Electronic Supplementary Information

Sodium Difluorophosphate: Facile Synthesis, Structure, and Electrochemical Behavior as an Additive for Sodium-ion Batteries

Huan Yang,[a] *Jinkwang Hwang,*[a] *Yuto Tonouchi,*[a] *Kazuhiko Matsumoto,*[*ab] *Rika Hagiwara*[ab]

[a] Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

[b] Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8510, Japan

[*]Corresponding author: E-mail: k-matsumoto@energy.kyoto-u.ac.jp

Table S1 Summary of crystallographic data and refinement results for NaDFP.

	NaDFP
formula	$NaPO_2F_2$
fw	123.96
T / K	113
crystal system	triclinic
space group	$P\bar{1}$
a / Å	6.708(5)
b / Å	6.844(6)
c / Å	8.540(7)
α / °	63.937(17)
β / °	78.750(13)
γ / °	83.826(17)
V / Å^3	343.3(5)
Z	4
ρ_{calc} / g cm^{-3}	2.385
μ / mm^{-1}	0.804
R_1 [a]	0.0369
wR_2 [b]	0.1062
cryst size / mm^3	0.30×0.10×0.10

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (˚) in NaDFP.

bond length (Å)		bond angles (˚)	
P1-O1	1.471(3)	O2-P1-O1	121.38(16)
P1-O2	1.466(3)	O2-P1-F1	109.86(16)
P1-F1	1.548(2)	O1-P1-F1	108.68(14)
P1-F2	1.557(2)	O2-P1-F2	109.52(13)
P2-O3	1.466(3)	O1-P1-F2	107.20(14)
P2-O4	1.467(3)	F1-P1-F2	97.54(13)
P2-F3	1.562(3)	O3-P2-O4	121.87(16)
P2-F4	1.555(2)	O3-P2-F4	108.79(14)
		O3-P2-F3	108.53(15)
		O4-P2-F4	109.27(14)
		O4-P2-F3	108.60(14)
		F4-P2-F3	96.89(13)

Table S3 Selected contact distances (Å) and angles (˚) in NaDFP.

bond length (Å)		bond angles (˚)	
Na1···O2	2.316(3)	O2···Na1···O4	93.44(11)
Na1···O4	2.350(3)	O2···Na1···O3	103.66(10)
Na1···O3	2.392(3)	O2···Na1···O1	174.62(10)
Na1···O1	2.400(3)	O2···Na1···F4	78.47(9)
Na1···F4	2.847(3)	O4···Na1···O3	93.06(11)
Na2···O3	2.303(3)	O4···Na1···O1	86.96(10)
Na2···O4	2.304(3)	O4···Na1···F4	152.54(9)
Na2···O1	2.364(3)	O3···Na1···O1	81.67(9)
Na2···F3	2.370(3)	O4···Na1···F4	152.54(9)
Na2···F2	2.375(3)	O1···Na1···F4	98.76(9)
		O3···Na2···O4	138.94(11)
		O3···Na2···O1	84.36(9)
		O3···Na2···F3	84.28(10)
		O3···Na2···F2	103.73(9)
		O4···Na2···O1	88.93(10)
		O4···Na2···F3	88.92(11)
		O4···Na2···F2	83.90(9)
		O1···Na2···F3	104.46(10)
		O4···Na2···F2	83.90(9)
		F3···Na2···F2	82.25(9)

Table S4 Assignments for the Raman and IR spectra of NaDFP.

Raman (cm^{-1})	IR (cm^{-1})[a]	Assignment[b] (C_{2v})
1304	1305 (1330 sh)	$\nu_{as}(PO_2)$
1140	1146 (1159 sh)	$\nu_{s}(PO_2)$
852	863 (880 sh)	$\nu_{as}(PF_2)$
818	836	$\nu_{s}(PF_2)$ + small $\delta_{s}(PO_2)$
520	499	$\delta_{s}(PF_2) - \delta_{s}(PO_2)$
502		$\rho_{r}(PF_2) - \rho_{w}(PO_2)$
		$\rho_{w}(PF_2) - \rho_{r}(PO_2)$
354		$\delta_{s}(PF_2) - \delta_{s}(PO_2)$
		$\rho_{t}(PF_2) - \rho_{t}(PO_2)$

[a]The abbreviation of sh denotes shoulder in the spectrum. [b]The symbols ν_{as}, ν_{s}, δ_{s}, ρ_{r}, ρ_{w}, and ρ_{t} denote asymmetric stretching, symmetric stretching, scissoring, rocking, wagging, and twisting modes, respectively. See the reference for assignments [K. Matsumoto and R. Hagiwara, Inorg. Chem., 2009, **48**, 7350-7358].

