[Supporting Information]

Na_2ZrCl_6 enabling highly stable 3 V all-solid-state Na-ion batteries

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1. Supporting Figures

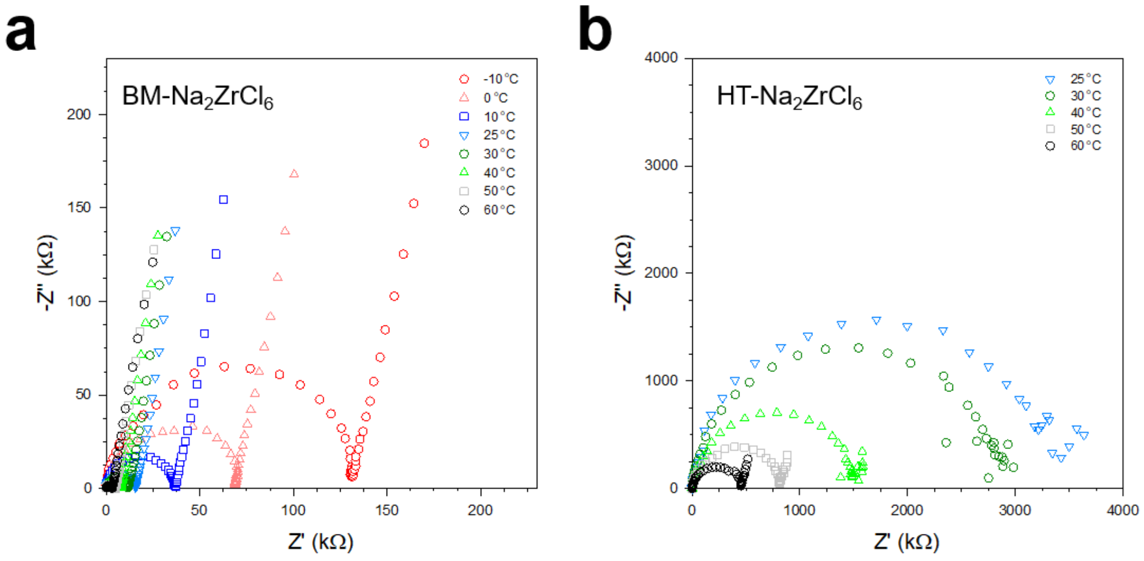

Figure S1. Typical Nyquist plots of ion-blocking Ti/SE/Ti symmetric cells.

