Supporting information

Supporting Information for "Design and Sintering of All-Solid-State Composite Cathodes with Tunable Mixed Conduction Properties via the Cold Sintering Process"

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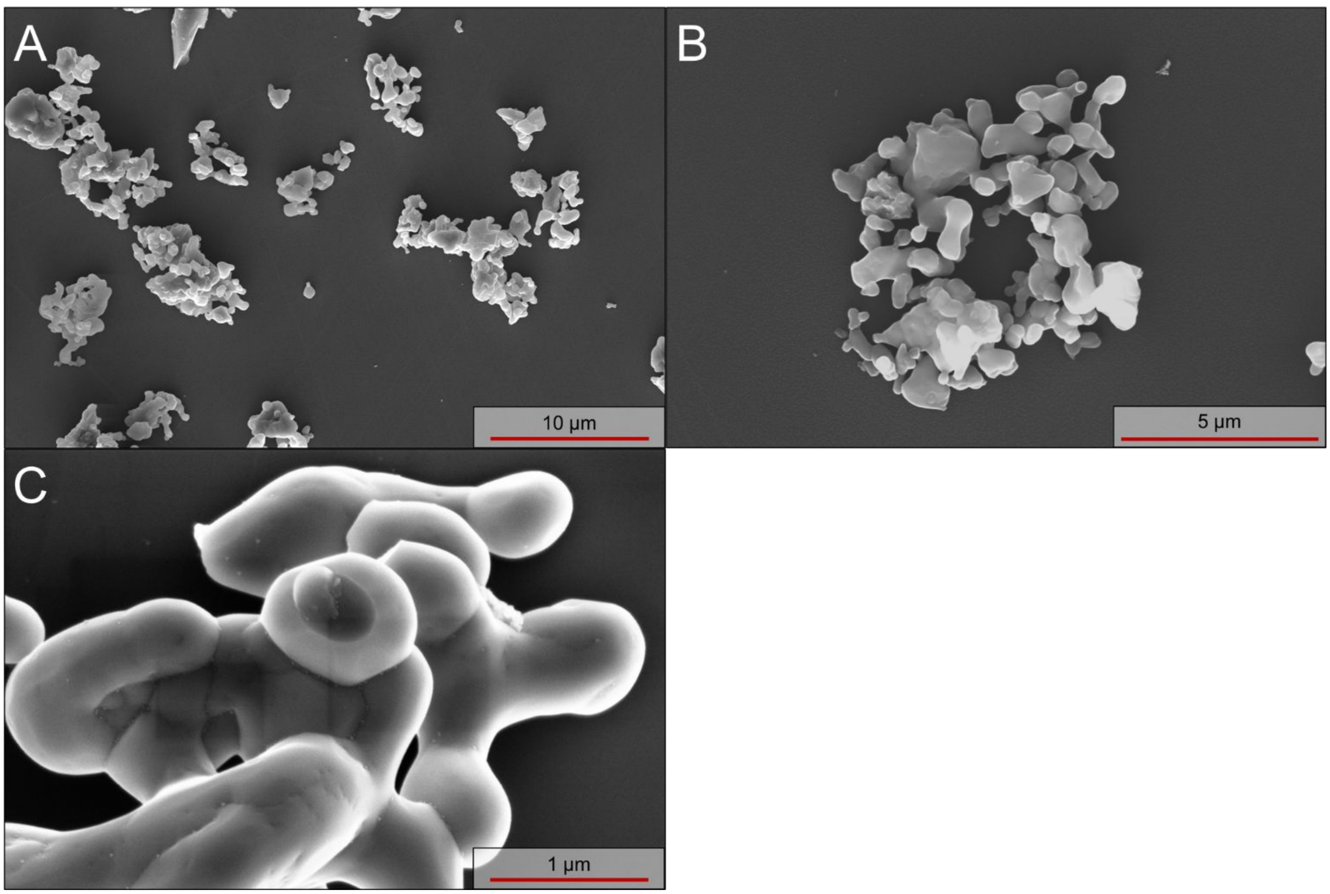

Figure S1 Scanning electron microscopy of sol-gel synthesized $Na_3V_2(PO_4)_3$ powder.

