Altering Na-ion Solvation to regulate Dendrite growth for a Reversible and Stable Room-temperature Sodium-Sulfur Battery

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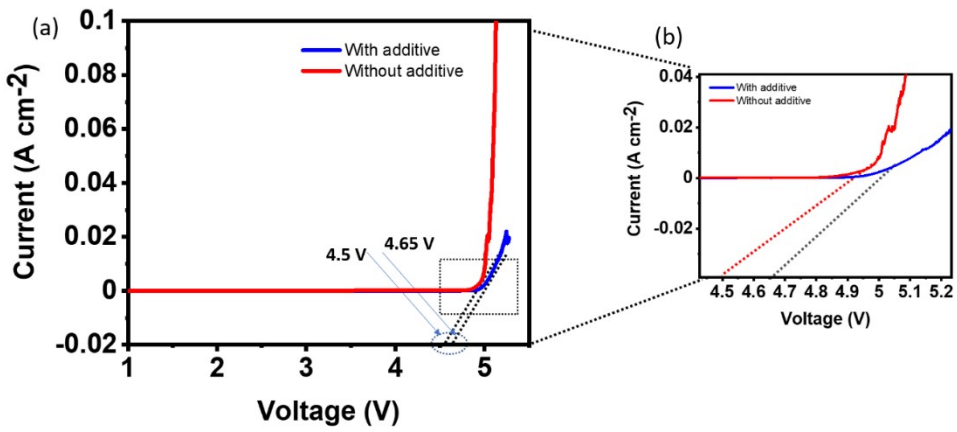

Fig. S1 Linear sweep voltammetry curve for electrolyte with additive and without additive. Na metal used as counter electrode whereas stainless steel used as working electrode

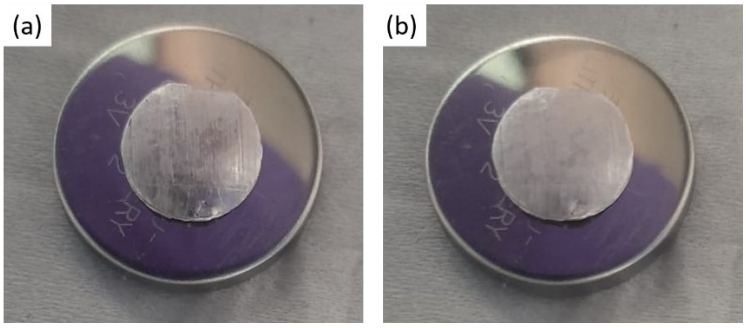

Fig. S2 Digital micrographs of a) a bare sodium metal, and b) sodium metal upon contact with NaI additive containing electrolyte. The sodium metal loses its luster; however, no apparent color change is caused by the NaI additives.

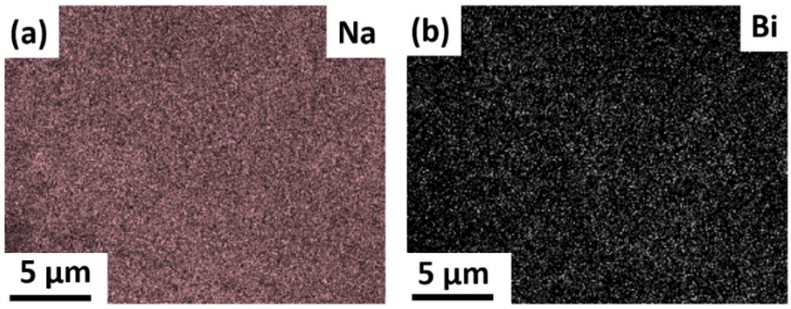

Fig. S3 EDX images of sodium metal anode top surface with additive. Here, Na and Bi, with Na comprising 68% and Bi 23% of the elemental composition on the metal anode