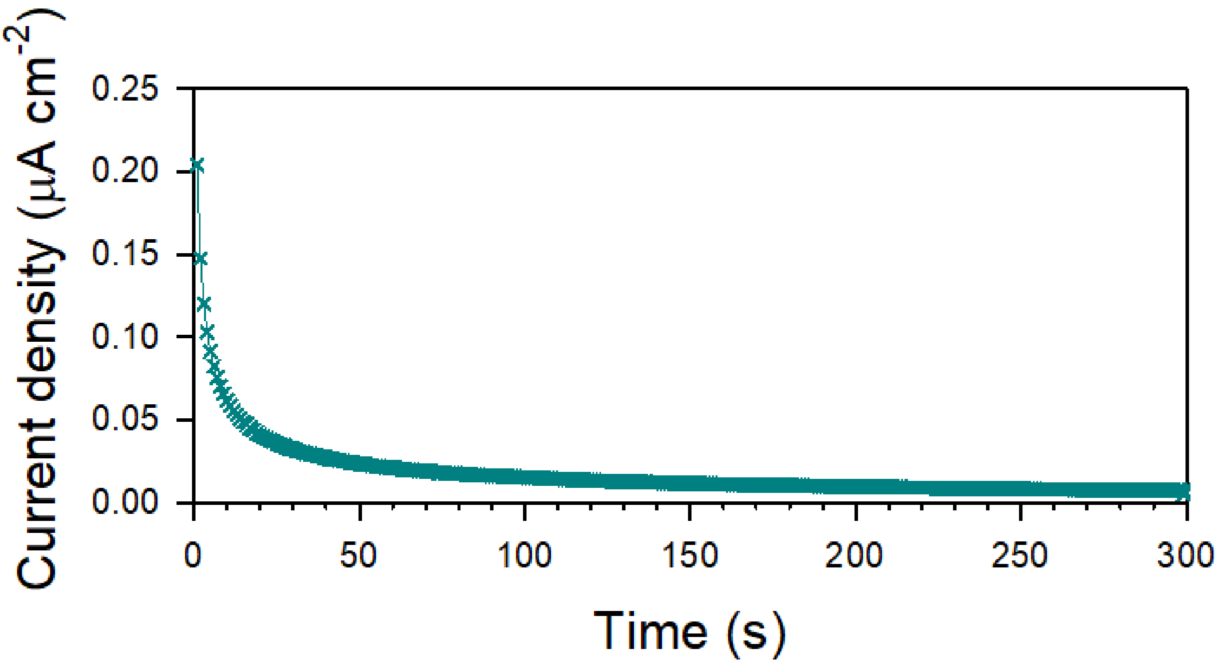

Figure S2. Chronoamperometry results for the Ti/SE/Ti symmetric cells with a voltage step of 1 V at room temperature for employing BM-Na_2ZrCl_6. Corresponding electronic conductiviteis were 2.09×10^{-10} S cm^{-1}.

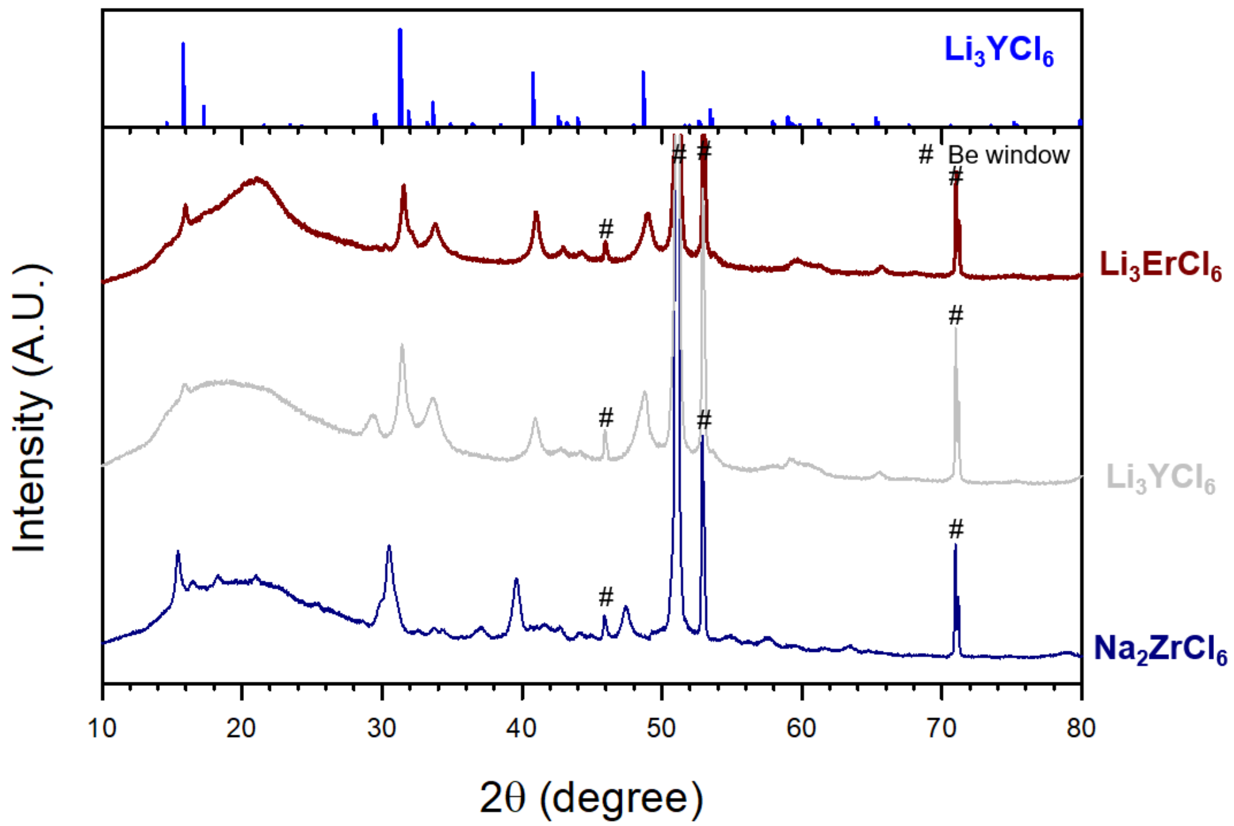

Figure S3. XRD patterns of BM-Li_3YCl_6, BM-Li_3ErCl_6 and BM-Na_2ZrCl_6. Bragg indexes for Li_3YCl_6 are also shown at the top.[38]