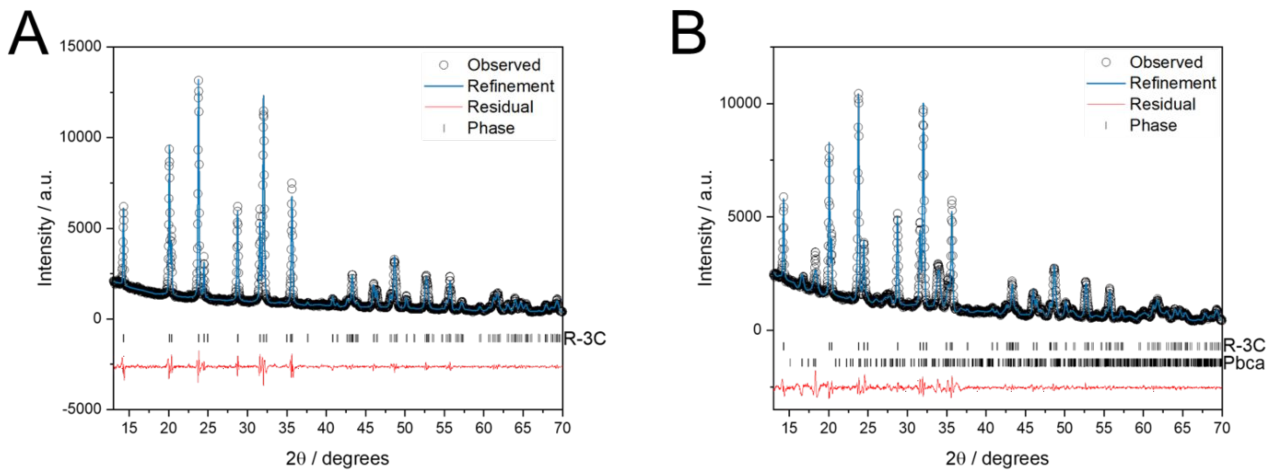

Figure S2 XRD Rietveld Refinements of the NVP powder (**a**) and an NVP pellet cold sintered at 375°C (**B**).

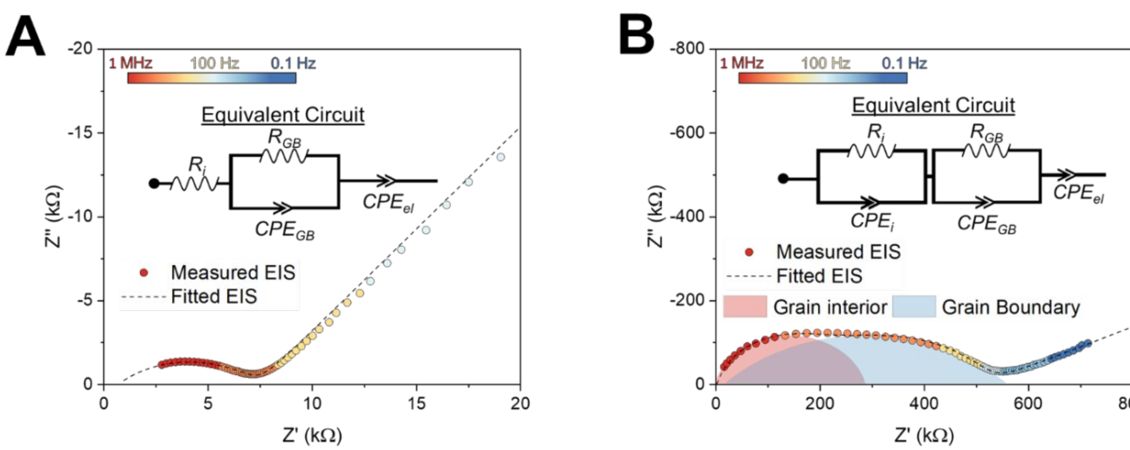

Figure S3 EIS of pure NVP, cold sintered at 375°C, 10 wt.% NaOH, 360 MPa, three hours. Resistance values given in Ohm’s. Equivalent circuits given in corresponding insets.

Table S1 Fitting parameters of pure NVP for EIS spectra depicted in Figure S3.

Pure NVP	*Interior*			*Grain boundary*			*Electrode*	
	R_i (Ω)	CPE_i-T	CPE_i-P	R_{GB} (Ω)	CPE_{GB}-T	CPE_{GB}-P	CPE_{el}-T	CPE_{el}-P
110°C	702	N/A	N/A	6538	1.06E-7	0.50	2.50E-5	0.52
23°C	2.61E6	1.14E-11	0.94	6.02E6	4.60E-10	0.77	8.48E-8	0.53

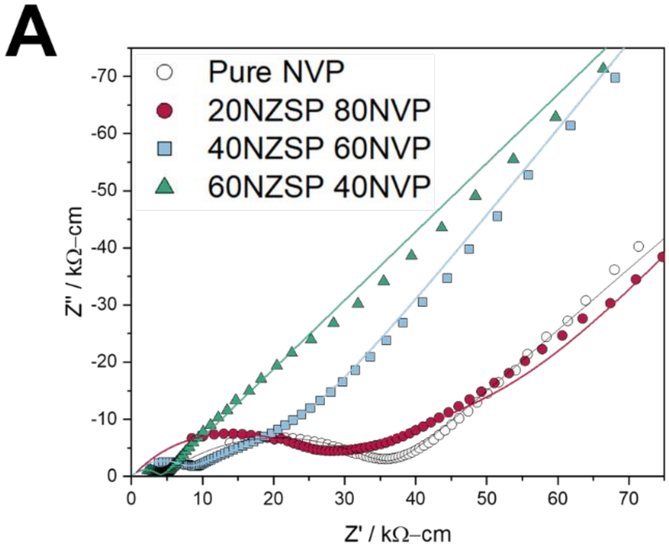

Figure S4 EIS of pure NVP, 20NZSP, 40NZSP, and 60NZSP samples at 110°C. Equivalent circuit fitting given in Table S2. Complex plane of EIS scaled by geometry (area/thickness, cm).