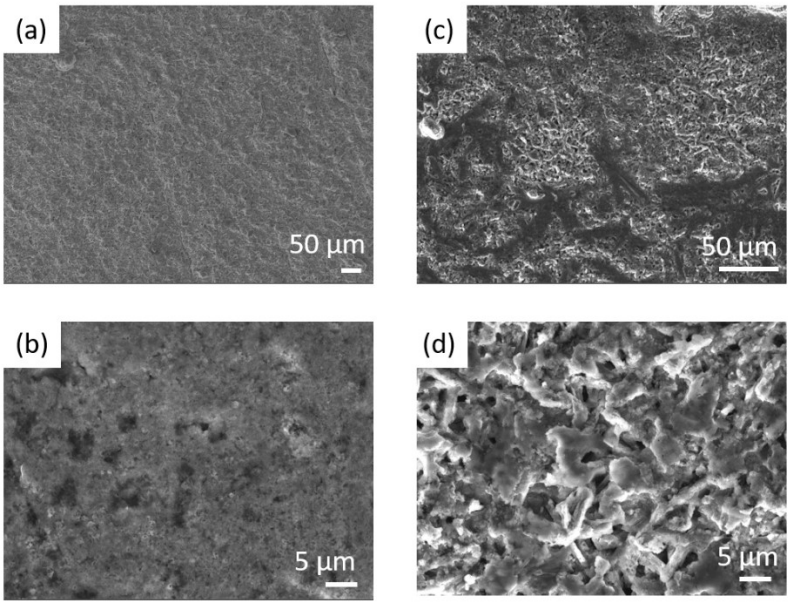

Fig. S4 FESEM images of Cu working electrode from half cells after 50 striping/plating cycles at 1 mA cm^{-2} current density and 1 mAh cm^{-2} capacity, while stripped to 1 V. (a, b) with additive (c, d) without additive

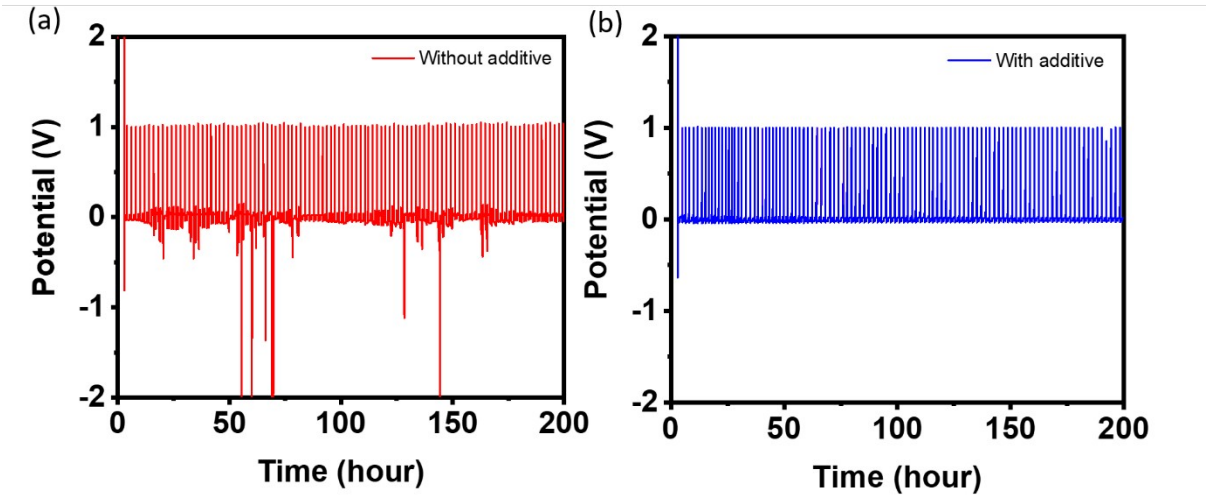

Fig. S5 Voltage vs time plots for Na//Cu half cells (a) without additive and (b) with additive at 1 mA cm^{-2} current density, 1 mA h cm^{-1} specific capacity and stripping up to 1 V.