Table S5 Ionic conductivity (mS cm^{-1}) and the VTF fitting parameters[a] for 1 M $NaPF_6$-EC/DMC (1:1, v:v) in neat and with 0.5 wt% and 1 wt% NaDFP and 0.5 wt % and 3 wt % FEC additives. All the fitting data have $R^2 > 0.99$.

Temperature (K)	Concentration				
	Neat	0.5 wt% NaDFP	1 wt% NaDFP	0.5 wt% FEC	3 wt% FEC
273	7.05	6.84	6.80	6.96	6.91
283	9.13	9.05	9.11	9.09	9.05
293	11.33	11.26	11.09	11.13	11.17
303	13.72	13.80	13.96	13.35	13.64
313	16.12	16.31	16.46	16.71	16.20
323	18.65	18.74	18.94	18.33	18.36
333	21.13	21.00	20.46	20.11	20.66
343	23.45	23.53	23.15	22.23	22.82
353	25.65	25.80	25.91	25.55	25.14

Concentration	A_σ (mS cm^{-1} $K^{1/2}$)	B_σ (K)	$T_{0\sigma}$ (K)
Neat	129	288	174
0.5 wt% NaDFP	118	261	181
1 wt% NaDFP	113	251	183
0.5 wt% FEC	120	279	175
3 wt% FEC	108	248	183

[a]See the references for the Vogel-Tammann-Fulcher (VTF) fitting. [H. Vogel, Phys. Z. 1921, **22**, 645−646. G. S. Fulcher, J. Am. Ceram. Soc. 1925, **8**, 339−355.]

Table S6 The first charge-discharge capacities and Coulombic efficiencies of the Na/HC cells with 1 M $NaPF_6$-EC/DMC (1:1, v:v) electrolytes with and without additives. The charge-discharge current density is 25 mA g^{-1}.

Electrolytes	Charge capacity (mAh g^{-1})	Discharge capacity (mAh g^{-1})	Coulombic efficiency (%)
neat electrolyte	342	260	75.8
0.5 wt% NaDFP	342	260	75.7
1 wt% NaDFP	342	260	76.1
0.5 wt% FEC	343	258	75.1
3 wt% FEC	344	256	74.6

Table S7. Fitting results of the EIS for the HC/HC symmetric cells in 1 M $NaPF_6$-EC/DMC with different weight ratios of NaDFP or FEC additive at 298 K.