Table S2 EIS fitting of EIS spectra given in Figure S4. R_i only discernible in the pure NVP sample. Some samples displayed some curvature at the transition from a semicircle to a purely CPE response, indicating a finite-length Warburg (open) response; these samples have a non-zero W_o-R value and the other electrode fitting parameters are italicized.

T = 110°C	*Interior*			*Grain boundary*			*Electrode*		
	R_i (Ω-cm)	CPE_i-T	CPE_i-P	R_{GB} (Ω-cm)	CPE_{GB}-T	CPE_{GB}-P	(W_0/CPE) -T	(W_o/CPE_{el})-P	W_o-R
Pure NVP	3271	N/A	N/A	30470	1.06E-7	0.50	2.50E-5	0.52	N/A
20NZSP	N/A	N/A	N/A	23650	1.60E-8	0.66	*0.117*	*0.31*	*1.34E4*
40NZSP	N/A	N/A	N/A	6031	4.97E-9	0.80	*1.75E-2*	*0.32*	*5552*
60NZSP	N/A	N/A	N/A	3789	9.47E-10	0.76	6.96E-7	0.41	N/A

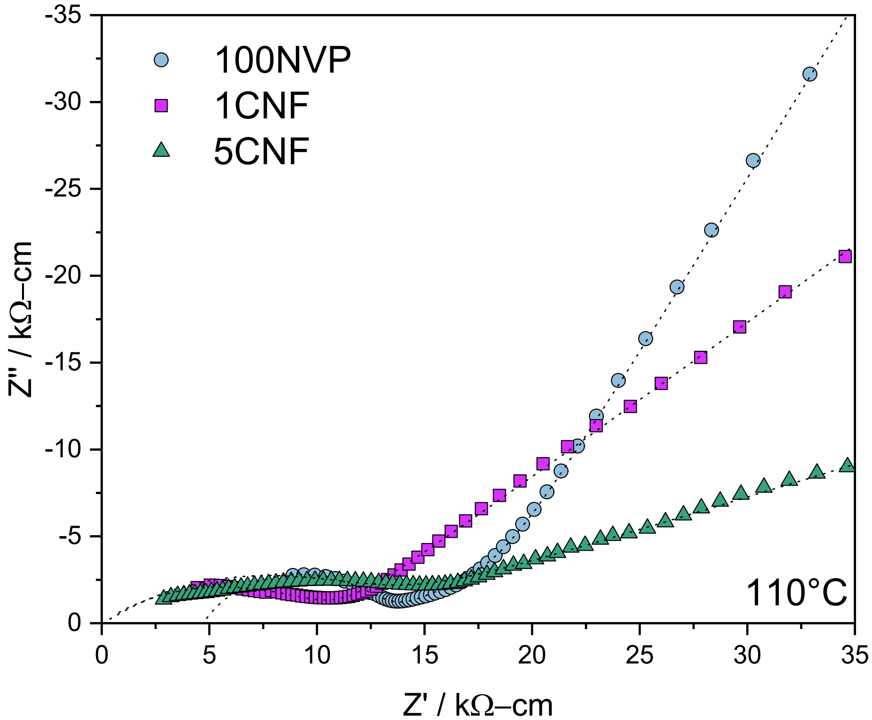

Figure S5 The EIS spectra of pure NVP, 1CNF, and 5CNF samples measured at 110°C. Complex plane of EIS scaled by geometry (area/thickness, cm)

Table S3 EIS fitting parameters of spectrum presented in Figure S5. R_i given where discernible.

T = 110°C	*Interior*			*Grain boundary*			*Electrode*	
	R_i *(Ω-cm)*	CPE_i*-T*	CPE_i*-P*	R_{GB} *(Ω-cm)*	CPE_{GB}*-T*	CPE_{GB}*-P*	CPE_{el}*-T*	CPE_{el}*-P*
Pure NVP	3271	N/A	N/A	30470	1.06E-7	0.50	2.50E-5	0.52
1CNF	N/A	N/A	N/A	11085	7.07E-7	0.43	4.17E-5	0.48
5CNF	N/A	N/A	N/A	10913	3.73E-6	0.46	4.62E-4	0.23

