Supporting Information

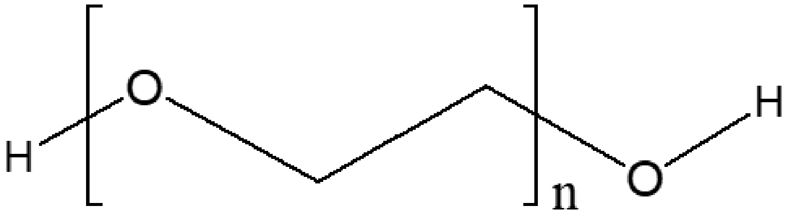

Figure S1. The molecular structure of PEG400.

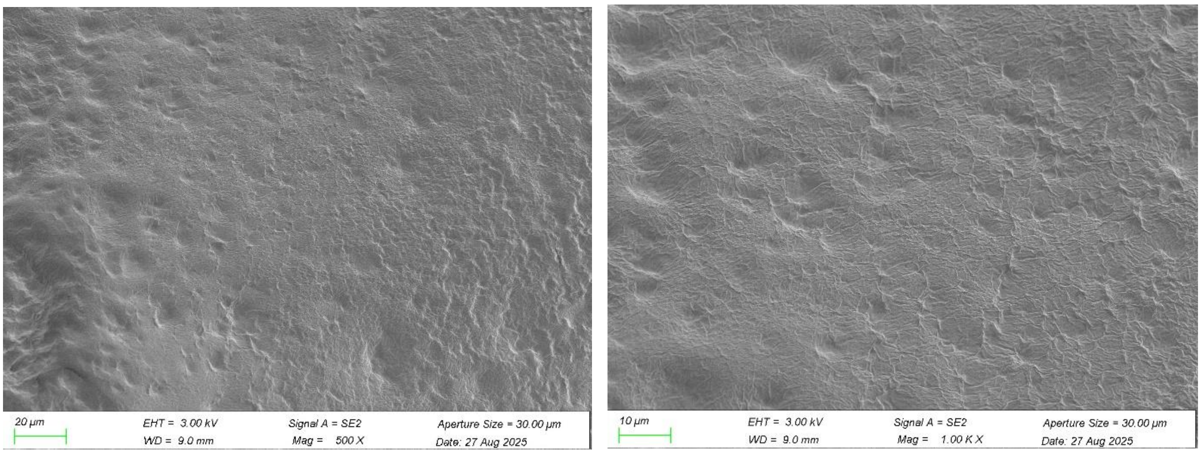

Figure S2. SEM images of V-SSE (0%).

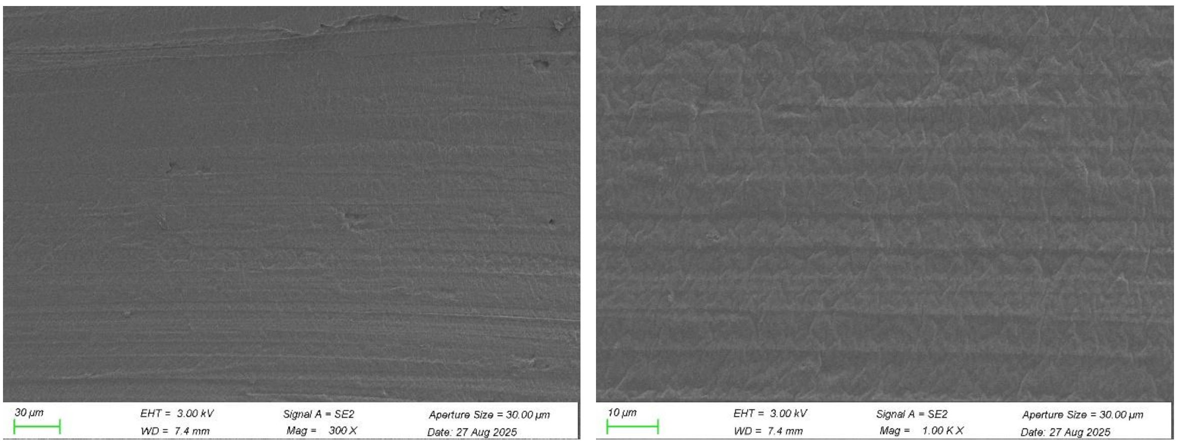

Figure S3. SEM images of V-SSE (19.87%).

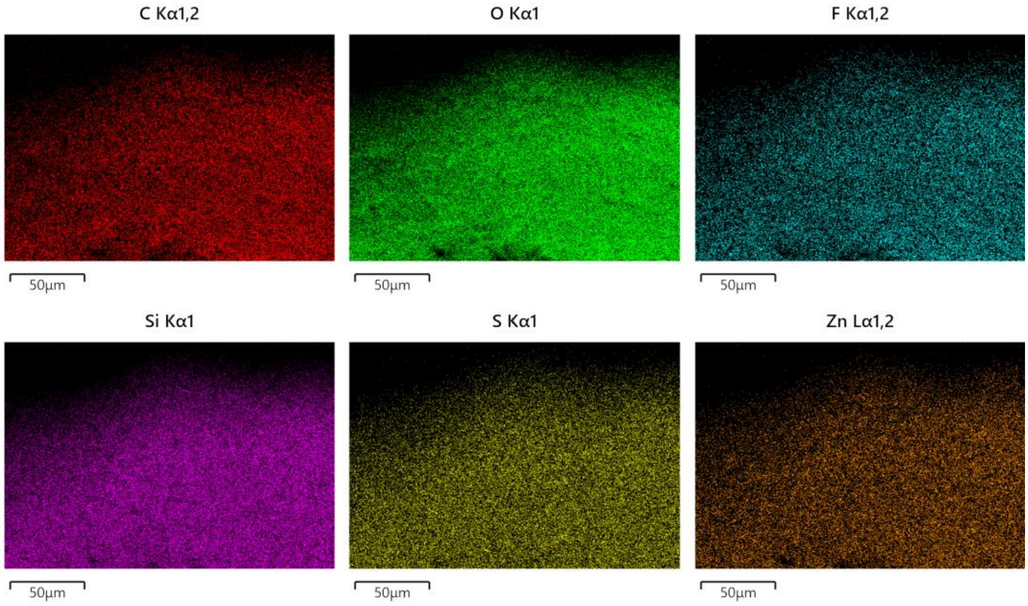

Figure S4. EDS mapping of V-SSE (0%).