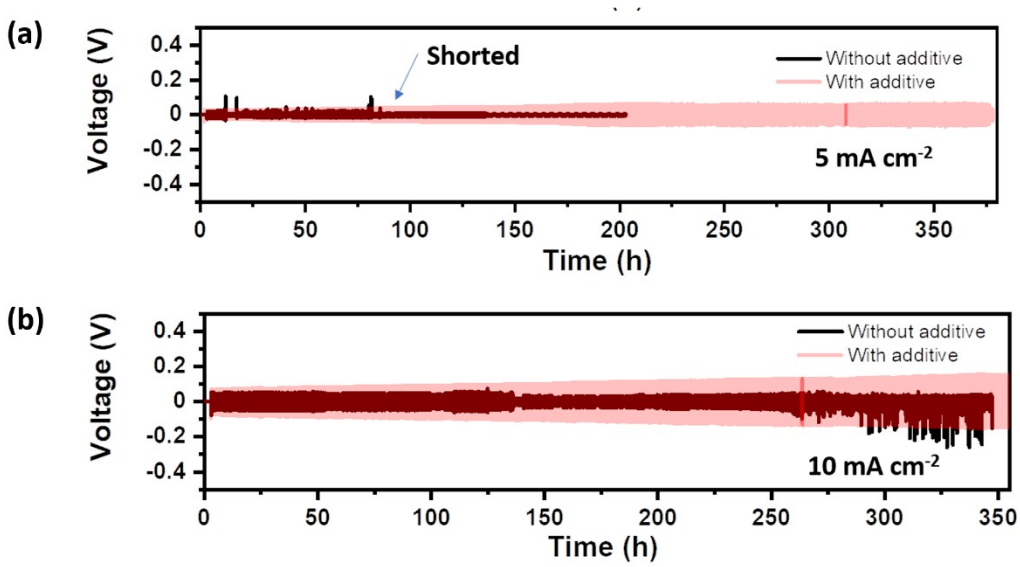

Fig. S6 (a) Stripping plating cycling performance of Na//Na symmetric cell at 5 mA cm^{-2} current density and 1 mA h cm^{-2} capacity (b) at 10 mA cm^{-2}

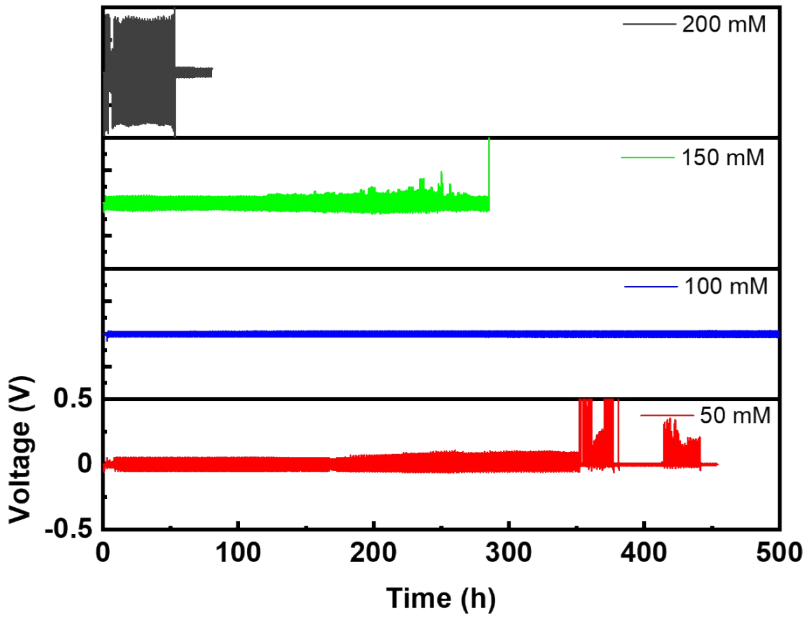

Fig. S7 Additive concentration optimization in Na//Na symmetric cell at 1 mA cm^{-2} current density. Concentration is varying from 50 to 200 mM.

Table-S1 Cyclic performance analysis of Na//Na symmetric cells with different types of additives.