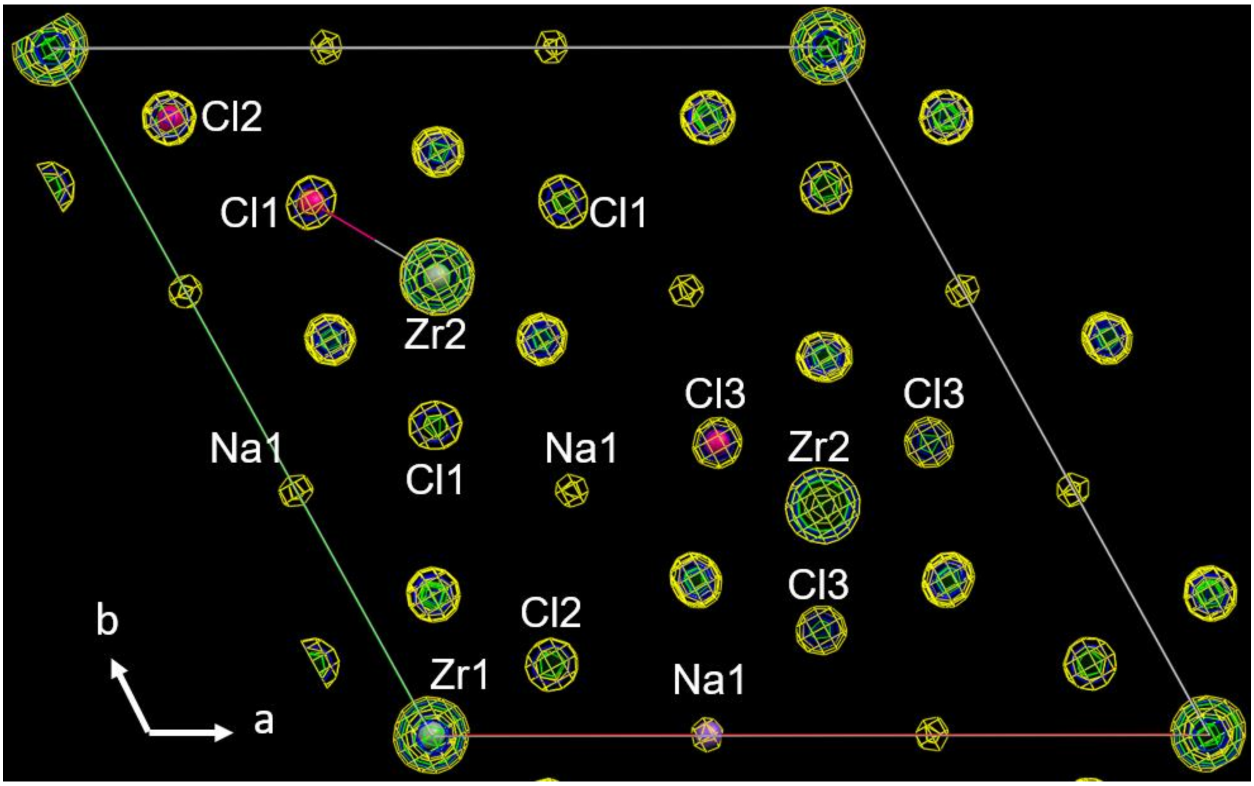

Figure S4. The (001) view of the observed Fourier map for Na_2ZrCl_6. The map with and thickness are 13 and 8 Å, respectively, with the center of the map at (0.5, 0.5, 0.5).