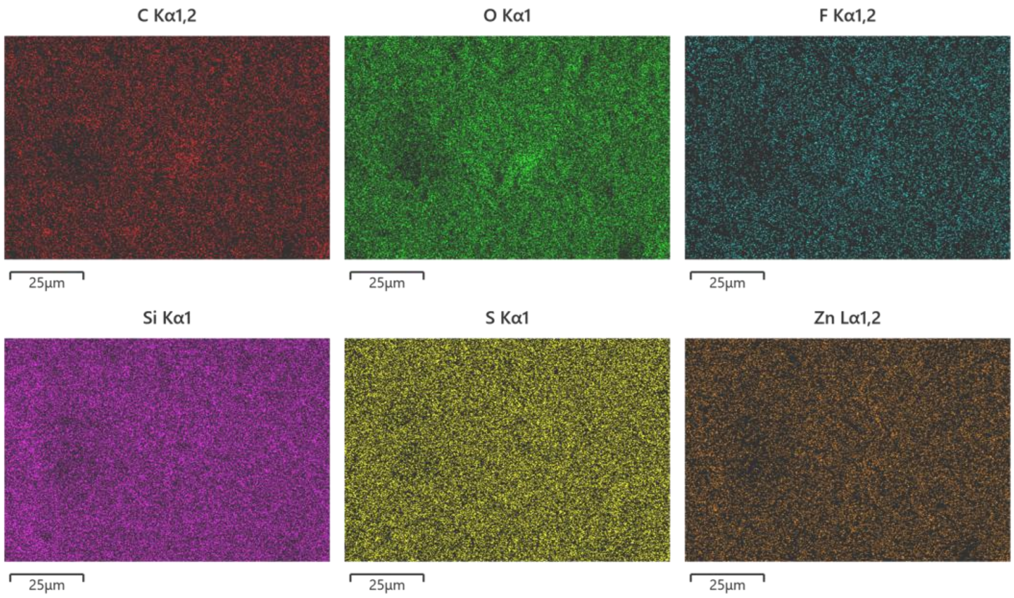

Figure S5. EDS mapping of V-SSE (19.87%).

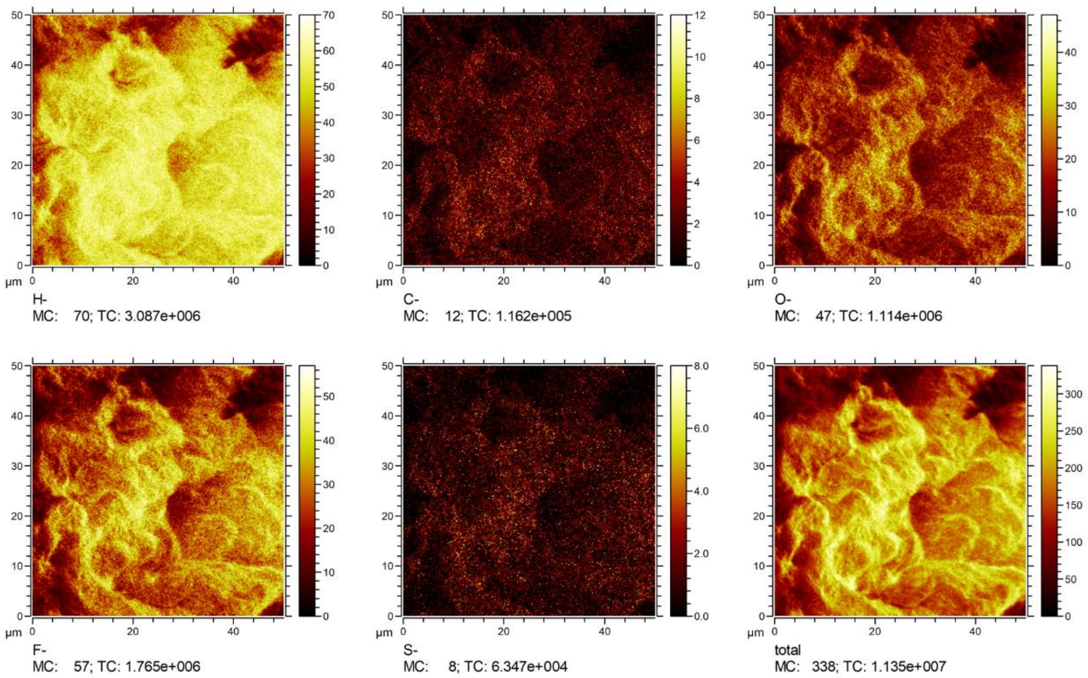

Figure S6. Elemental mapping of V-SSE (19.87%) based on time-of-flight secondary ion mass spectrometry (TOF-SIMS) using negative ion modes.

