Supplementary materials

Accelerating Interfacial Desolvation Kinetic by NaF-Rich Composite Sodium for High-Performance All-Climate Sodium-Metal Batteries

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1. Experimental Section

Preparation of NaF: Firstly, deionized water and anhydrous ethanol were mixed with a volume ratio of 2:1, and 0.06 M NaOH solution was prepared by dissolving a certain amount of NaOH in the above mixed solution. After that, 0.3 %vol hydrofluoric acid (HF, \geq 40 wt%) was added and stirred for 20 minutes at 25 °C. Secondly, the above solution was placed in a refrigerator at -50 °C for 24 h and freeze-dried in a freeze dryer for 2 days at a vacuum degree of 5~20 Pa and temperature of -45 °C to evaporate the excess liquid. Afterward, NaF powders can be collected.

Preparation of flocculent NaF@Na anode: A certain amount of flocculent NaF were evenly dispersed on the fresh Na foil and repeatedly rolled for 30 times to obtain the NaF@Na foil. The NaF@Na composite anodes with diverse Na:NaF weight ratio (10:1, 10:2, 10:3) are synthesized, denoted as NaF@Na-1, NaF@Na-2, and NaF@Na-3, respectively. The thickness of the final NaF@Na foil was about 200~400 µm. The above steps were all carried out in a glovebox filled with an Ar atmosphere.

Preparation of NVP cathode: The NVP cathode was prepared through mixing NVP, acetylene black, and Poly (vinylidene fluoride) (PVDF) in N-methylpyrrolidone (NMP) at a mass ratio of 8:1:1 and then pasted onto Al foil. The NVP cathode was punched into disks with diameter of 12 mm, of which the NVP mass loading was around 1.0~1.5, 4.5~5.5 and 8~10 mg cm⁻² in different cell configurations, respectively.

Cell assembly and electrochemical measurements: All cells were assembled into coin-type cells (CR2032) in a glovebox with an Ar atmosphere. The electrolyte is 1 M NaClO₄ in propylene carbonate (PC) with 5 wt% fluoroethylene carbonate (FEC) and separator is glass fiber (GF) membrane. The full cells were assembled with NVP as cathode, Na metal or NaF@Na as anode and GF as separator; all cells were pre-cycled for activation at 0.1 C for three cycles and measured between 2.5~4.0 V. Galvanostatic charge/discharge measurements were performed with a Neware electrochemical testing system. Electrochemical impedance spectroscopy (EIS) test was measured in Autolab electrochemical workstation at range of 0.1 Hz-1 MHz.

Materials Characterization: X-ray diffraction (XRD, Panalytical X'pert Powder) was tested to reveal the phase components of materials. Scanning electron microscope

(SEM, ZEISS AURIGA FIB/SEM) and Energy Disperse Spectroscopy (EDS) mapping were applied to research the surface morphology of the materials. X–ray photoelectron spectroscopy (XPS) text (XPS, ESCA-LAB 250Xi) was employed to study the chemical state of the obtained composite modified materials. The molecular dynamics were performed using the software package GROMACS (version 2021.3)¹⁻⁴. The molecules were optimized in Gaussian 16 first. The system was constructed by packmol⁵, and concomprised specific molecules in a cubic box with the edge size of 5 nm. The atomic interactions were parameterized by the optimized potentials for liquid simulations all-atom (OPLS–AA) force field⁶, and RESP2 charge obtained from Multiwfn⁷ was applied in the calculations. After the energy minimization, the systems were pre-balanced in NPT ensemble with Berendsen method for 2 ns. Then, the production run was carried out in the NVT ensemble at 300 K with the time step of 1 fs. The temperature of the system was controlled by a V-rescale thermostat (τ_T =1 ps). After 20 ns of simulation, the RDF of the particles were analyzed by the toolkits of GROMACS.

The desolventization process were simulated with CP2K package (version 7.1) in the framework of semiempirical quantum mechanical methods GFNn-xTB. A plane–wave density cutoff of 500 Ry was adopted. The long range van der Waals interaction is described by the DFT-D3 approach. All the structures fully relaxed firstly by CP2K with BFGS scheme, and the force convergence criterion was set to 4.5×10^{-4} hartree/bhor. Then the molecular dynamic simulations were carried out based on the optimized structures. The temperature of the system was controlled by Nose–Hoover thermostat and the time step was set to 1fs/frame.

2. Supplementary Figures



Figure S1. Scheme of the preparation of NaF@Na by rolling method.



Figure S2. (a.b) SEM images of the obtained NaF in this work. (c) The average particle size of NaF.



Figure S3. The partial enlarged view of Figure 2b in the high frequency.



Figure S4. Nyquist plots of NaF@Na||NaF@Na and Na||Na cells after cycling 200 h.



Figure S5. Rate performance of the Na||Na symmetrical cell.



Figure S6. (a) Cycling performance of the Na||Na and NaF@Na||NaF@Na symmetrical cells at an operating condition of 0.1 mA cm⁻² and 0.1 mAh cm⁻². The enlarged galvanostatic voltage profiles at (b) 342-348 h, (c) 1894-1900 h and (d) 3794-3800 h.



Figure S7. SEM images of the NaF@Na surface and its corresponding EDS elemental mapping of Na, O and F.



Figure S8. High-resolution XPS spectra of the anodes before cycling, (a) Na and (b) NaF@Na.



Figure S9. High-resolution XPS spectra of (a) Na 1s, (b) F 1s after cycling for the NaF@Na anodes.



Figure S10. High-resolution XPS spectra of (a) Na 1s, (b) F 1s after 20 cycles at 0.2 C, -40 °C for the NaF@Na anodes.