Cell type	Salt	Solvent	Additive	Current density (mA cm^{-2})	Capacity (mA h cm^{-2})	Overpotential (m V)	Cycle life (h)
Na//Na (This work)	**1 M NaOTf**	**Diglyme**	**100 mM BiI_3**	**1**	**1**	**90**	**1600**
Na//Na[1]	1 M $NaPF_6$	EC/PC	FEC	1	1	100	100
Na//Na[2]	1 M $NaPF_6$	Diglyme	0.033 M Na_2S_6	2	1	38	400
Na//Na[3]	1 M $NaClO_4$	EC/DEC	0.05 M $SnCl_2$	0.5	1	100	500
Na//Na[4]	4 M NaFSI	DMC	1% SbF_3	0.5	0.5	25	1000
Na//Na[5]	1 M NaTFSI	FEC	0.75 % $NaAsF_6$	0.5	1	500	350
Na//Na[6]	2 M $NaPF_6$	DME/FEPE	1% SbF_3	0.5	0.5	200	1200
Na//Na[7]	0.3 M $NaPF_6$	EC/PC	Acetamide (BSTFA)	0.5	0.5	120	350
Na//Na[8]	1 M NaOTf	Diglyme	50 mM 9-Fluorenone	1	1	25-30	1200
Na//Na[9]	1 M $NaPF_6$	EC/PC	2% TMDT	0.5	1	400	450
Na//Na[10]	0.8 M NaPF6	TMP/FEC (7:3)	DTD as co-solvent	0.5	1	200	1350

Na//Na[11]	1 M $NaPF_6$	EC/PC	Perfluorobenzene	1	1	600	300
Na//Na[12]	1 M $NaPF_6$	VC	N-methyl-N-(trimethylsilyl)trifluoroacetamide	0.1	0.1	400	800

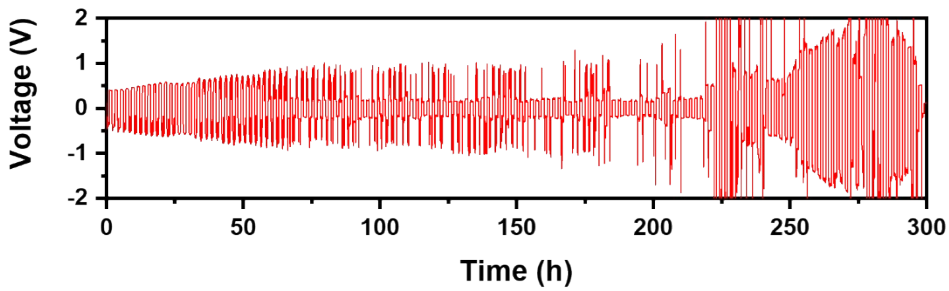

Fig. S8 Na//Na symmetric cell cycling performance in ester electrolyte (EC/DMC) at 1 mA cm^{-2} current density and 1 mAh cm^{-2} capacity.

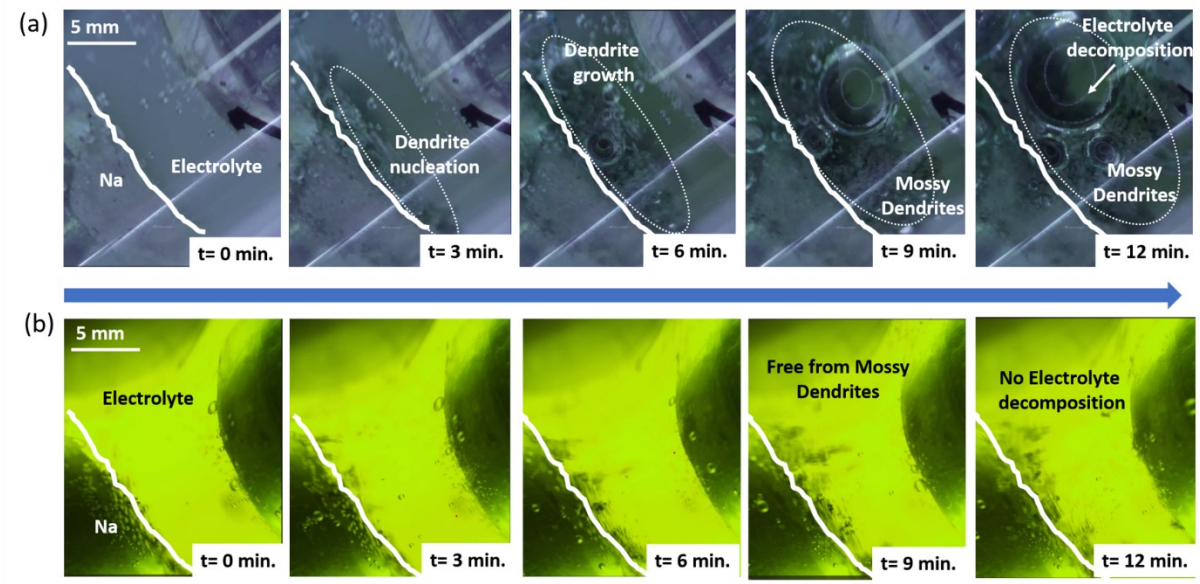

Fig. S9 In-situ optical testing for visualizing dendrite growth pattern over sodium metal anode (a) In conventional electrolyte without additive with mossy dendrites and bubble formation (b) In additive based electrolyte after a different span of time at 5 mA cm^{-2} current density.