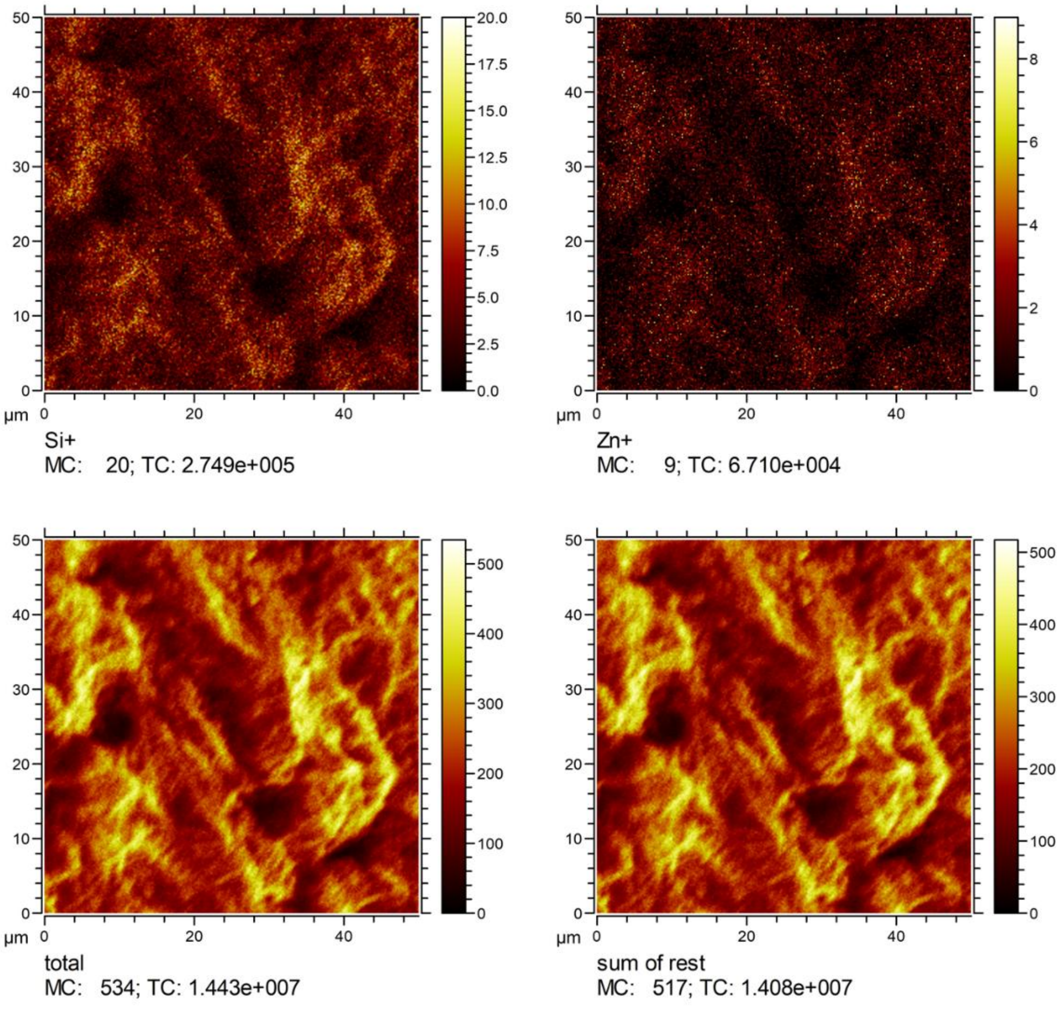

Figure S7. Elemental mapping of V-SSE (19.87%) based on time-of-flight secondary ion mass spectrometry (TOF-SIMS) using positive ion modes.

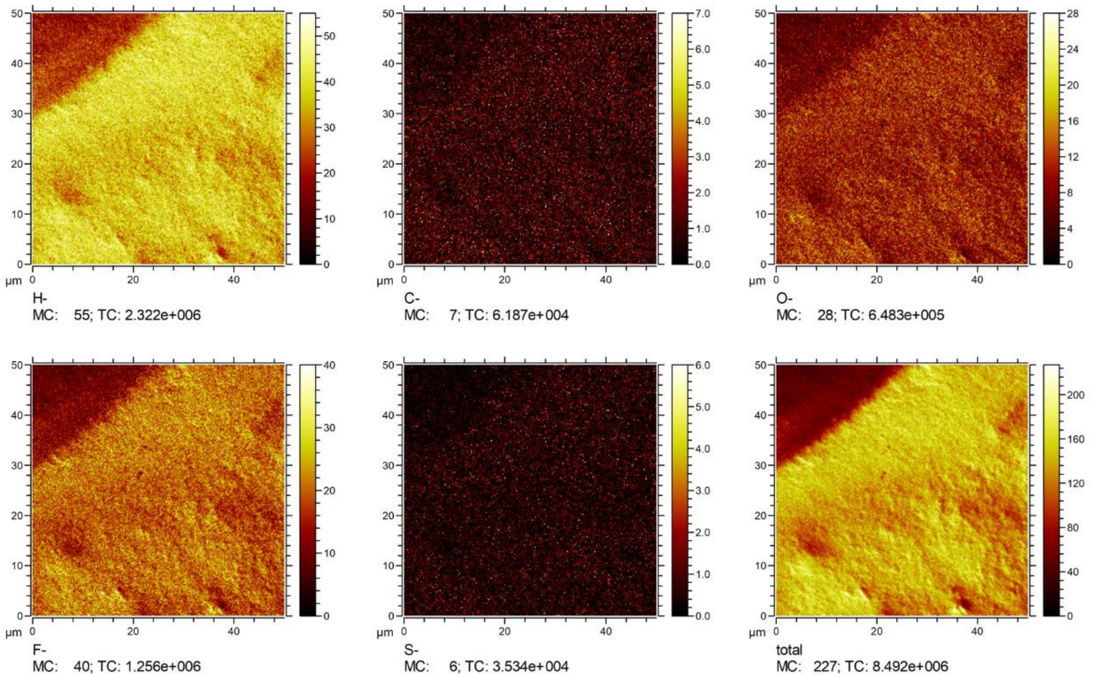

Figure S8. Elemental mapping of V-SSE (0%) based on time-of-flight secondary ion mass spectrometry (TOF-SIMS) using negative ion modes.

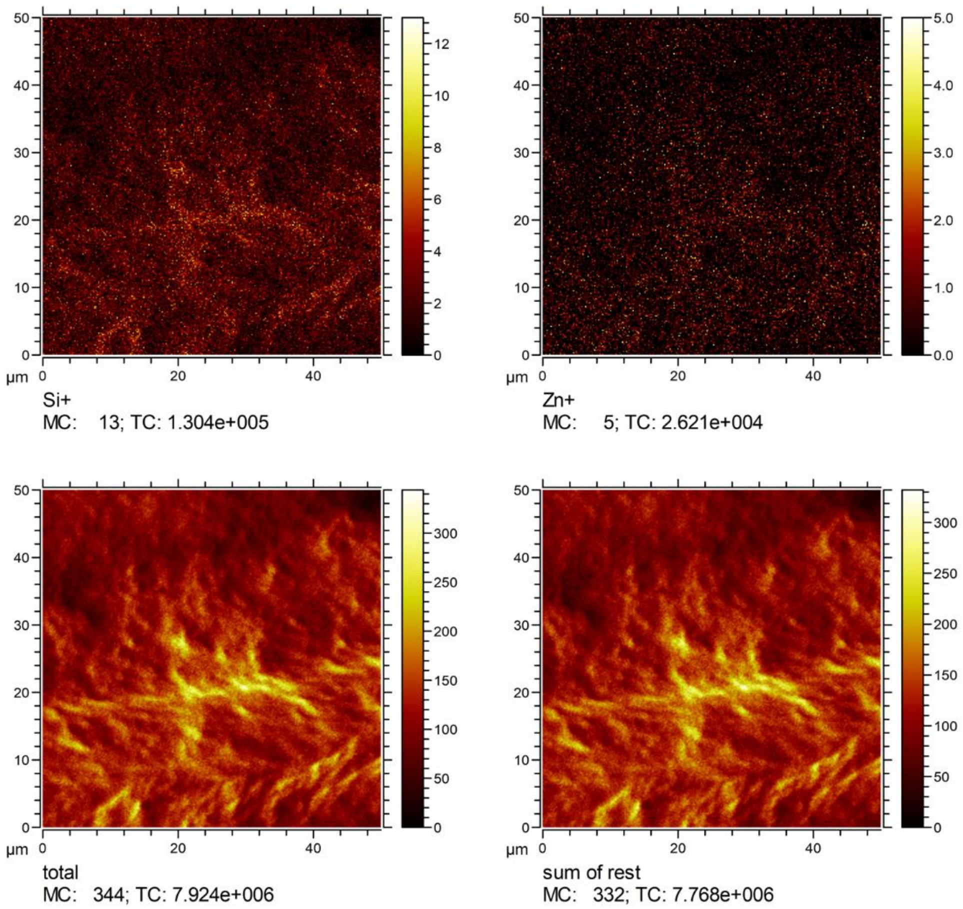

Figure S9. Elemental mapping of V-SSE (0%) based on time-of-flight secondary ion mass spectrometry (TOF-SIMS) using positive ion modes.

