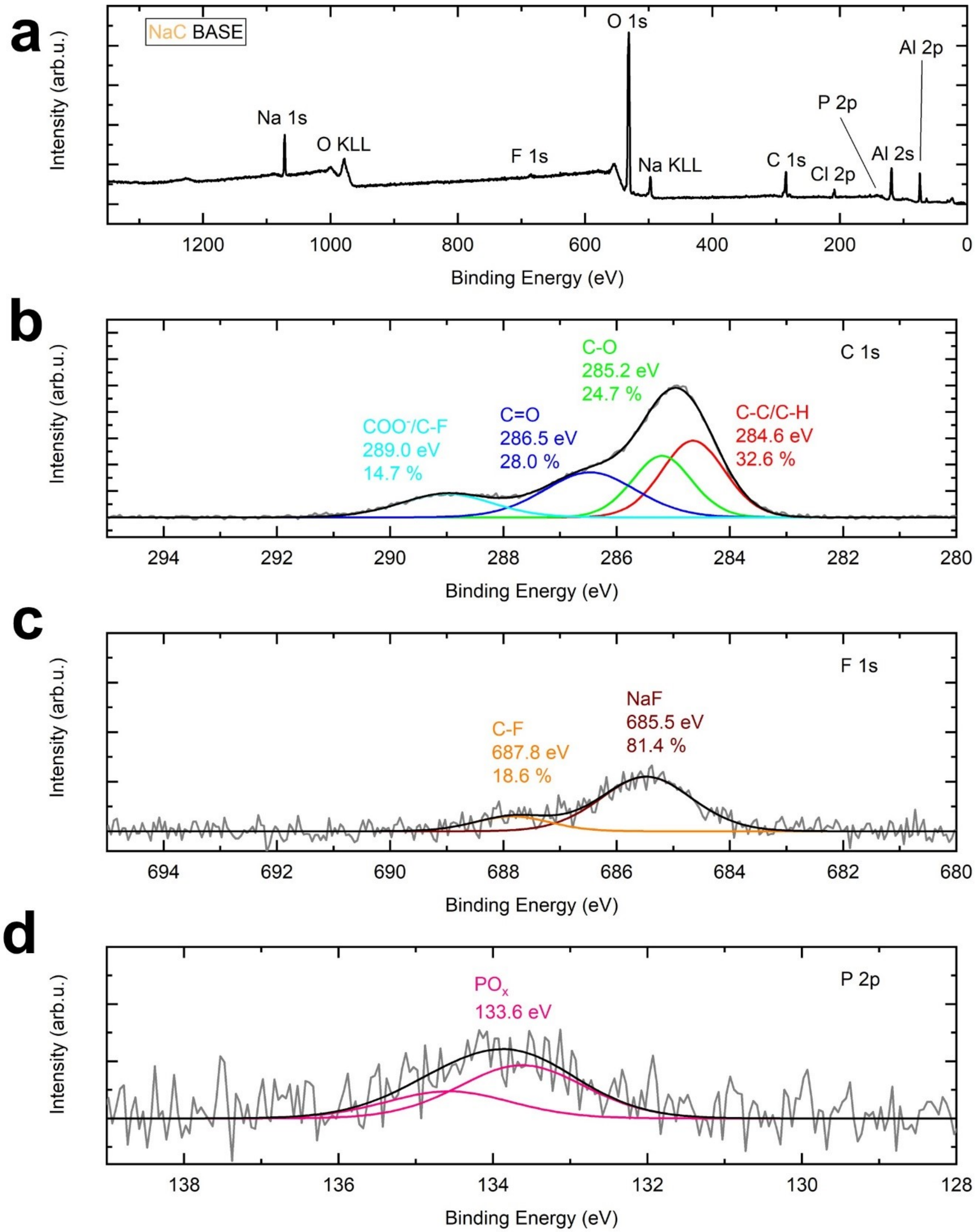

Figure S 6. Post-mortem XP spectra of a BASE after cycling, which had been in contact with NaC and the cathode. a) Survey spectrum. b) Spectrum of the C 1s level. c) Spectrum of the F 1s level. d) Spectrum of the P 2p level.

