Supporting Information:

## In-situ formed Self-embedded Ion/Electron Conductive Skeleton Enabling Highly-Stable Sodium Metal Anode

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Figure S1. Nitrogen adsorption-desorption isotherms and pore size distribution of the Sn powder.



Figure S2. Optical images of Na foil, Sn powder on Na foil, and NSN-3D IECF composite anode.



Figure S3. The local magnification of the XRD.



Figure S4. (a) XRD patterns of NSN-3D IECF with different Sn powers weight ratios; (b) Voltage-time profiles of NSN-3D IECF with different Sn powers weight ratios.



Figure S5. SEM images of (a) 5 wt% and (b) 10 wt% Sn powder weight ratios.



Figure S6. SEM images of (a) Bare Na and (b) NSN-3D IECF.



Figure S7. XRD pattern of the NS-3D IECF.



Bulk Na (100) E<sub>b</sub>=-1.31 eV

Figure S8. The binding energy of the Na atom on the (a, b) NSN-3D IECF and (c, d) Na.



Figure S9. Top-view SEM images of bare Na electrodes after (a) stripping 5 mA h cm<sup>-2</sup> Na; (b) plating 5 mA h cm<sup>-2</sup> Na; Top-view SEM images of NSN-3D IECF electrodes after (c) stripping 5 mA h cm<sup>-2</sup> Na; (d) plating 5 mA h cm<sup>-2</sup> Na; Cross-sectional SEM images of bare Na electrodes after (e) stripping 5 mA h cm<sup>-2</sup> Na; (f) plating 5 mA h cm<sup>-2</sup> Na; Cross-sectional SEM images of NSN-3D IECF electrode after (g) stripping 5 mA h cm<sup>-2</sup> Na; h cm<sup>-2</sup> Na; (h) plating 5 mA h cm<sup>-2</sup> Na;



Figure S10. (a) Na stripping/plating cycling of symmetric cells at 1 mA cm<sup>-2</sup> with areal capacity fixed at 10 mA h cm<sup>-2</sup>; (b) Na stripping/plating cycling of symmetric cells at 10 mA cm<sup>-2</sup> with areal capacity fixed at 10 mA h cm<sup>-2</sup>.



Figure S11. Nyquist plots of the bare Na and NSN-3D IECF symmetric cells after 5, 10, and 50 cycles.



Figure S12. XPS spectra of NSN-3D IECF and bare Na electrodes after 10 plating/stripping cycles at 1 mA cm<sup>-2</sup> and 1 mA h cm<sup>-2</sup>.



Figure S13. Na stripping/plating cycling of symmetric cells at 5 mA cm<sup>-2</sup> with areal capacity fixed at 5 mA h cm<sup>-2</sup> in carbonate-based electrolytes.



Figure S14. Top-view SEM images of (a, b) NSN-3D IECF electrode and (c, d) bare Na electrode after galvanostatic plating/stripping 20 cycles at 1 mA cm<sup>-2</sup> and 1 mA h cm<sup>-2</sup> in carbonate electrolyte.



Figure S15. Nyquist plots of the (a) NSN-3D IECF and (b) Bare Na symmetrical battery after 5, 10, and 50 cycles in carbonate electrolyte.



Figure S16. Nyquist plots of the (a) Bare Na||NVPOF and (b) NSN-3D IECF||NVPOF full cells after 5, 10, and 50 cycles at 1 C.



Figure S17. Cycling performance of the NSN-3D IECF||NVPOF and Na||NVPOF full cells at 1 C.



Figure S18. Corresponding charge/discharge profiles at different cycles.



Figure S19. Corresponding charge/discharge profiles at different cycles.



Figure S20. Top-view SEM image of the (a, b) NSN-3D IECF||NVPOF and (c, d) Na||NVPOF full cell after cycling 100 cycles at 5 C.



Figure S21. Cycling performance of the NSN-3D IECF||NVPOF and Na||NVPOF full cells at 10 C.

Sample	NSN-3	D IECF	Bare Na		
Cycle	$R_{s}(\Omega)$	$R_{ct}(\Omega)$	$R_{s}(\Omega)$	$R_{ct}(\Omega)$	
5th cycle	2.414	1.797	7.105	14.36	
10th cycle	2.415	1.461	10.69	34.32	
50th cycle	2.488	0.448	8.834	64.4	

Table S1. The fitted parameters for Figure S11.

Table S2. The fitted parameters for Figure S15.

Sample	NSN-3D IECF			Bare Na		
Cycle	$R_{s}\left(\Omega\right)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	$R_{s}(\Omega)$	$R_{\mathrm{SEI}}\left(\Omega ight)$	$R_{ct}(\Omega)$
5th cycle	2.429	101.2	104.7	3.645	222.6	694.7
10th cycle	2.758	137.1	76.76	3.78	330.2	1248
50th cycle	4.342	63.06	66.86	4.438	150.7	909.6

Table S3. The fitted parameters for Figure S16.

Sample	NSN-3D IECF  NVPOF			Bare Na  NVPOF		
Cycle	$R_{s}\left(\Omega ight)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	$R_{s}\left(\Omega ight)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$
5th cycle	2.368	512.3	492.7	1.91	650.2	143.4
10th cycle	3.823	502.2	400.1	2.381	631.3	1701
50th cycle	4.596	239.1	285.8	5.259	899.6	1603