Insight into the interfacial reaction mechanism of FEC and NaF on Na for high performance sodium metal batteries

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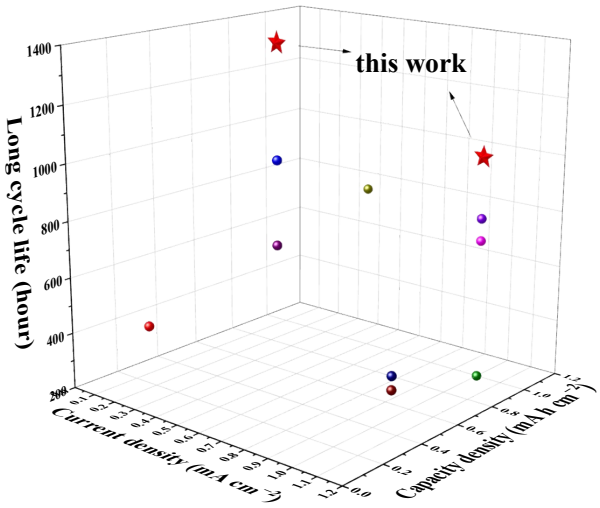

Figure S1. Performance comparisons of the literature on SEI.

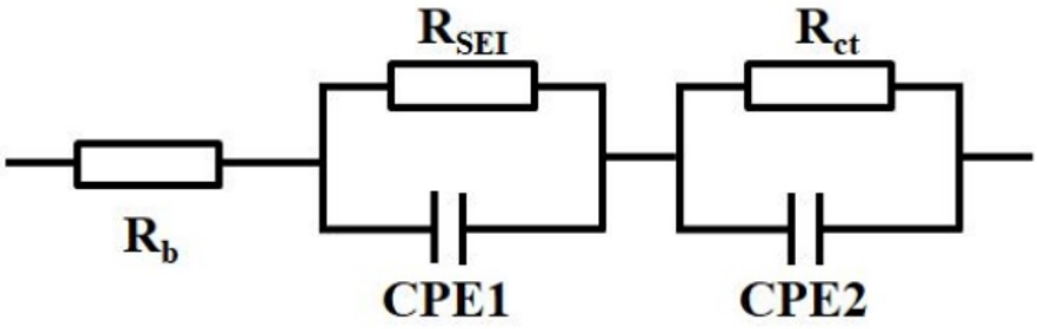

Figure S2. Equivalent circuit model for EIS plots of symmetric batteries of different materials at different cycles.

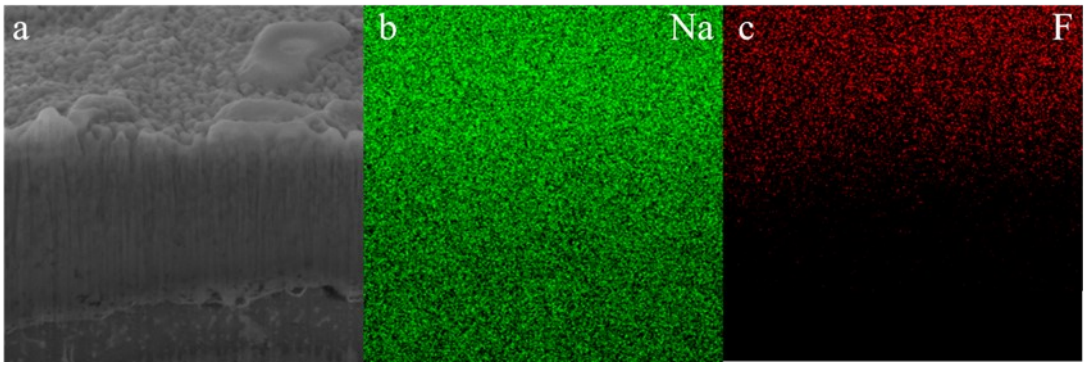

Figure S3. (a) Cross-sectional SEM image of NaF@Na anode after cycling with FEC and element mapping corresponding (b) Na and (c) F.

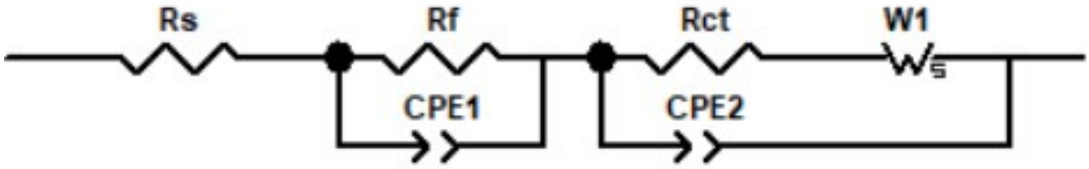

Figure S4. Equivalent circuit model for EIS plots of symmetric batteries of different materials at different temperatures.

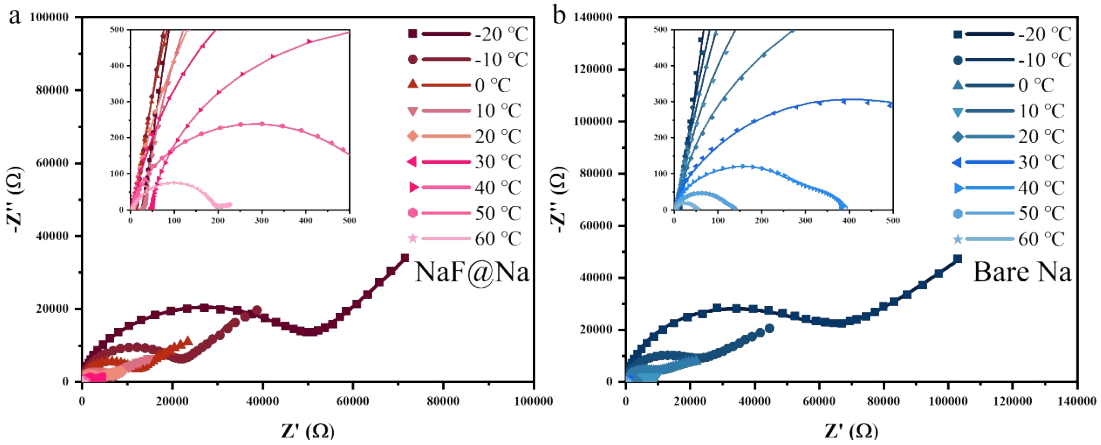

Figure S5. Nyquist plots of symmetric cells with (a) NaF@Na and (b) bare Na electrodes at different temperatures.