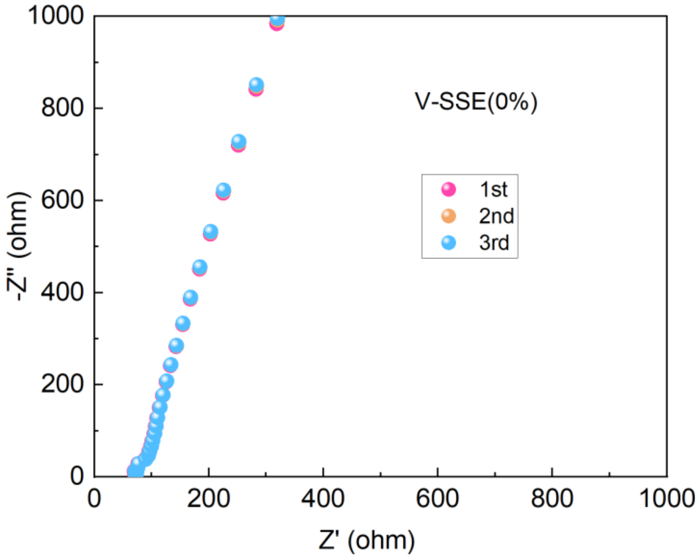

Figure S10. Electrochemical impedance spectra of SS|V-SSE|SS cells using V-SSE (0%). Note: SS, stainless steel.

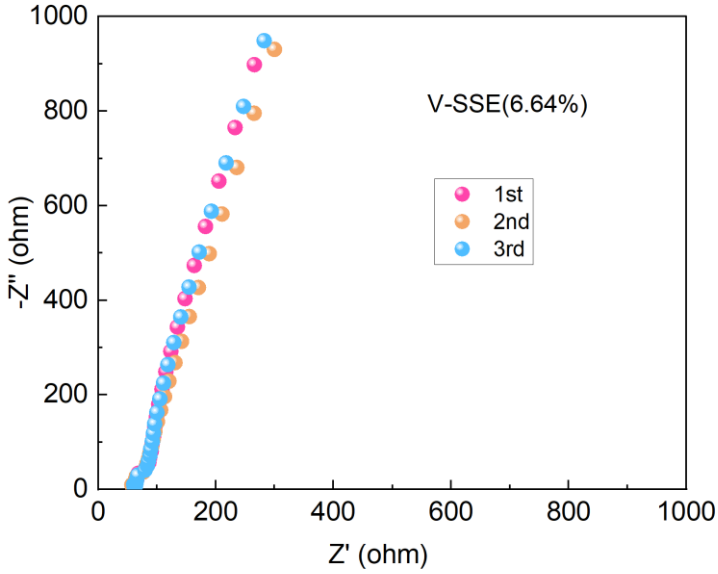

Figure S11. Electrochemical impedance spectra of SS|V-SSE|SS cells using V-SSE (6.64%). Note: SS, stainless steel.

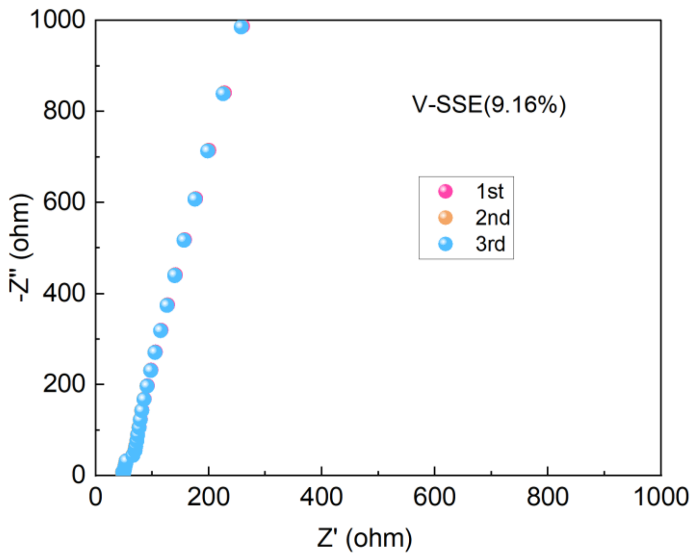

Figure S12. Electrochemical impedance spectra of SS|V-SSE|SS cells using V-SSE (9.16%). Note: SS, stainless steel.

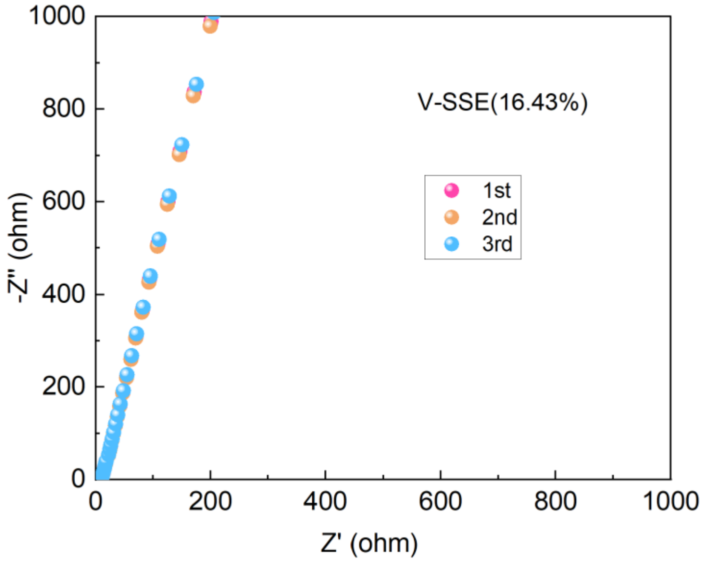

Figure S13. Electrochemical impedance spectra of SS|V-SSE|SS cells using V-SSE (16.43%). Note: SS, stainless steel.

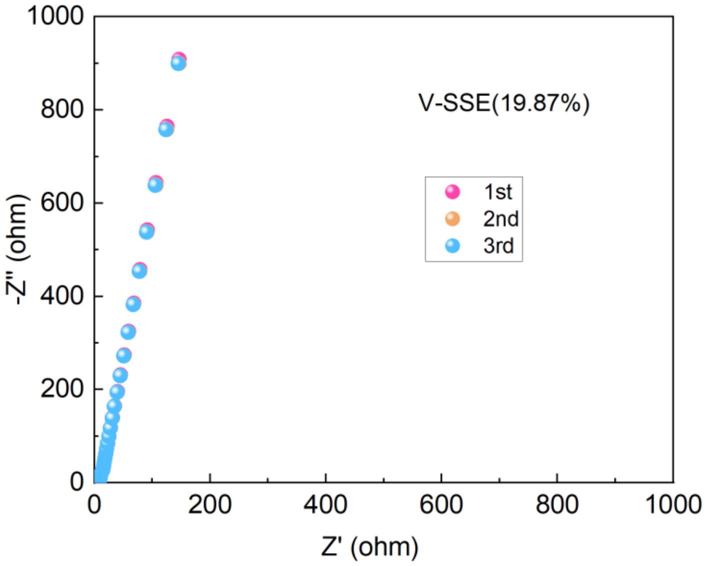

Figure S14. Electrochemical impedance spectra of SS|V-SSE|SS cells using V-SSE (19.87%). Note: SS, stainless steel.