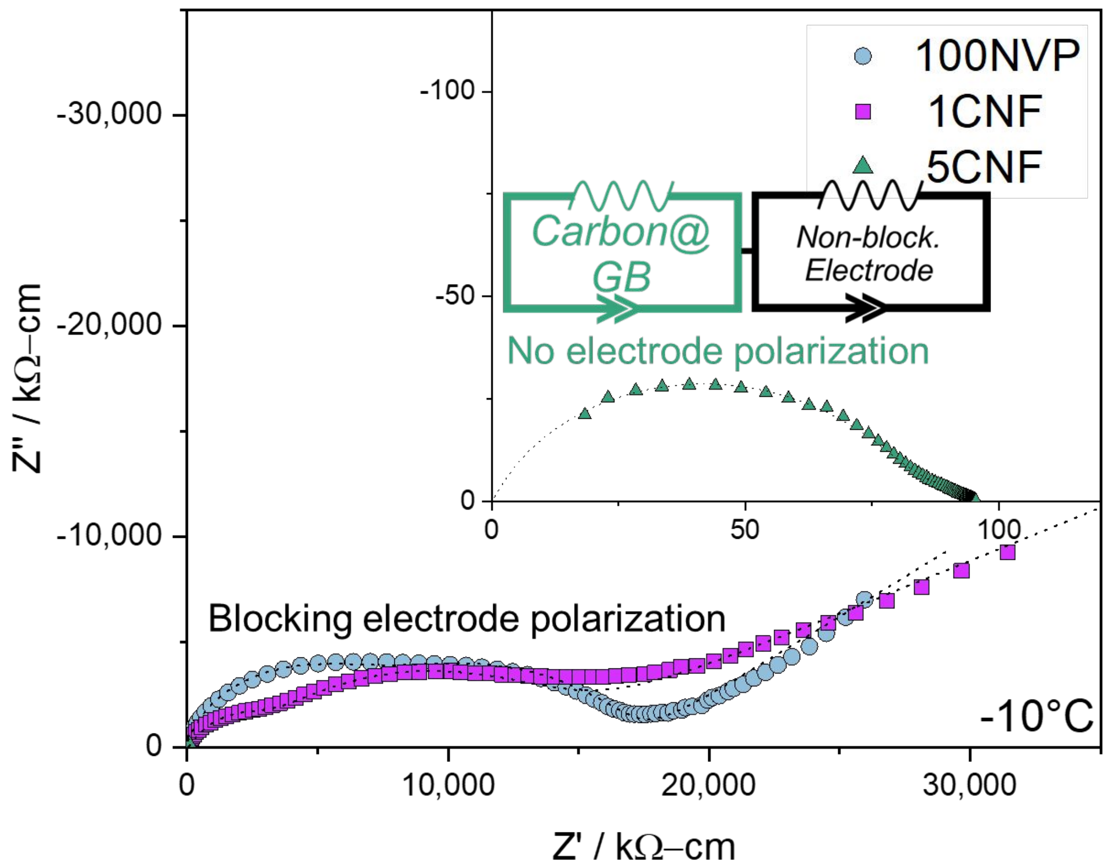

Figure S6 EIS spectra of pure NVP, 1CNF, and 5CNF samples at -10°C. Equivalent circuit and fitting parameters given in Table S4 and S5. Complex plane of EIS scaled by geometry (area/thickness, cm)

Table S4 EIS fitting parameters for pure NVP and 1CNF at -10°C, depicted in Figure S6

T = -10°C	*Interior*			*Grain boundary*			*Electrode*	
	R_i (Ω-cm)	*CPE_i-T*	*CPE_i-P*	*R_{GB} (Ω-cm)*	*CPE_{GB}-T*	*CPE_{GB}-P*	*CPE_{el}-T*	*CPE_{el}-P*
Pure NVP	1.22E7	1.14E-11	0.94	2.80E7	4.60E-10	0.77	8.48E-8	0.53
1CNF	2.61E6	3.78E-11	0.91	1.12E7	2.60E-9	0.73	3.36E-9	0.41

Table S5 EIS fitting parameters for the 5CNF sample at -10°C, as depicted in Figure S6.

T = -10°C	*High Frequency (HF)*			*Low Frequency (LF)*		
	R_{HF} (Ω-cm)	*CPE_{HF}-T*	*CPE_{HF}-P*	*R_{LF} (Ω-cm)*	*CPE_{LF}-T*	*CPE_{LF}-P*
5CNF	8.43E4	3.24E-9	0.72	1.03E4	3.36E-6	0.64