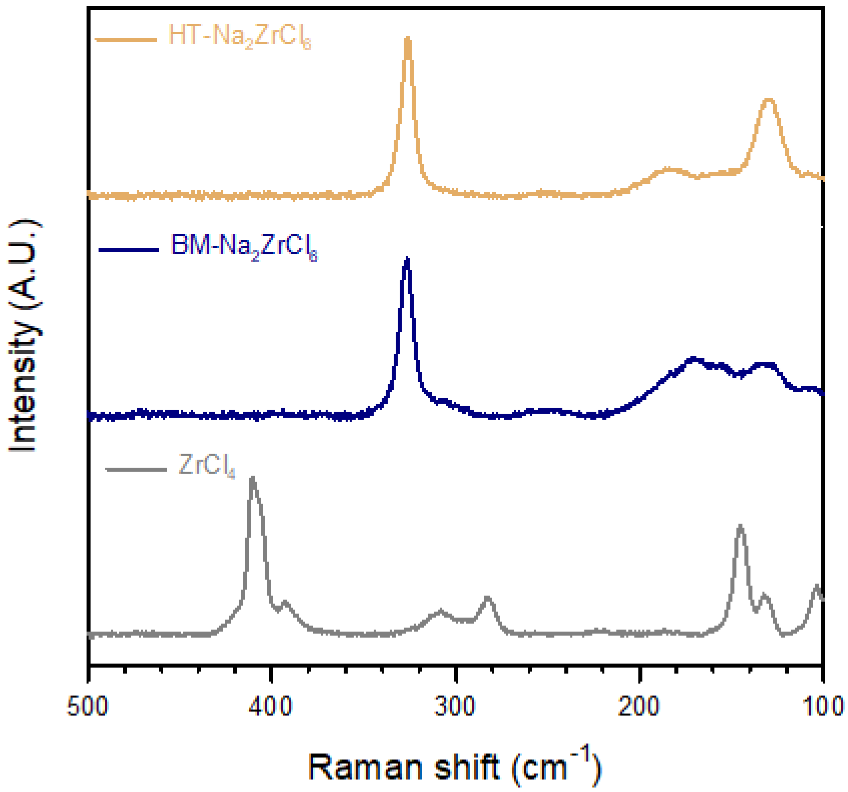

Figure S5. Raman spectra for ball-milled, heat-treated Na_2ZrCl_6 and $ZrCl_4$.

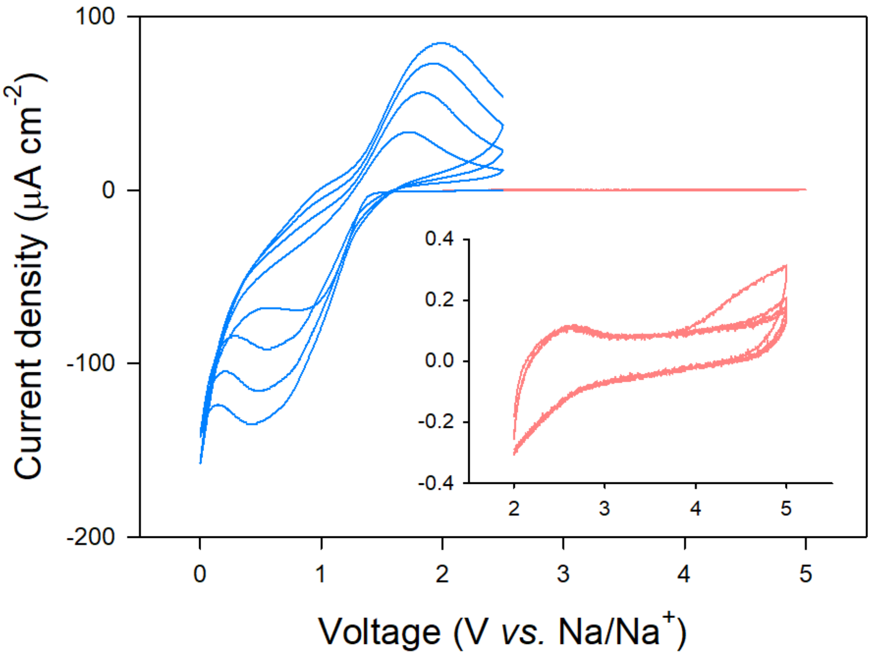

Figure S6. Cyclic voltammetry curves for Ti/Na_2ZrCl_6/Na_3PS_4/Na-Sn all-solid-state cells in the negative potential range (0.0-2.5 V (vs. Na/Na^+)) and in the positive potential range (2.0-5.0 V (vs. Na/Na^+)) at 10 mV s^{-1} and 30 ^oC. The enlarged view in the positive voltage range is shown in the inset. 30 mg of Na_2ZrCl_6, 150 mg of Na_3PS_4, and 40 mg of Na-Sn with nominal composition of Na_3Sn were used.