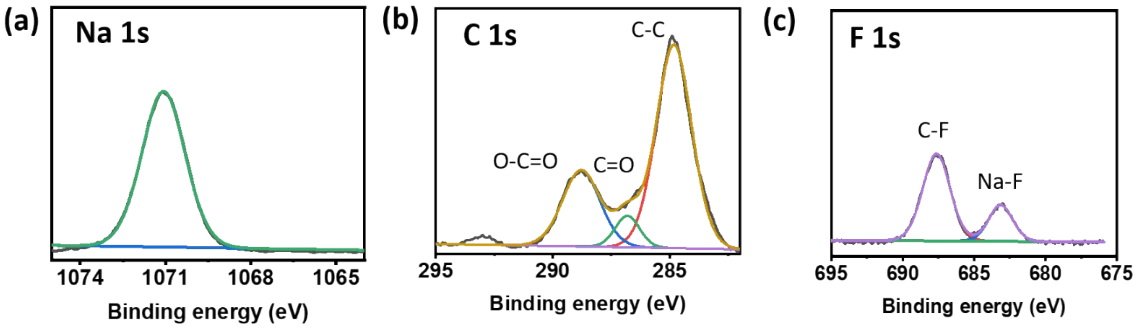

Fig. S10 XPS spectra of reference Na metal anode after cycling (a) Na 1s (b) C 1s (c) F 1s

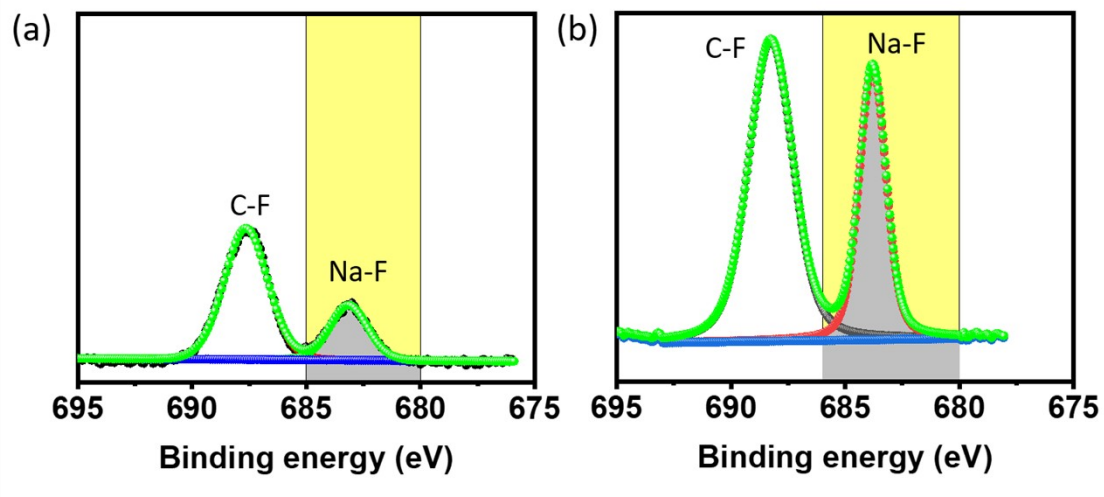

Fig. S11 (a) XPS spectra for F 1s from sodium metal anode in reference electrolyte after cycling (b) XPS spectra for F 1s from sodium metal anode in additive based electrolyte after cycling

Table-S2 XPS data tabulated in the form of elements, peak position, peak assignment and possible species