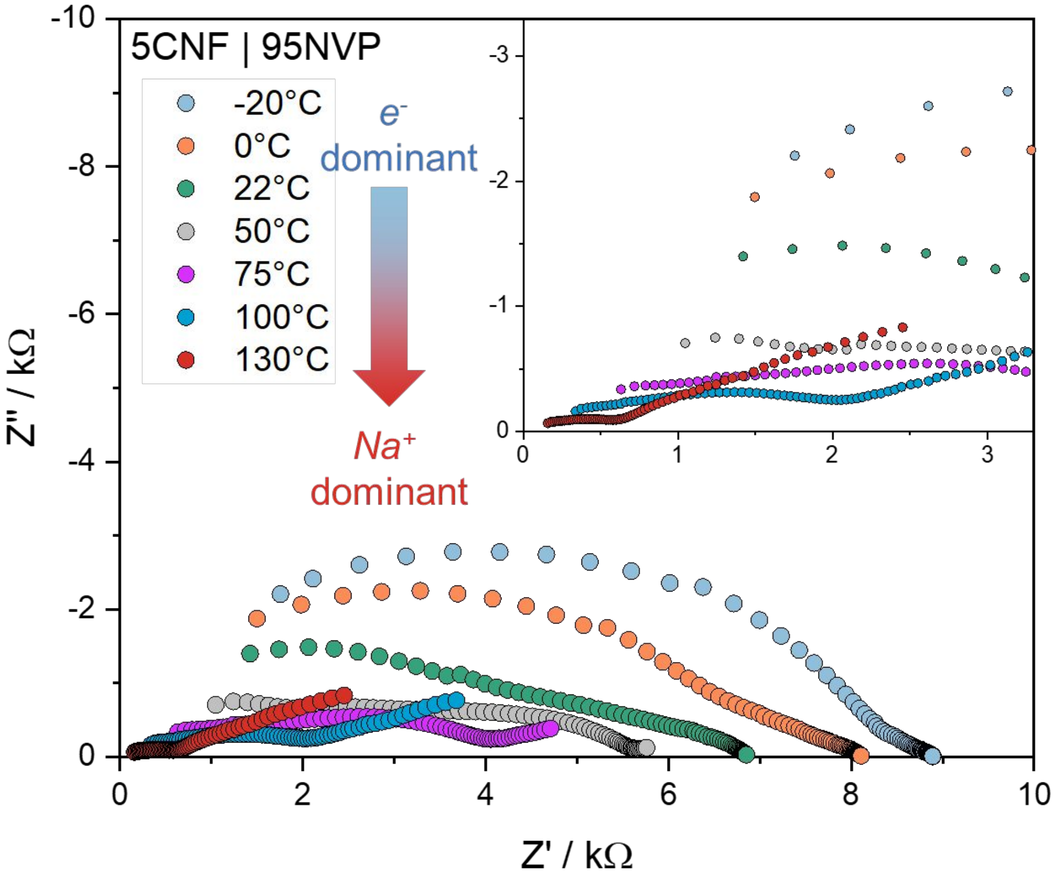

Figure S7 EIS spectrum of the 5CNF sample from -20°C to 130°C, illustrating the changes in the shape of the complex plane response. The equivalent circuits corresponding to each spectra presented are given in Table S6.

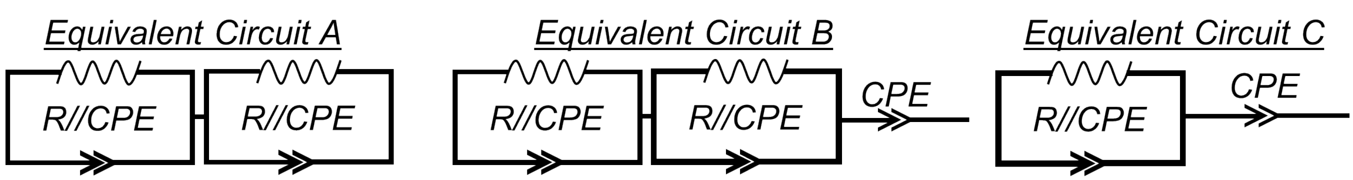

Table S6 The 5CNF sample displays a range of complex plane EIS responses across the -20°C to 130°C temperature range. Three simple equivalent circuits are selected and matched to the EIS spectra of different temperatures, as indicated in this table.