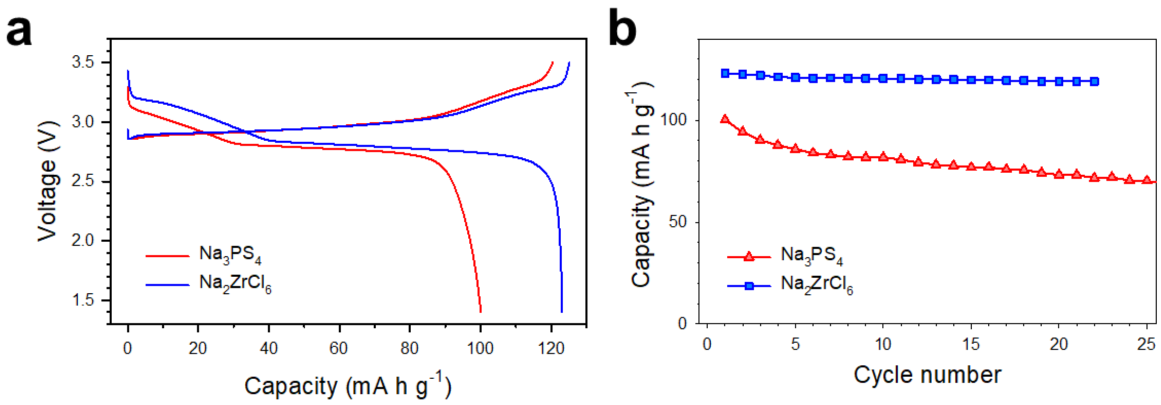

Figure S7. Electrochemical performance at 60 ^{o}C for $NaCrO_2$/Na-Sn all-solid-state cells employing Na_3PS_4 or BM-Na_2ZrCl_6. a) First–cycle charge–discharge voltage profiles at 0.1C and b) corresponding cycling performance.

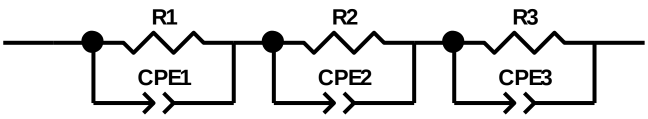

Figure S8. Equivalent circuit model used for fitting Nyquist plots, shown in Figure 4d, e, g, h, for Na^+ non-blocking e^--blocking symmetric cells of Na-Sn/Na_3PS_4/electrode/Na_3PS_4/Na-Sn for $NaCrO_2$ or RuO_2 electrodes using Na_3PS_4 or BM-Na_2ZrCl_6 before cycling and after charge.

2. Supporting Tables

Table S1. Selected interatomic distances (Å) in the structure of Na_2ZrCl_6 at room temperature.

Na-Cl	2.860 (1) × 2 2.764 (5) × 2 2.669 (5) × 2
Zr1-Cl	2.511 (4) × 6
Zr2-Cl	2.453 (5) × 3 2.475 (5) × 3

Table S2. Fitted results of the EIS data shown in Figure 4d, e, g, h. Equivalent circuit model is shown in Figure S8.

Electrode	SOC	R_1 [Ω]	$R_{electrode}$ [Ω]	Density of electrode [g cm^{-3}]	Na^+ conductivity of electrode [S cm^{-1}]
$NaCrO_2/Na_3PS_4$	Pristine	1632	374	3.12	7.3×10^{-6}
	After 1st cycle	1472	339		8.0×10^{-6}
$NaCrO_2/Na_2ZrCl_6$	Pristine	1632	760	3.28	3.4×10^{-6}
	After 1st cycle	1483	213		1.2×10^{-5}
RuO_2/Na_3PS_4	Pristine	1297	3934	5.55	3.9×10^{-7}
	After charge	1547	7220		2.1×10^{-7}
RuO_2/Na_2ZrCl_6	Pristine	1323	3978	5.61	3.8×10^{-7}
	After charge	1640	4199		3.6×10^{-7}