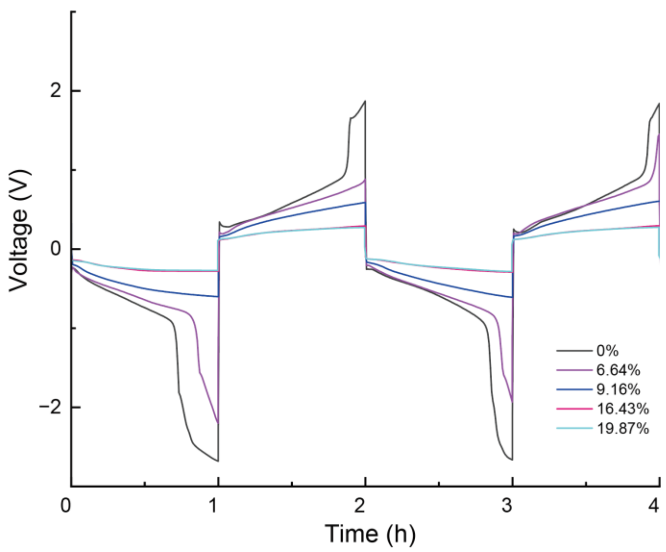

Figure S15. Voltage–time profiles of Zn||Zn symmetric cells with V-SSE under 1 mA cm^{-2} and 1 mAh cm^{-2} cycling conditions.

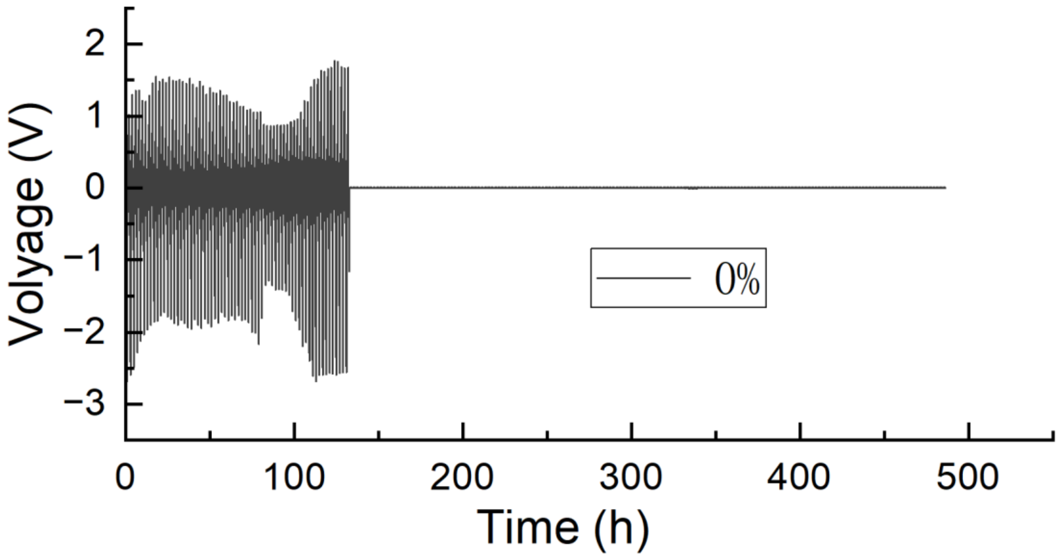

Figure S16. Voltage–time profiles of Zn||Zn symmetric cells with V-SSE (0%) under 1 mA cm^{-2} and 1 mAh cm^{-2} cycling conditions.

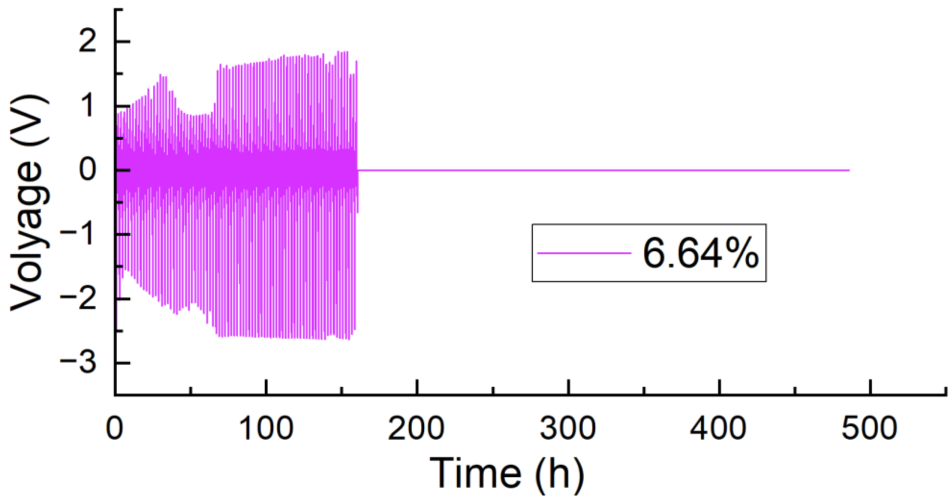

Figure S17. Voltage–time profiles of Zn||Zn symmetric cells with V-SSE (6.64%) under 1 mA cm^{-2} and 1 mAh cm^{-2} cycling conditions.

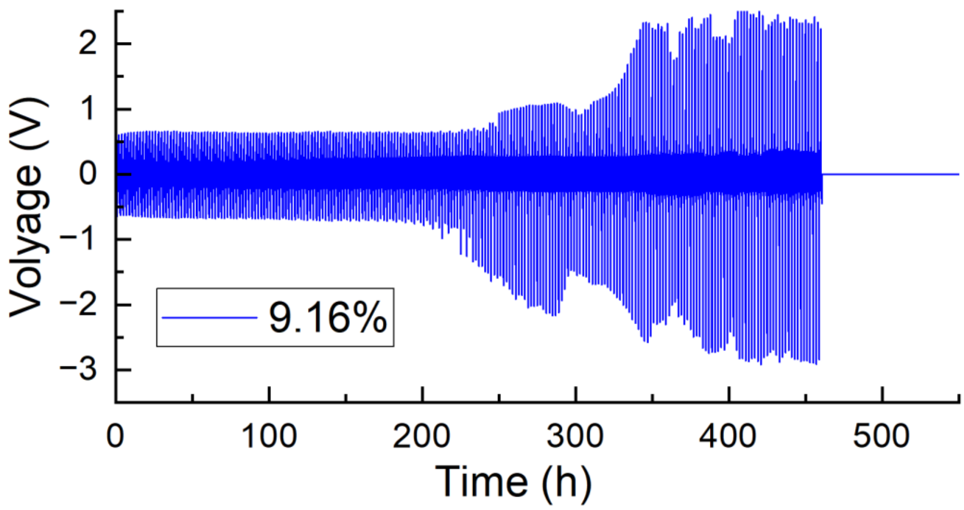

Figure S18. Voltage–time profiles of Zn||Zn symmetric cells with V-SSE (9.16%) under 1 mA cm^{-2} and 1 mAh cm^{-2} cycling conditions.