	-20°C	0°C	22°C	50°C	75°C	100°C	130°C
Equivalent Circuit	A	A	A	B	B	C	C

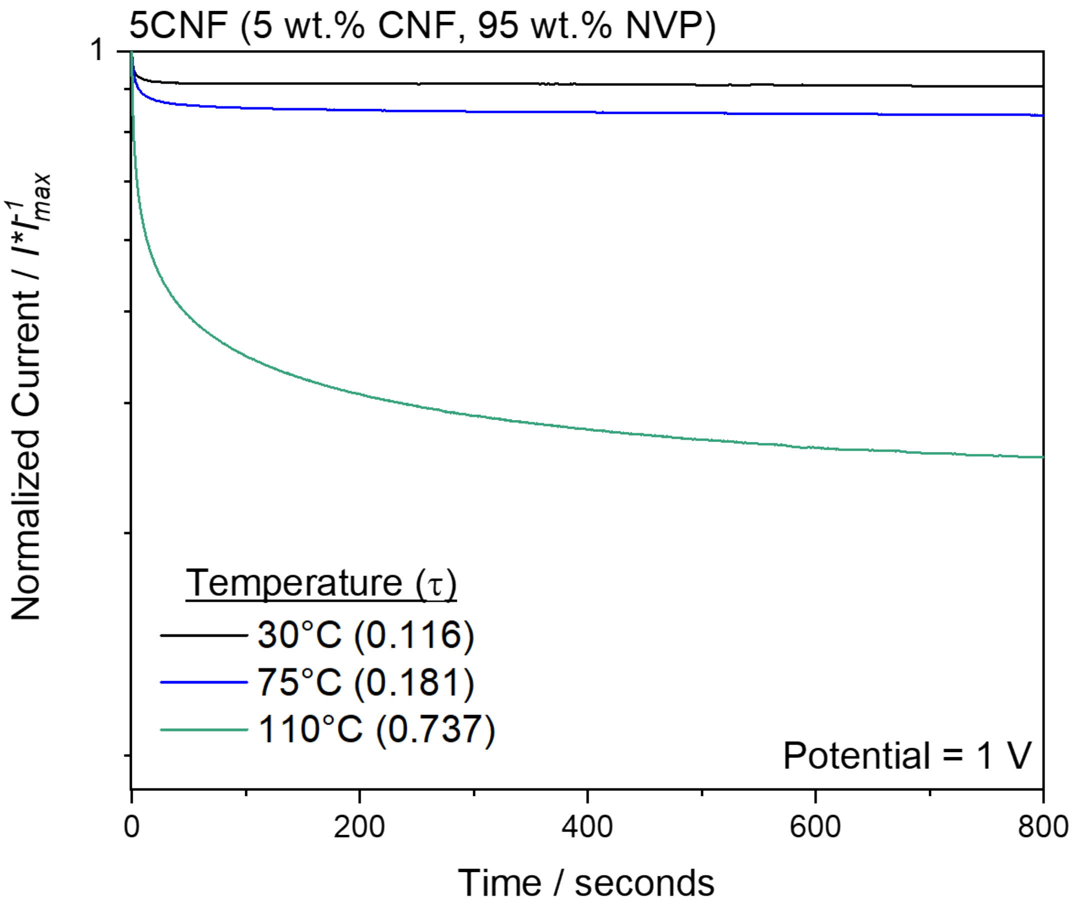

Figure S8 Transference number measurements of the 5CNF sample at 30°C, 75°C, and 110°C. The transference number (τ) increases from 0.116 to 0.737 as the temperature is increased and the conductivity changes from electron-dominated to ion-dominated.