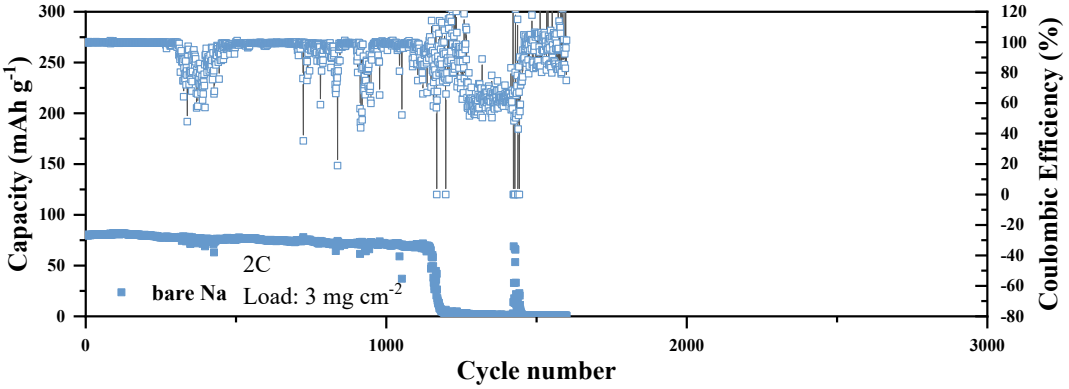

Figure S6. Cycling performance of NVP-based full cells with bare Na anodes without FEC at 2C.

Table S1. Performance comparisons of the literature on SEI.

Components	Electrolyte	Symmetric Cells Test	Electrochemical	Ref.

of SEI		Condition		Performances (hour)	
		Current density (mA cm^{-2})	Capacity density (mA h cm^{-2})		
Al_2O_3	1.0 M $NaClO_4$ in EC/DEC	0.25	0.125	450	1
Bi	1.0 M $NaSO_3CF_3$-G2	0.5	0.5	1000	2
BiOCl	1.0 M $NaClO_4$ in EC/DEC 1/1 vol % with 5% FEC	1.0	1.0	700	3
graphene	1.0 M $NaFP_6$ in EC/DEC	1.0	1.0	200	4
perfluorobenzene	1 M NaPF6 in EC/PC (1:1)	1.0	0.5	350	5
red phosphorus (P)	1M NaTFSI FEC-DMC (3:7 by volume)	1.0	1.0	780	6
SbF_3	1.0 M $NaClO_4$ in EC: PC (1:1 by volume) with 2% FEC	0.5	0.5	700	7
SnS	1.0 M $NaClO_4$ in EC: DEC (1:1 by volume) with 55% FEC	1	0.5	300	8
FEC	1 M NaPF6 in EC/DMC (1:2)	0.5	1	800	9

Table S2. Electrolyte resistance and interfacial resistance of symmetric batteries of different materials at different cycles.

		Cycle resistance(Ω)		
Materials	Numbers of cycles	R_e	R_{SEI}	R_{ct}
Bare Na	1st	2.332	52.77	260.2
	50th	5.784	23.42	82.96
	100th	8.051	20.27	239.9
	150th	3.773	371.8	471.4
NaF@Na	1st	8.086	180	213.1
	50th	6.172	24.45	198
	100th	9.79	22.25	176.5
	150th	7.888	19.31	93.59

Table S3. Electrolyte resistance of symmetric batteries of different materials at different temperatures.

Materials	Different degree (℃/K)	Resistance(R_{ct}/Ω)
Bare Na	-20/253	55918
	-10/263	17904
	0/273	6375
	10/283	1889
	20/293	420.9
	30/303	688
	40/313	120
	50/323	95
	60/333	32
NaF@Na	-20/253	34346
	-10/263	19743
	0/273	9262
	10/283	5946
	20/293	3049
	30/303	1645
	40/313	930.3
	50/323	429.1
	60/333	150.4

Structural models

Based on the result of XRD and XPS, a (3×2) supercell of Na(110) surface with five

unit layer slab (containing 60 atoms) used to simulate Na anode, and a (2×2) supercell of NaF(111) surface with five unit layer slab (to ensure structural symmetry, the bottom layer F was removed, containing 144 atoms) was used to simulate NaF electrode. A FEC molecule is placed about 4 Å away from the surfaces of the two models. To avoid interactions between periodic images, a vacuum space of 20 Å was added on the z direction. During AIMD simulations, the bottom three layers were fixed, while the upper two layers and the FEC thereon were allowed to be fully relaxed. The adsorption energy (ΔE_{ads}) is calculated as follows:

$$\Delta E_{ads}=E_{slab\text{-}fec}-E_{slab}-E_{fec}$$

where $E_{slab\text{-}fec}$, E_{slab}, and E_{fec} represent the energy of the total systems after adsorption, clean slab, and FEC molecule, respectively.

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