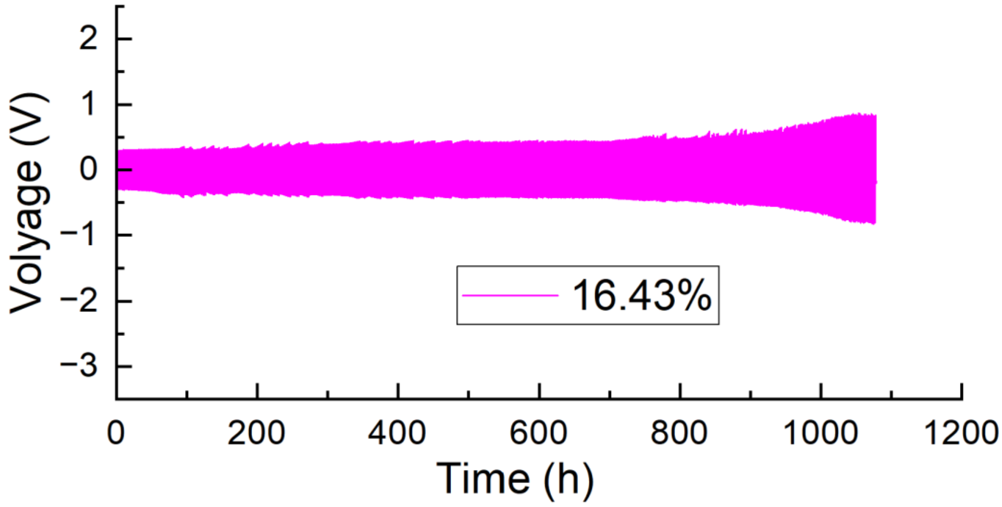

Figure S19. Voltage–time profiles of Zn||Zn symmetric cells with V-SSE (16.43%) under 1 mA cm^{-2} and 1 mAh cm^{-2} cycling conditions.

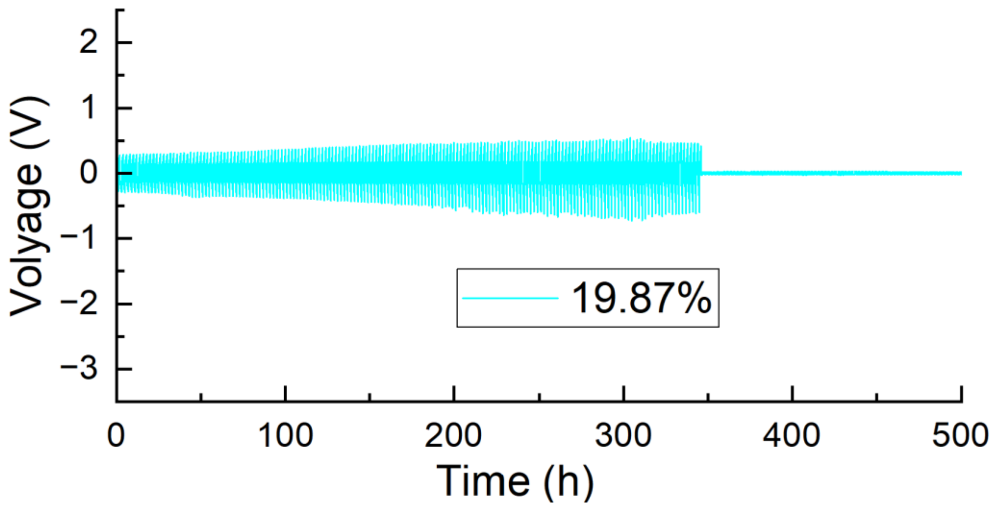

Figure S20. Voltage–time profiles of Zn||Zn symmetric cells with V-SSE (19.87%) under 1 mA cm^{-2} and 1 mAh cm^{-2} cycling conditions.

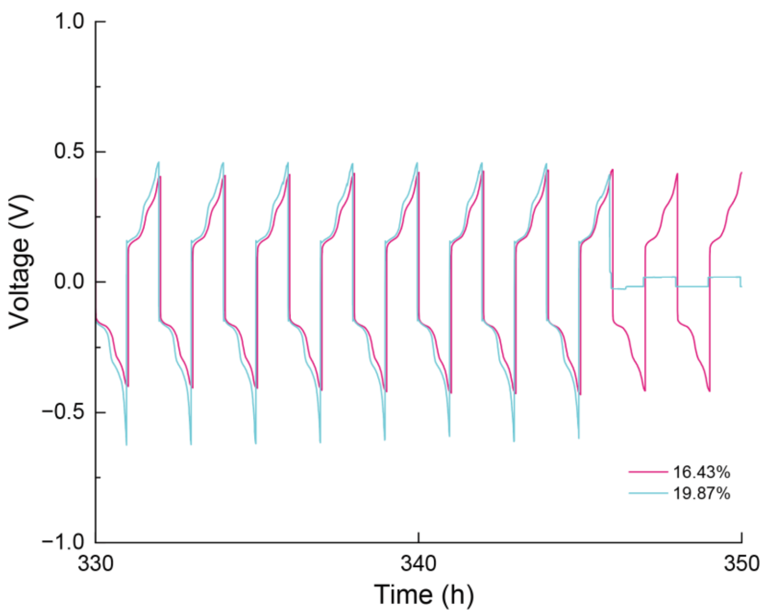

Figure S21. Voltage–time profiles of Zn||Zn symmetric cells during late cycle with V-SSE (16.43% vs. 19.87%) under 1 mA cm^{-2} and 1 mAh cm^{-2} cycling conditions.