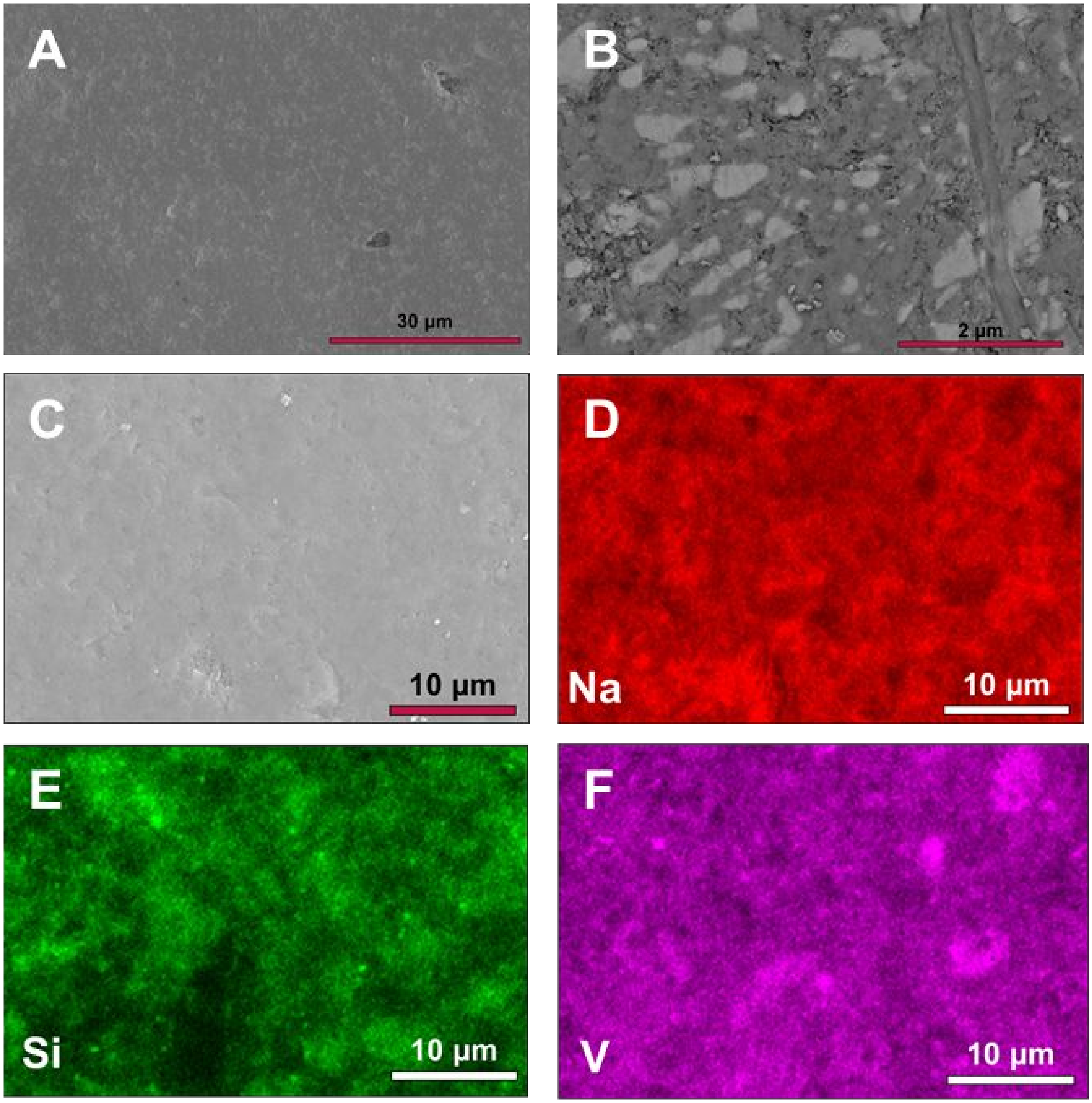

Figure S9 SEM images of a polished sample containing 90 wt.% NVP and 10 wt.% NZSP. High density is apparent from secondary electron imaging (**A**). Z-contrast in backscatter imaging allows for the denser Zr-rich NZSP within the sample to appear lighter within the microstructure (**B**). EDS imaging allows for chemical mapping of the two phases in areas which might appear otherwise homogenous (**C-F**).

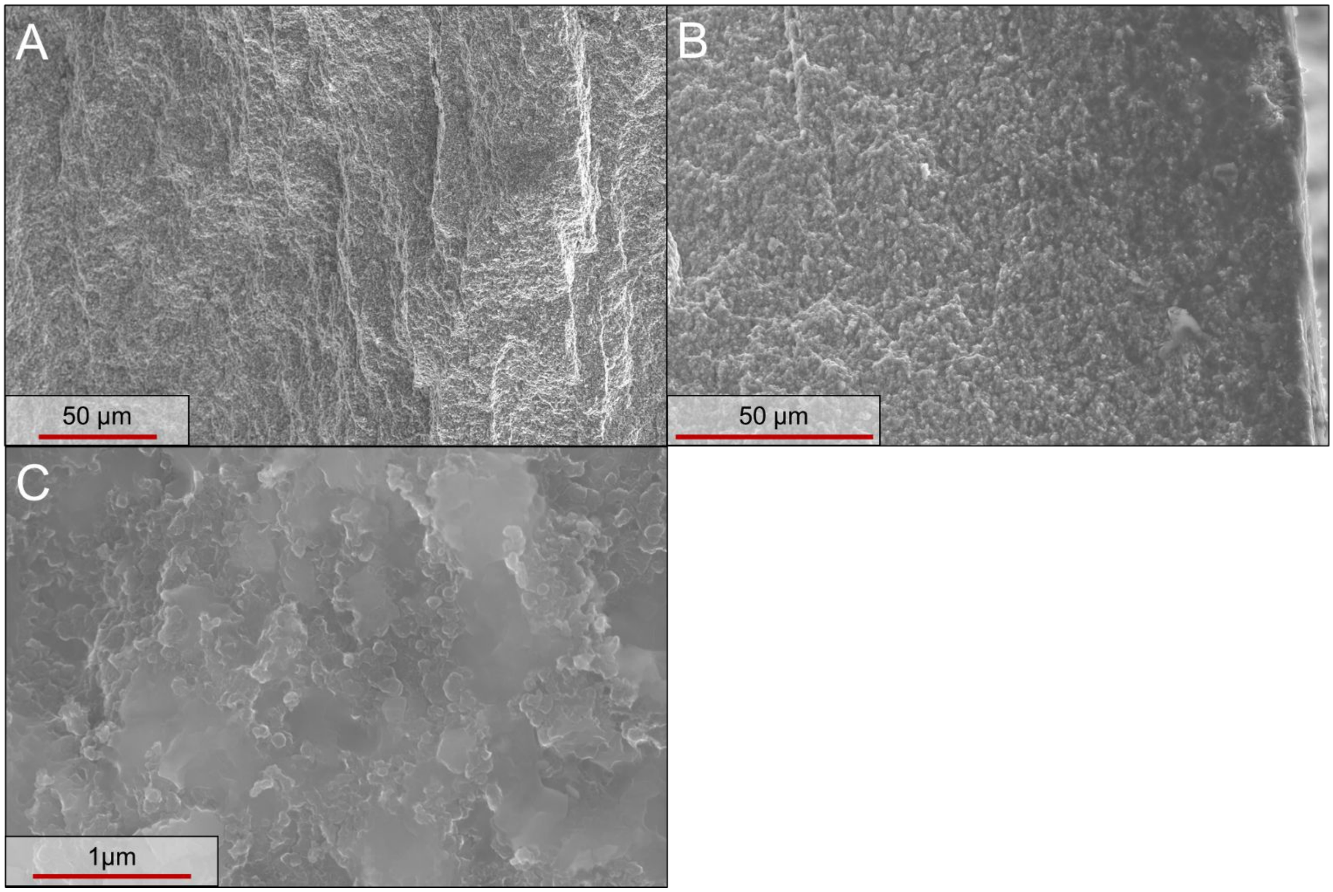

Figure S10 A cold sintered composite cathode was cycled 150 times (as detailed in the main body) and the half cell was subsequently disassembled. SEM images from the bulk of the pellet (**A**,**C**) and the edge of the pellet (**B**) illustrate that the surface is free of pores/cracks even after extensive cycling.