Figure S11. (a) Long-term cycle performance of the Na||NVP and NaF@Na||NVP full cells at 100 C with a NVP loading of 1.1 mg cm⁻². The corresponding galvanostatic charge-discharge profiles at different cycles for (b) Na||NVP and (c) NaF@Na||NVP full cell.



Figure S12. The galvanostatic charge-discharge profiles at various cycles of the NaF@Na||NVP full cell at 5 C with a NVP loading of 8 mg cm⁻².

Figure S13. The galvanostatic charge-discharge profiles at various cycles of (a) the Na||NVP and (b) NaF@Na||NVP full cells with a NVP loading of 5.2 mg cm⁻² at 10 C and 60 °C.

Figure S14. (a) Cycle performance of the NaF@Na||NVP full cell with a NVP loading of 8.0 mg cm⁻² at 1 C and 60 °C; (b) The corresponding galvanostatic charge-discharge profiles at different cycles.

Figure S15. (a) Cycle performance of the for NaF@Na||NVP cell at 1 C/-20 °C with a NVP loading of 1.3 mg cm⁻². (b) The corresponding galvanostatic charge-discharge profiles of (a).

Figure S16. Galvanostatic charge-discharge profiles of the NaF@Na||NVP full cell under low temperature: (a) 0.5 C and -20 °C with a NVP loading of 4.3 mg cm⁻² and (b) 0.2 C and -40 °C with a NVP loading of 1.2 mg cm⁻².

Figure S17. MD simulations for the desolvation process of $Na[PC]_4[ClO_4^-]$ solvation structure on the anode surface of (a) bare Na and (b) NaF@Na at -40 °C and 2000 fs.

Figure S18 MD simulations for the desolvation process of $Na[PC]_4[ClO_4^-]$ solvation structure on the anode surface of bare Na at (a) 1000 fs, (b) 2000 fs and (c) 3000 fs in difference directions.

Figure S19. MD simulations for the desolvation process of $Na[PC]_4[ClO_4^-]$ solvation structure on the anode surface of NaF@Na at (a) 1000 fs, (b) 2000 fs and (c) 3000 fs in difference directions.

Figure S20. Galvanostatic charge-discharge voltage profiles of the NaF@Na||NVP pouch cell with a NVP loading of 1.1 mg cm⁻² at 1 C under different cycles.

Anode	Voltage windows/V	NVP loading/mg cm ⁻²	Rate/C	Discharge capacities/mAh g ⁻¹ /Cycles number	Refs.
NaF/Co/Na	2.3-4.0	4.5	15	70.0/1000	8
Na ₃ P@Na	2.5-3.7	5.5	15	89.3/400	9
CF@ZnS@Na	2.6-3.8	4.0	20	90.0/3000	10
vfP/Na	2.5-4.0	2.0-2.2	3	103.0/1500	11
Na-SnNCNF	2.6-3.8	2.0	10	94.0/1000	12
Sb@HPCNF-Na	2.5-3.8	1.0-2.0	5	90.1/1000	13
Na-C ₃ N ₄	2.5-3.8	13.0	3	95.0/1200	14
Ti ₃ C ₂ T _x /CNT-Na	2.5-4.0	11.0	5	40.0/5000	15
Ni ₃ S ₂ /Ni ₃ P@NF@Na	2.3-3.9	3.0	20	69.0/10000	16
MoS ₂ @NCF/Na	2.5-3.8	3.6-4.2	3	100.0/1300	17
SnCl ₄ @Na-rGO	2.5-4.0	1.2-1.5	1	106.0/600	18
Na ₂ S/V/Na	2.5-4.0	3.0	5	90.0/1800	19
NaF@Na	ıF@Na 2.5-4.0	1.0-1.5	50 100	62.3/6000 55.0/4000	This
		10.0	0.2	72.8/200	WORK

Table S1. Cathode materials (the loading of cathode), voltage windows, rate, discharge capacities and cycles of the reported full batteries using different anodes at RT.

Published articles	Temperature /°C	NVP loading/mg cm ⁻²	Cycles number	Discharge capacities/ mAh g ⁻¹	Rate/C	Refs.
FB-ester-based electrolyte	60	2	500	104	1	20
NaTFSI in IL/TFEE electrolyte	60	2.3	250	102	0.5	21
MTE electrolyte	60	4.0	700	107	1	22
NZSP@PP separator	60	1.4	180	100	1	23
IOHL-Na	55	3	600	105	10	24
NaTFSI-SFH	60	3	500	117	1	25
NaF@Na	60	5.2	2400	106	10	This work

Table S2. Comparison of temperature, the NVP loading, cycle numbers, specific capacity and rate performance at 60 $^{\circ}$ C, 10 C of this work with recent published articles.

Published articles	Temperature /°C	NVP loading/mg cm ⁻²	Cycles number	Capacities retention/ %	Rate/C	Refs.
WT electrolyte	-20	2	500	93	0.5	20
ES6-BLTE electrolyte	-20	2.3	50	92	0.1	21
TILE electrolyte	-40	2	200	88.2	0.1	26
Na-SF in 0.8- FEH electrolyte	-20	2	600	88.7	0.5	27
1 M NaOTf- DEGDME	-40	2	100	95	0.2	28
NaF@Na	-20	4.3	700	93	0.5	This
	-40	1.2	400	90	0.2	work

Table S3. Comparison of temperature, the NVP loading, cycle numbers, capacity retention and rate performance at -40 °C, 0.5/0.2 C of this work with recent published articles.

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