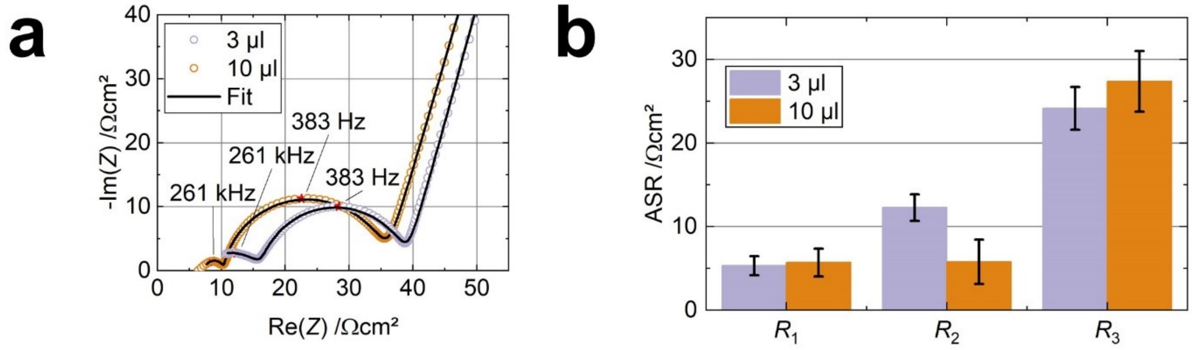

Figure S 7. a) Nyquist plot of a symmetrical cell (PE|LOE|BASE|LOE|PE) measured at 80 °C. The spectrum of the cell with 3 µl LOE on both positive electrodes is shifted to the right, indicating higher resistances than the cell with 10 µl LOE. The same electrolyte and two positive electrodes were used for both measurements. b) Evaluation of the Nyquist plot shows a significant reduction (n = 3) in R_2 when additional NaC is added to the cathode.

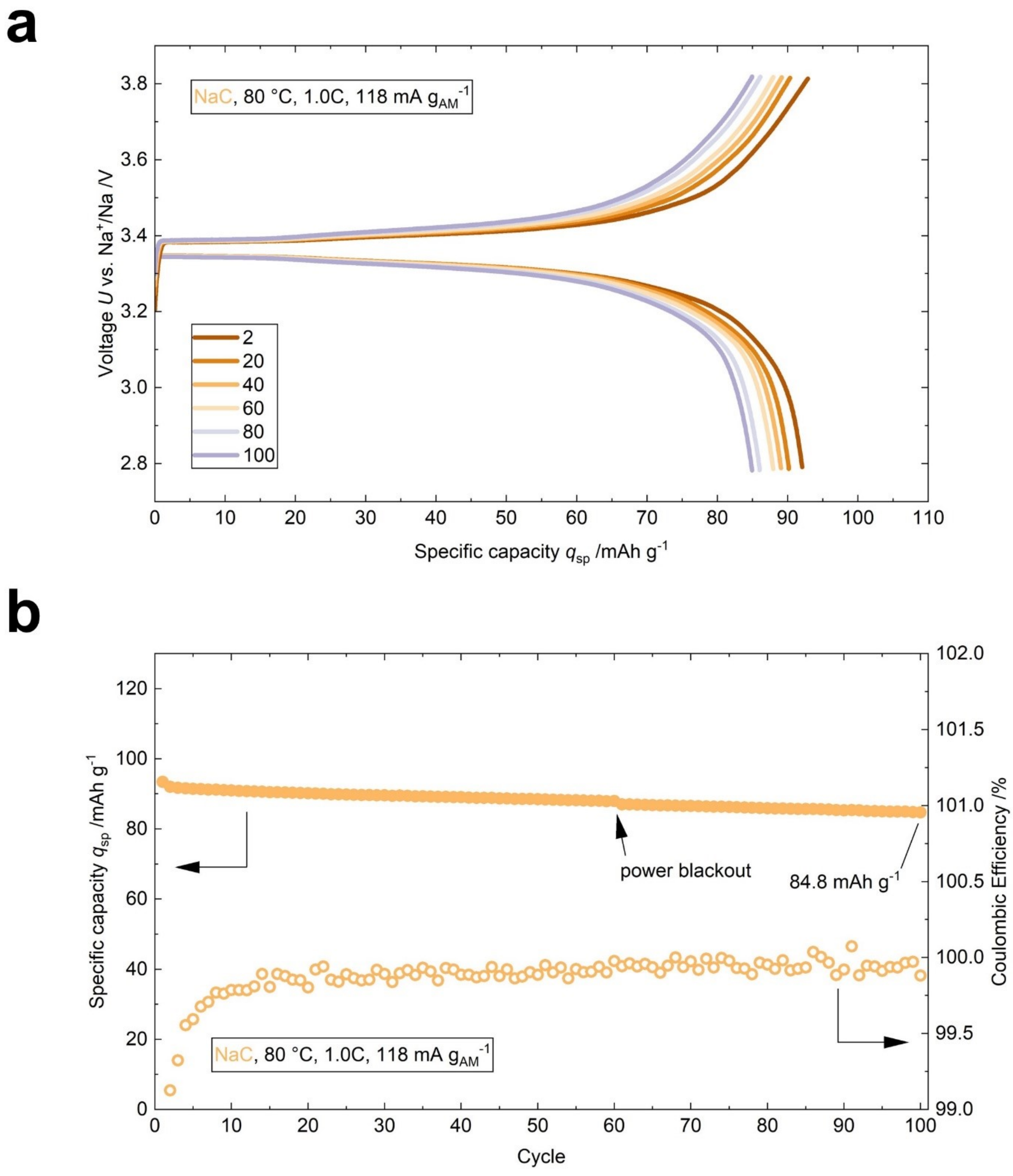

Figure S 8. GCPL data of the three-electrode cell (Cell 2) cycled at 80 °C with 1.0C. a) The voltage profiles of the hundred cycles show a less distinct plateau. b) The cell delivers a specific discharge capacity of 84.8 mAh g^{-1} after 100 cycles with a high Coulombic Efficiency close to 100%.