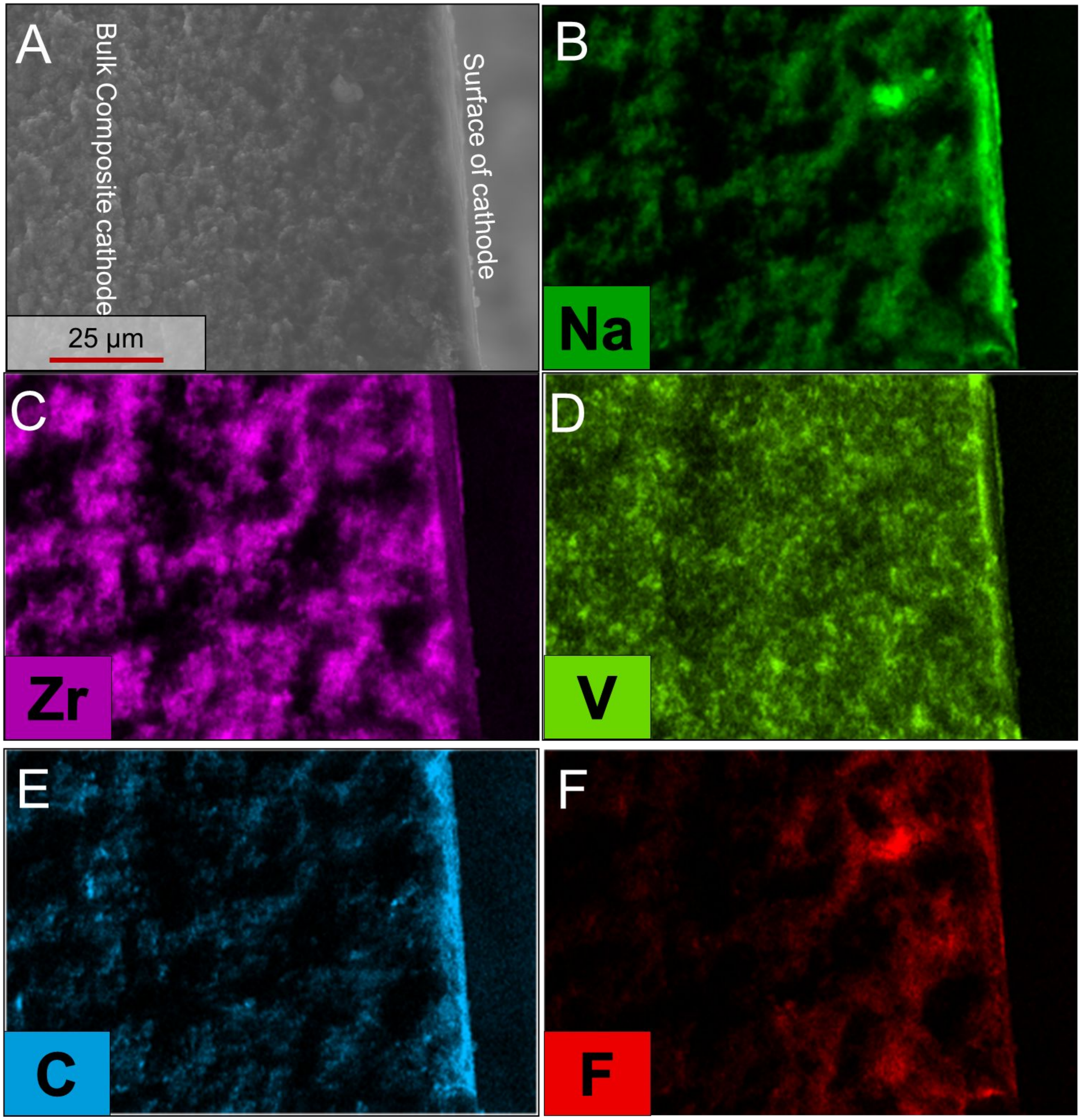

Figure S11 EDS of the surface/edge of the cold sintered cathode pellet after 150 cycles is depicted. The bulk triphasic cathode contains clear signatures of the distinct phases, namely $Na_3V_2(PO_4)_3$ (**B**, **D**), $Na_3Zr_2Si_2PO_{12}$ (**C**), and carbon (**E**). Contamination/infiltration of the liquid electrolyte ($NaClO_4$ in propylene carbonate and fluoroethylene carbonate) is clearly limited to the surface of the monolithic pellet, as implied by the fluorine signature (**F**). The scale bar of (**A**) is applicable to all images.