Electrolyte		1st cycle	3rd cycle	10th cycle	20th cycle
neat	R_{bulk} / Ω	3.2	3.3	3.9	3.8
	R_h/ Ω	6.0	7.6	9.6	10.1
	$C.F._h$ / Hz	8612	5833	2763	2763
	Q_h / F $s^{\alpha-1}$	3.6×10^{-6}	3.4×10^{-6}	3.4×10^{-6}	3.7×10^{-6}
	α_h	1	1	1	1
	R_{ct}/ Ω	60.3	64.5	74.2	99.5
	$C.F._{ct}$ / Hz	51.9	51.9	51.9	35.1
	Q_{ct} / F $s^{\alpha-1}$	0.2×10^{-3}	0.2×10^{-3}	0.2×10^{-3}	0.3×10^{-3}
	α_{ct}	0.7	0.7	0.7	0.7
0.5 wt% NaDFP	R_{bulk} / Ω	3.2	2.8	3.2	3.1
	R_h/ Ω	5.8	6.0	6.2	6.4
	$C.F._h$ / Hz	12763	18906	18906	18906
	Q_h / F $s^{\alpha-1}$	3.2×10^{-6}	4.0×10^{-6}	4.6×10^{-6}	3.7×10^{-6}
	α_h	1.0	1.0	1.0	0.8
	R_{ct}/ Ω	30.8	43.7	47.5	50.4
	$C.F._{ct}$ / Hz	51.9	51.9	51.9	35.1
	Q_{ct} / F $s^{\alpha-1}$	0.8×10^{-3}	0.5×10^{-3}	0.6×10^{-3}	0.3×10^{-3}
	α_{ct}	0.7	0.7	0.6	0.8
1 wt% NaDFP	R_{bulk} / Ω	3.107	3.057	3.025	3.149
	R_h/ Ω	3.8	4.1	4.7	4.3
	$C.F._h$ / Hz	12763	18612	18612	18612
	Q_h / F $s^{\alpha-1}$	4.1×10^{-6}	2.2×10^{-6}	2.6×10^{-6}	$2.9'10^{-6}$
	α_h	1.0	0.8	1.0	1.0
	R_{ct}/ Ω	27.9	30.4	31.1	32.8
	$C.F._{ct}$ / Hz	250.4	250.4	250.4	250.4
	Q_{ct} / F $s^{\alpha-1}$	0.7×10^{-3}	0.4×10^{-3}	0.4×10^{-3}	0.5×10^{-3}
	α_{ct}	0.7	0.736 4	0.5	0.7
0.5 wt% FEC	R_{bulk} / Ω	4.2	4.6	4.9	4.6
	R_h/ Ω	6.6	7.4	8.1	13.4
	$C.F._h$ / Hz	12763	12959	8612	5833
	Q_h / F $s^{\alpha-1}$	4.0×10^{-6}	4.0×10^{-6}	3.7×10^{-6}	2.7×10^{-6}
	α_h	1.0	1.0	1.0	1.0
	R_{ct}/ Ω	135.2	169.7	177.3	212.5
	$C.F._{ct}$ / Hz	23.6	16.8	10.8	4.9
	Q_{ct} / F $s^{\alpha-1}$	0.2×10^{-3}	0.3×10^{-3}	0.2×10^{-3}	0.3×10^{-3}
	α_{ct}	0.8	0.8	0.8	0.7
3 wt% FEC	R_{bulk} / Ω	5.9	6.7	7.3	8.0
	R_h/ Ω	8.0	8.3	12.4	15.3
	$C.F._h$ / Hz	12763	8763	854	861
	Q_h / F $s^{\alpha-1}$	3.1×10^{-6}	3.2×10^{-6}	4.9×10^{-6}	3.6×10^{-6}
	α_h	1.0	1.0	1.0	1.0
	R_{ct}/ Ω	159.4	209.8	231.8	292.9
	$C.F._{ct}$ / Hz	16.0	11.4	16.3	10.8
	Q_{ct} / F $s^{\alpha-1}$	0.2×10^{-3}	0.2×10^{-3}	0.2×10^{-3}	0.2×10^{-3}
	α_{ct}	0.8	0.8	0.7	0.7

[a] *C.F.*, *Q*, and α denote characteristic frequency, CPE parameter, and CPE exponent, respectively.

Table S8 Binding energy and assignments of the XPS results on the HC electrode after 20 cycles in 1 M $NaPF_6$-EC/DMC (1:1, v:v) electrolytes with and without additives.

	F 1s		O 1s		P 2p	
Neat	686.9	Na_xPF_y / $Na_xPF_yO_z$ (99%)	533.3	C–O (36%)	137.4	Na_xPF_y (96%)
	683.8	NaF (1%)	531.7	C=O (64%)	136.5	
					134.1	$Na_xPF_yO_z$ / P–O (4%)
					133.4	
3 wt%	687.3	Na_xPF_y / $Na_xPF_yO_z$ (88%)	533.2	C–O (42%)	137.7	Na_xPF_y (71%)
FEC	684.0	NaF (12%)	531.5	C=O (58%)	136.8	
					134.3	$Na_xPF_yO_z$ / P–O (29%)
					133.3	
1 wt%	687.1	Na_xPF_y / $Na_xPF_yO_z$ (77%)	533.1	C–O (48%)	137.8	Na_xPF_y (32%)
NaDFP	683.9	NaF (23%)	531.6	C=O (32%)	136.9	
			530.7	P–O (20%)	134.6	$Na_xPF_yO_z$ / P–O (68%)
					133.7	

Table S9 XPS quantification of elements on the HC electrode after 20 cycles in 1 M $NaPF_6$-EC/DMC (1:1, v:v) electrolytes with and without additives.