Element	Peak position	Peak assignment	Species
C	289.1/286.4/284.8 eV	O-C=O/C=O/C-C	$NaSO_3CF_3$/RC_2Na
O	535.6/532.5/531.1	O-H/Na-O/Na-C	$NaOH$/Na_2O/Na_2CO_3
Na	1071	Na-F/Na-O	NaF/Na_2O
I	630.59/619.09	I $3d_{5/2}$ / I $3d_{3/2}$	NaI
Bi	166.72/163.64/161/158.4	Bi $4f_{5/2}$ (Bi_2O_3)/Bi $4f_{5/2}$ / Bi $4f_{7/2}$ (Bi_2O_3)/Bi $4f_{7/2}$	Na_3Bi / Bi_2O_3
F	688.25/683.79 eV	C-F/Na-F	$NaSO_3CF_3$/NaF
S	170.33/169.02 eV	S $2p_{1/2}$ / S $2p_{3/2}$	$NaSO_4$

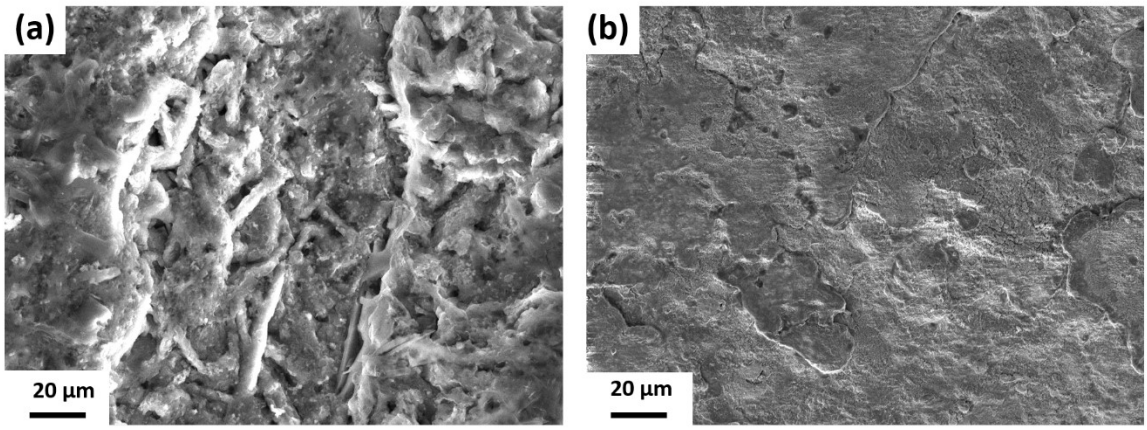

Fig. S12 FESEM images of sodium metal surface after 50 plating/stripping cycles in symmetric cell configuration (a) without additive (b) with additive

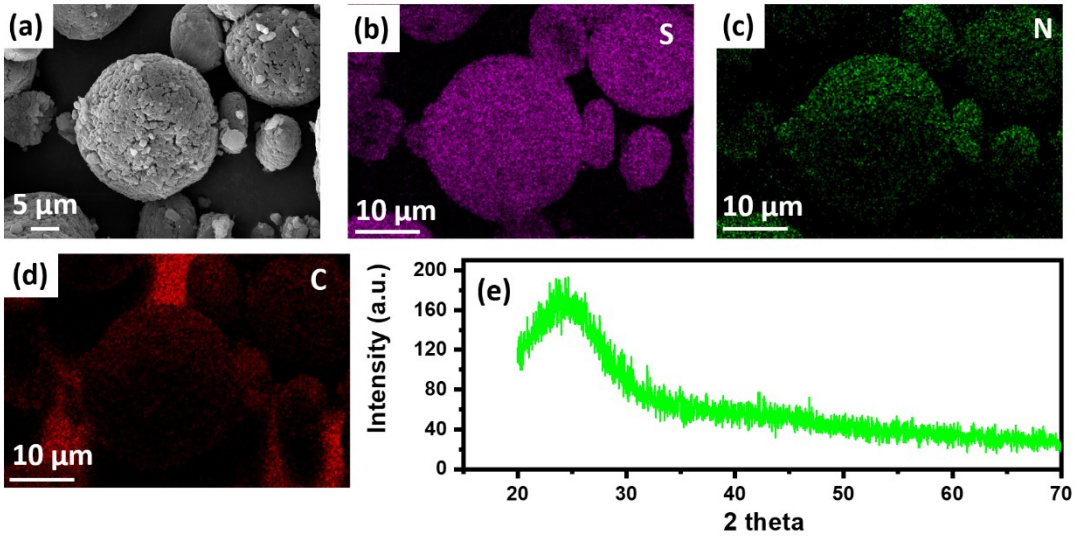

Fig. S13 (a) FESEM image of as synthesized SPAN material (b-c) corresponding EDX images (e) XRD spectra of the SPAN material