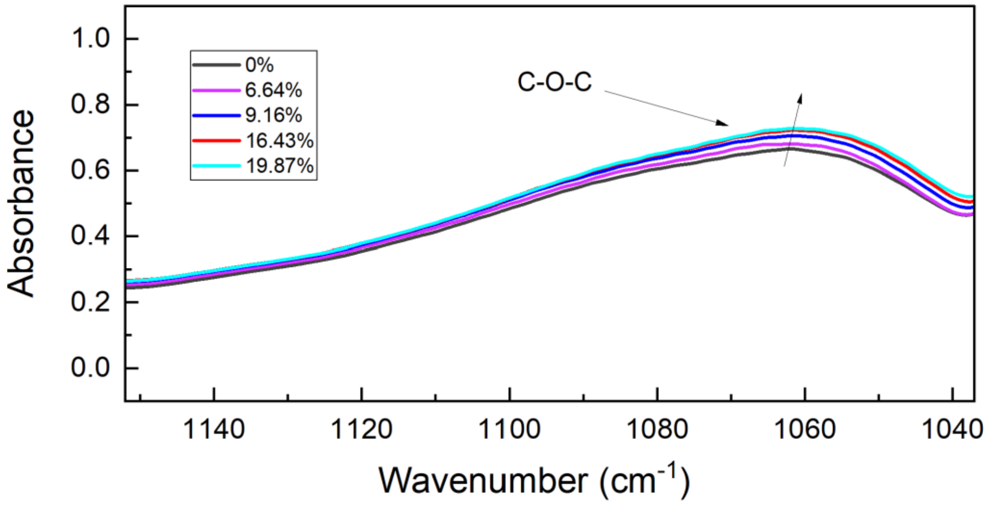

Figure S22. FTIR of V-SSE with different water content.

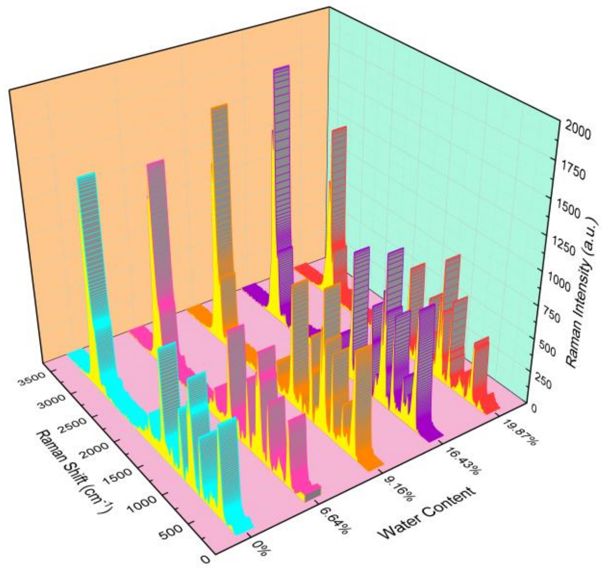

Figure S23. Raman spectra of V-SSE with different water content.

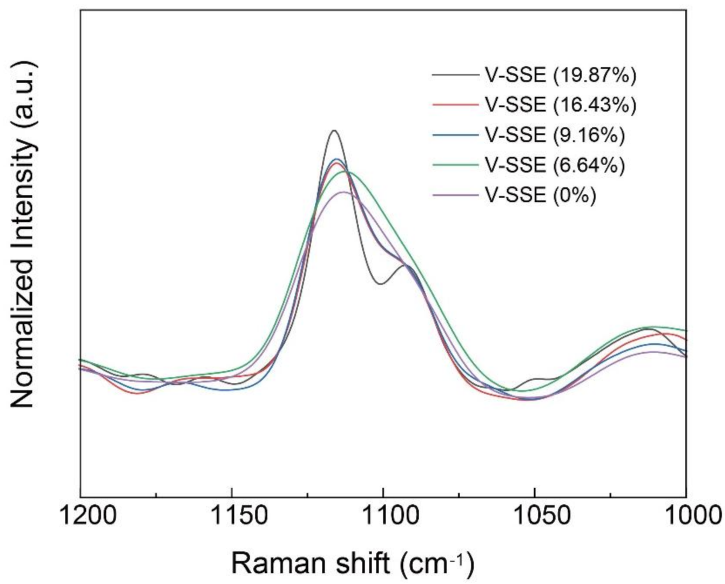

Figure S24. Raman spectra of V-SSE with different water content.

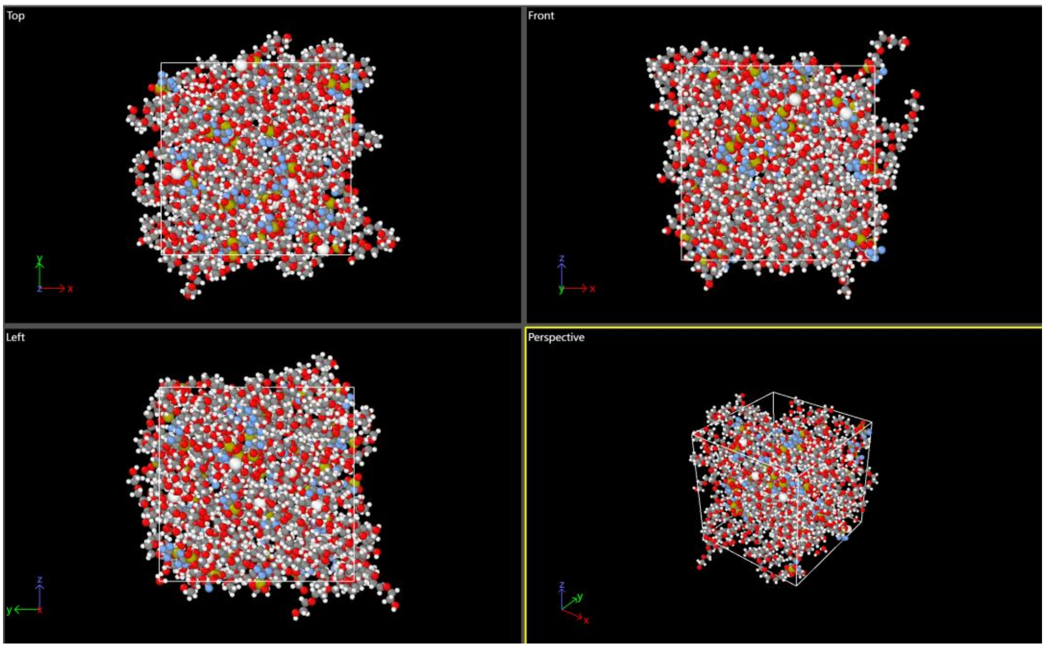

Figure S25. A typical V-SSE structure with H_2O:EO = 1:3.

