Supporting information

Amphiphilic Interface for Constructing Uniform Composite Solid-State

Electrolyte towards Long-Life All-Solid-State Sodium Metal Batteries

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Scheme S1 Oxidative ring-opening self-polymerization of dopamine.



Fig. S1 (a) XRD pattern of sol-gel synthesized NZSP filler; (b) SEM morphology and elements distribution of synthesized NZSP filler; (c) Nyquist plots of synthesized NZSP pellet.



Fig. S2 ATR-FTIR spectra of PDA@NZSP and NZSP.



Fig. S3 Contact angle between the PEO acetonitrile solution and NZSP pellet (a) or PDA@NZSP pellet (b).



Fig. S4 Optical images of PCSE composite solid-state electrolyte membrane.



Fig. S5 TGA curves of CSE and PCSE in the temperature range from 25-600°C.



Fig. S6 Nyquist plots of SUS|PCSE|SUS (a, b) and SUS|CSE|SUS (c, d) in the temperature range from 30-75°C.



Fig. S7 SEM morphology of the sodium metal anode disassembled from Na|CSE|Na (a) and Na|PCSE|Na (b) after 50 deposition/dissolution cycles.



Fig. S8 (a) Charge/discharge profiles of Na|PCSE|NVP and Na|CSE|NVP at 10th cycle with a rate of 1 C; (b) charge/discharge profiles of Na|PCSE|NVP with different number of cycles.



Fig. S9 CV curves of Na|PCSE|NVP and Na|CSE|NVP with different scanning rates.



Fig. S10 Charge/discharge profiles of Na|CSE|NVP with different rates.



Fig. S11 Discharge profiles of Na|PCSE|NVP at 30°C.

	Na	Zr	Р	
Element mass ratio (%)	13.29	37.02	5.67	

Table S1 Mass ratio of each element in sol-gel product

 Table S2
 Fitted bulk impedance of SUS|PCSE|SUS and SUS|CSE|SUS at different temperature

Fitted bulk impedance (Ω)										
Temperatur	20	25	40	15	50	55	60	65	70	75
e (°C)	30	33	40	43	30	33	60	03	/0	13
PCSE	908.8	412.6	170.8	62.2	33	15.4	11.9	9.3	6.3	4.6
CSE	31949	1101	2410	718	130.9	54.3	31.2	24.1	19.3	13.6
		3								

The thickness of PCSE and CSE membrane was 118 and 98 μ m, respectively. The contact area between the electrolyte membrane and the SUS electrode is 1.96 cm².

Table S3 Bulk and interfacial impedance of Na|PCSE|Na and Na|CSE|Na before and after 30 cycles

	$R_{\mathrm{b0}}~(\Omega)$	R_{b1} (Ω)	$R_{\rm i0}~(\Omega)$	$R_{\rm il}$ (Ω)
PCSE	10.99	10.89	52.46	128.07
CSE	16.61	15.79	124.62	188.78

 $R_{\rm b}$ represents the bulk impedance, $R_{\rm i}$ represents the interfacial impedance, $_0$ indicates initial state, $_1$ indicates after 30 charge/discharge cycles

Table S4 Bulk and interfacial impedance of Na|PCSE|NVP and Na|CSE|NVP before and after 100 cycles

	$R_{\rm b0}~(\Omega)$	R_{b1} (Ω)	$R_{\rm i0}~(\Omega)$	$R_{\rm il}$ (Ω)
PCSE	12.64	14.89	65.20	21.73
CSE	16.31	18.98	99.38	105.96

 $R_{\rm b}$ represents the bulk impedance, $R_{\rm i}$ represents the interfacial impedance, $_0$ indicates

initial state, 1 indicates after 100 charge/discharge cycles

			0 /			
Solid electrolyte	Cathode	Temperatur e (°C)	Rate (C)	Initial capacity	Cycles	Capacity retention (%)
				$(mAh g^{-1})$		
1.FMC-ASPE ¹	NVP	80	0.5	107.5	400	89
2.NZ-PEO@IL*2	NVP	60	0.5	104.5	150	90
3.PEPA@NC ³	FeHCF	60	0.2	100	350	77.2
$4.BPCE^4$	NVP	50	0.5	107	300	88.5
5.PEO-NaClO ₄ - Na ₃ Zr ₂ Si ₂ PO ₁₂ ⁵	MnHCF	60	0.5	109.3	300	83
6.CPE-IL40*6	NVP	60	0.1	98	70	86.7
7. SPE ⁷	NaNFM	60	0.1	102.4	80	90
8.PEO/NZTO ⁸	NVP	80	0.2	95	100	89.4
9.PEO- β -Al ₂ O ₃ ⁹	NVP	60	0.2	93.1	100	83.6
10.PEO-P-N ¹⁰	NVP	60	1	102	500	87.2
$11.ATFPE^{11}$	NVP	60	1	87.3	1000	78.2
12.2N8D+FEC*12	NVP	60	0.5	108	200	50.3
13.CPE ¹³	NVP	60	0.5	102	250	86
14.PE-PEO /NaTFSI ¹⁴	NVP	80	0.1	115	200	88.7
15.BSPCE ¹⁵	NVP	60	0.1	115.7	200	86.8
16.PSZ ¹⁶	NVP	80	0.5	92.3	200	95
17.M1 ¹⁷	NaFe(SO ₄) ₂	60	0.1	84	60	89.3
This work	NVP	60	1	107.9	1350	80.5

Table S5 A comparison of the conditions and cycling performance of Na|PCSE|NVP with recently published PEO-based sodium solid-state electrolytes (* denotes quasi-solid-state design)

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