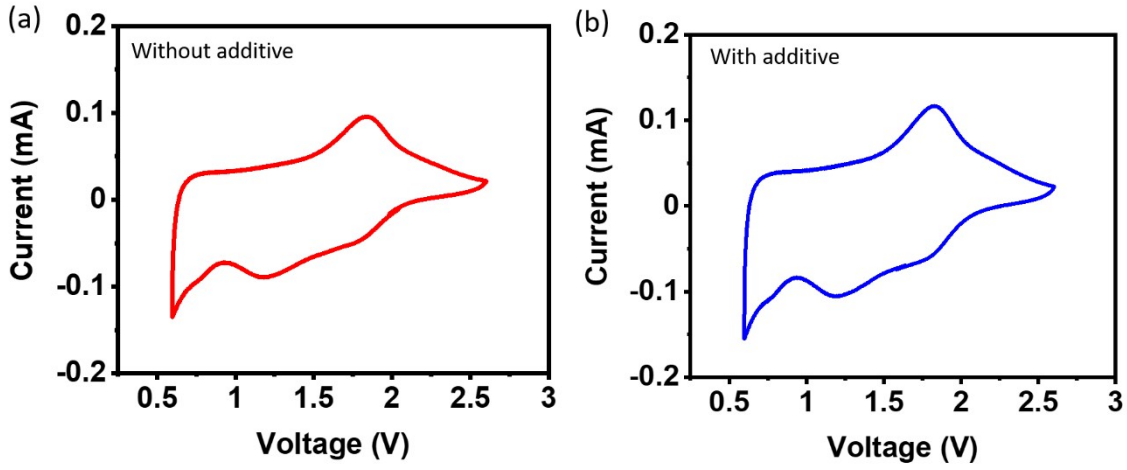

Fig. S14 (a) Cyclic voltammetry curves for Na-SPAN full cells without additive (b) with additives. CV was captured at 0.1 mA s^{-1} scan rate.

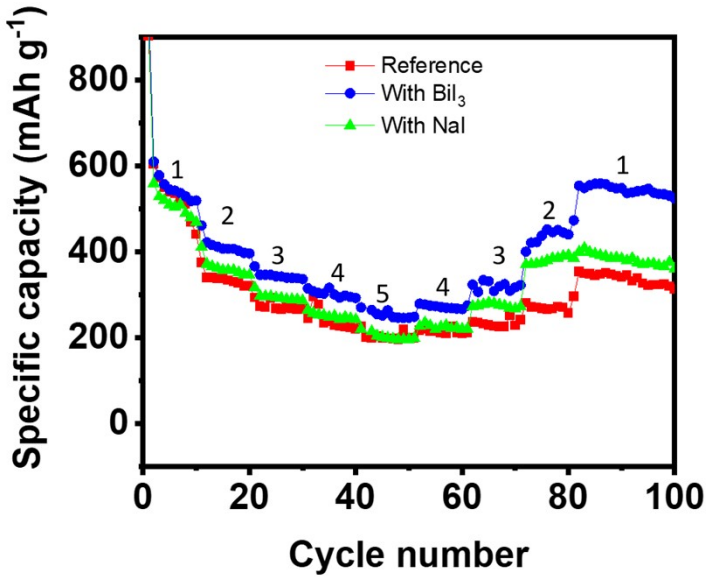

Fig. S15 Rate performance analysis for Na//SPAN full cells with BiI_3, NaI and reference electrolyte. Where 1-5 corresponds to 160 mA g^{-1}, 320 mA g^{-1}, 640 mA g^{-1}, 800 mA g^{-1}, and 1000 mA g^{-1} current density, respectively

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