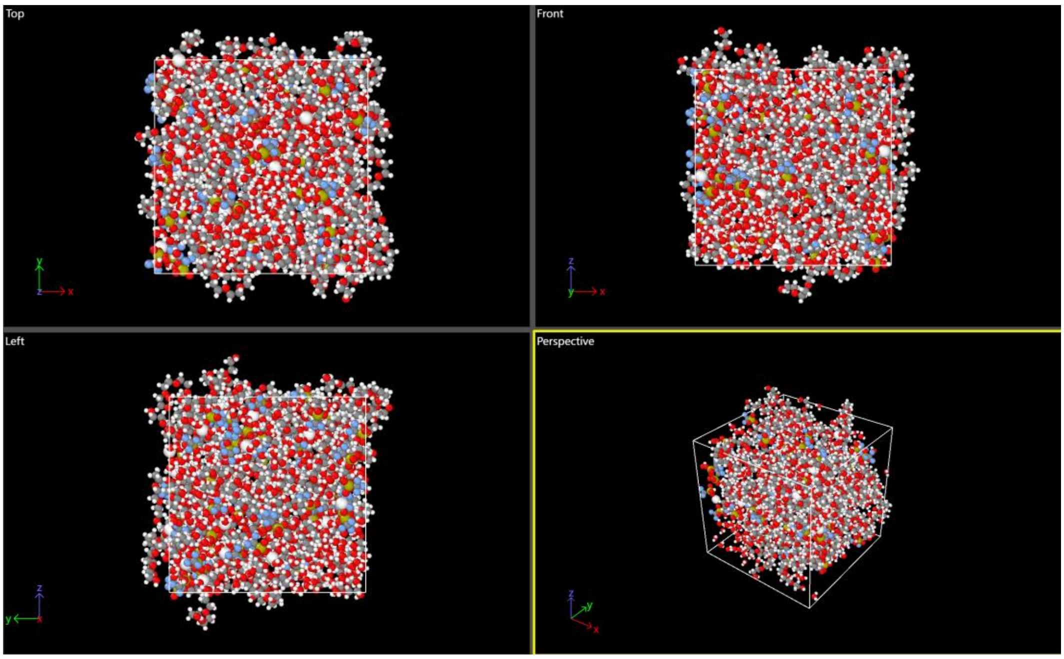

Figure S26. A typical V-SSE structure with H_2O:EO = 1:1.

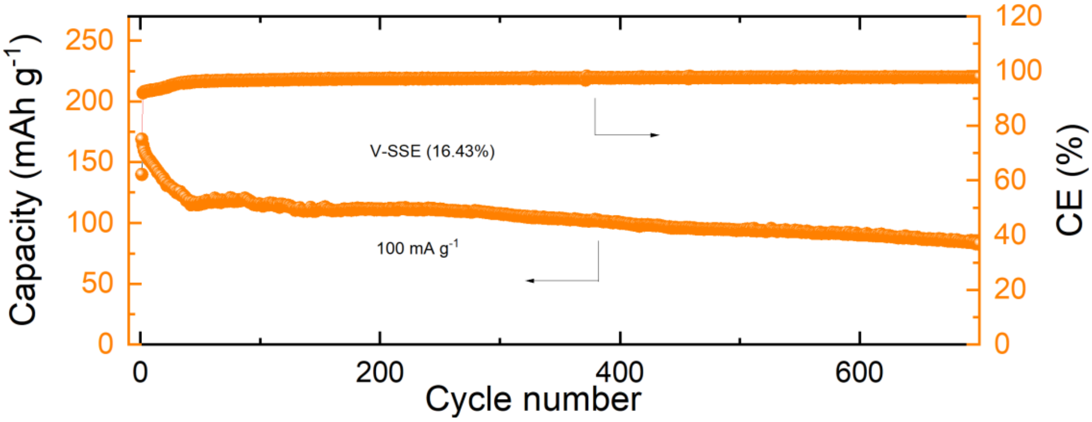

Figure S27. Long-cycle performance of Zn||I_2 full cells with V-SSE (16.43%) at 100 mA g^{-1}.

Table S1. T2 relaxation time of V-SSE samples.

Samples	Relaxation Time 1 (ms)	Peak Ratio (%)	Relaxation Time 2 (ms)	Peak Ratio (%)	Relaxation Time 3 (ms)	Peak Ratio (%)
V-SSE (0%)	0.034	0.087	2.674	99.913	_	_
V-SSE (6.64%)	0.059	1.381	3.144	98.619	_	_
V-SSE (9.16%)	0.097	1.464	3.697	98.536	_	_
V-SSE (16.43%)	0.082	1.754	0.675	0.635	6.01	97.61
V-SSE (19.87%)	0.082	1.139	0.933	0.41	7.663	98.451

Table S2. Ionic conductivity of V-SSE versus water content.

Samples	Ionic Conductivity (mS cm^{-1})			Average Ionic Conductivity (mS cm^{-1})	Standard Deviation
	First Test	Second Test	Third Test		
V-SSE (0%)	0.145	0.143	0.143	0.144	0.001
V-SSE (6.64%)	0.167	0.170	0.165	0.167	0.002
V-SSE (9.16%)	0.229	0.230	0.227	0.229	0.002
V-SSE (16.43%)	1.04	1.03	1.04	1.04	0.008
V-SSE (19.87%)	1.36	1.35	1.34	1.35	0.012

Table S3. Positron annihilation lifetime spectrum test results.

Samples	First Lifespan (ns)	Intensity (%)	Second Lifespan (ns)	Intensity (%)	Third Lifespan (ns)	Intensity (%)
V-SSE (19.87%)	0.214	22.2	0.450	54.0	2.640	23.8
V-SSE (16.43%)	0.221	22.9	0.451	53.1	2.658	24.0
V-SSE (9.16%)	0.266	36.2	0.506	40.2	2.659	23.5
V-SSE (6.64%)	0.191	18.7	0.442	57.0	2.583	24.4
V-SSE (0%)	0.228	26.3	0.463	50.3	2.554	23.4

Table S4. Comparison on the performance of the proposed V-SSE against other recently reported solid-state zinc-ion electrolytes.

Solid-State Zinc-Ion Electrolytes	Ionic Conductivity at RT（S cm^{-1}）	Electrochemical Window (V)	Environmental Friendliness/Energy Consumption of Preparation Process	Fabrication Pressure for the Electrolyte Membrane (MPa)	Ref.
"polymer-in-salt" solid electrolyte	1.6×10^{-3}	9	Use organic solvent (DMF)	30-40	[57]
PVDF-TrFE-CTFE	1.07×10^{-3}	2.7	Use organic solvent (DMF) and need heat treatment (70 °C)	—	[28]
MSZCs	1.2×10^{-4}	—	Need heat treatment (100 °C)	—	[29]
$ZnPS_3$	2.0×10^{-3} (30 °C)	—	Use organic solvent (CS_2) and need heat treatment (500 °C)	—	[58]
KL-Zn	5.08×10^{-3}	2.73 V	Need heat treatment (80 °C)	20	[59]
ZMCs	6.02×10^{-4}	2.55	Need heat treatment (65 °C)	—	[60]
V-SSE	1.35×10^{-3}	2.82	No organic solvents, no heat treatment	< 0.1	This work