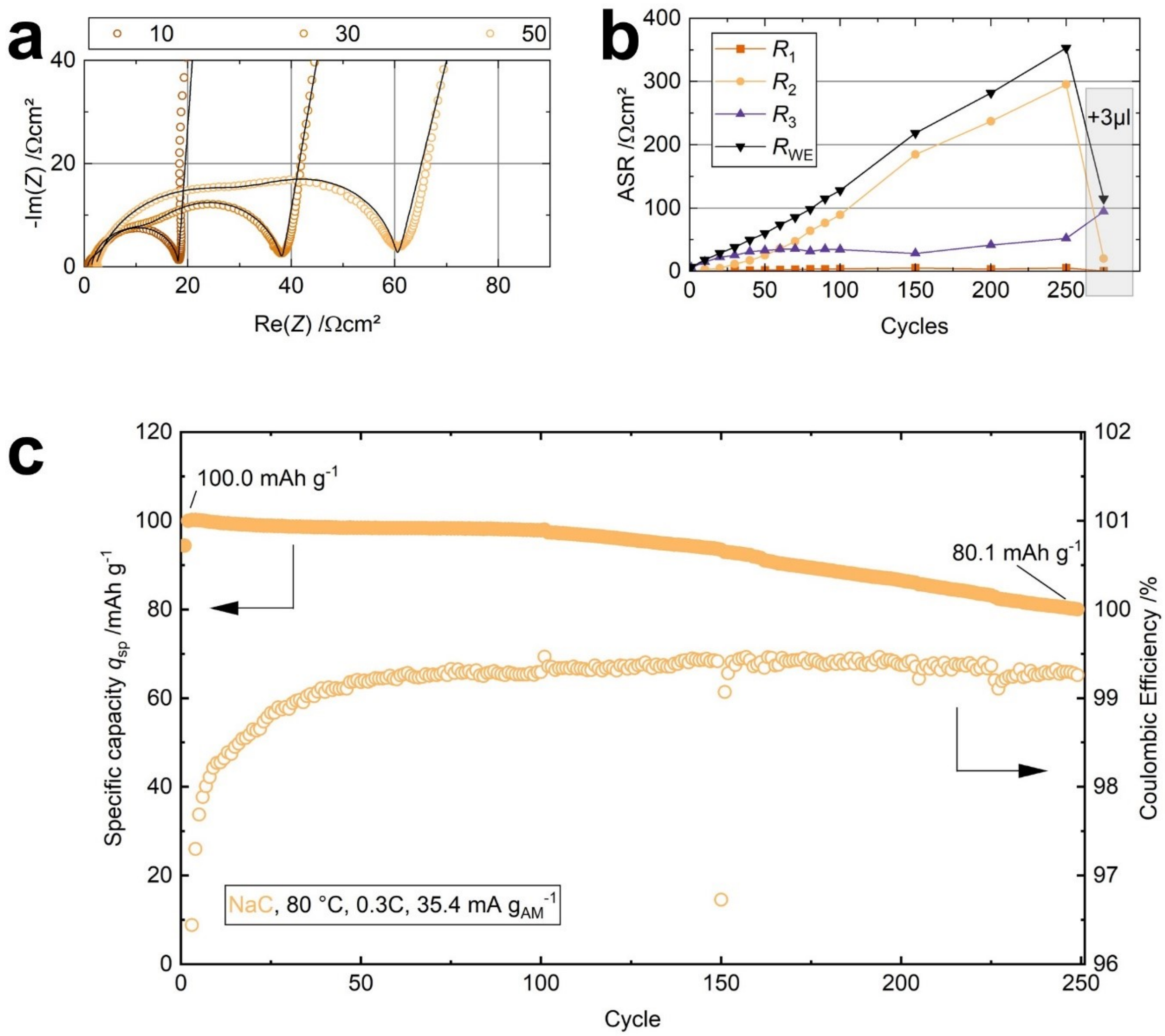

Figure S 9. Three-electrode measurement of the cell with 15 µl LOE (Cell 3). a) Only one semicircle is visible after ten cycles, corresponding to the charge-transfer resistance R_3. After thirty cycles, a second semicircle, correlated to R_2, has evolved at medium frequencies. After fifty cycles, both semicircles are nearly equal in size, indicating similar resistances of the underlying processes. b) As cycling continues, the interface resistance R_2 increases while R_3 stabilizes. R_2 dominates the cell´s internal resistance. R_1 stays constant, while R_3 increases slightly. After adding 3 µl of NaC, R_2 is drastically reduced. No cycling was performed after adding the LOE; the resistance is shown at the 275th cycle for comparison. c) The cell was cycled for 250 cycles. The measurement was manually stopped after 100 cycles and 150 cycles for evaluation. The slope indicates that the interruptions were not beneficial for the cell performance. The cell delivers 80.1 mAh g^{-1} after 250 cycles at 80 °C and 0.3C, corresponding to 80% capacity retention. The CE is 99.3% in the 250th cycle.