	C	O	F	Na	P
Neat	30	22	16	28	4
3 wt% FEC	37	22	17	22	2
1 wt% NaDFP	39	23	20	13	6

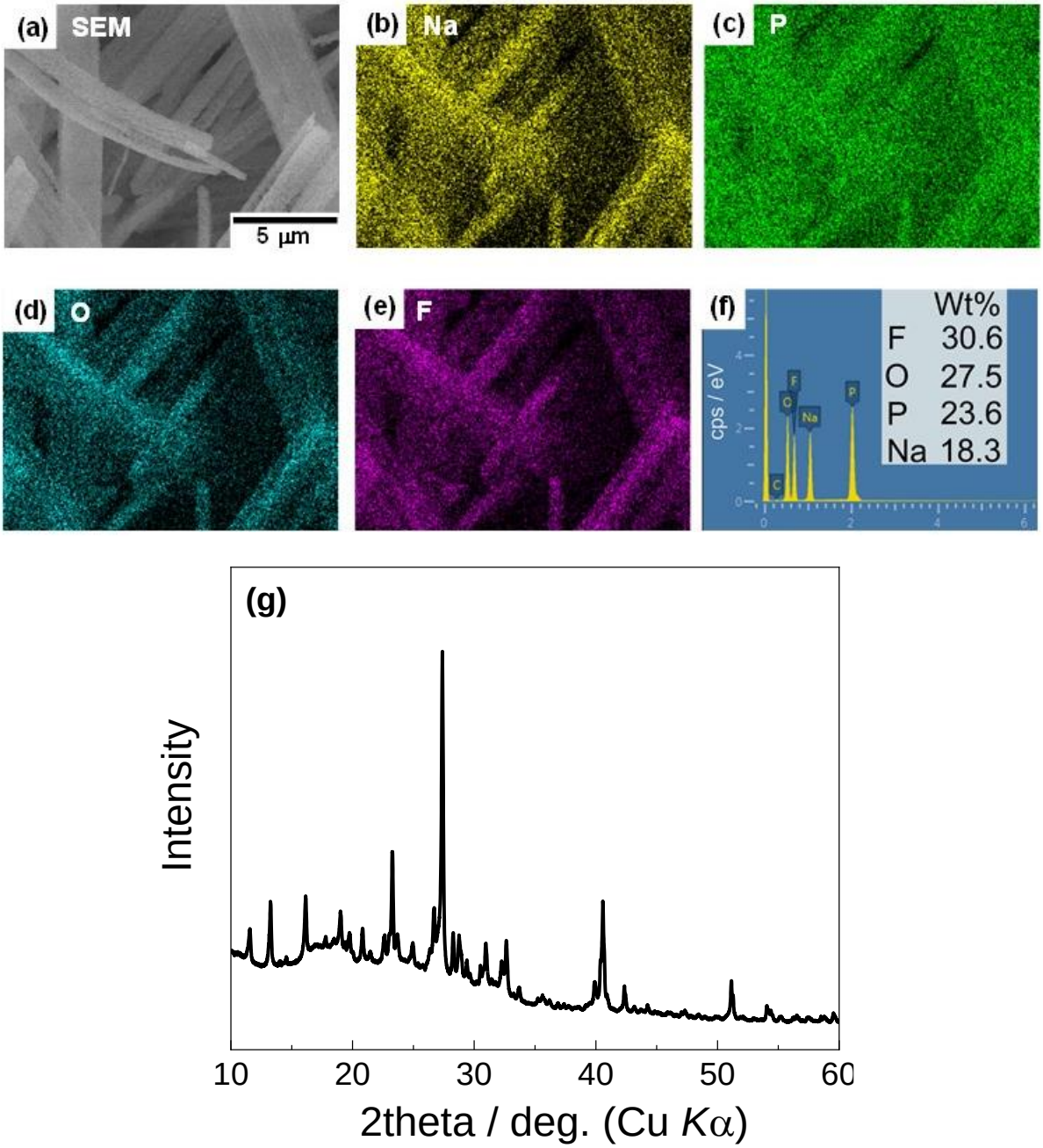

Fig. S1 (a) SEM image, (b−f) EDX mappings of the elements and the elemental composition present in the prepared NaDFP, and (g) X-ray powder diffraction patterns of the prepared NaDFP.

Brief comments: Potassium from the starting material was not detected. The elemental composition of prepared NaDFP and theoretical composition has similar values. (cf. Element: observed vs. theoretical; Na: 18.3 vs. 18.5 wt%, P: 23.6 vs. 25.1 wt%, O: 27.5 vs. 25.8 wt%, and F: 30.6 vs. 30.6 wt%)

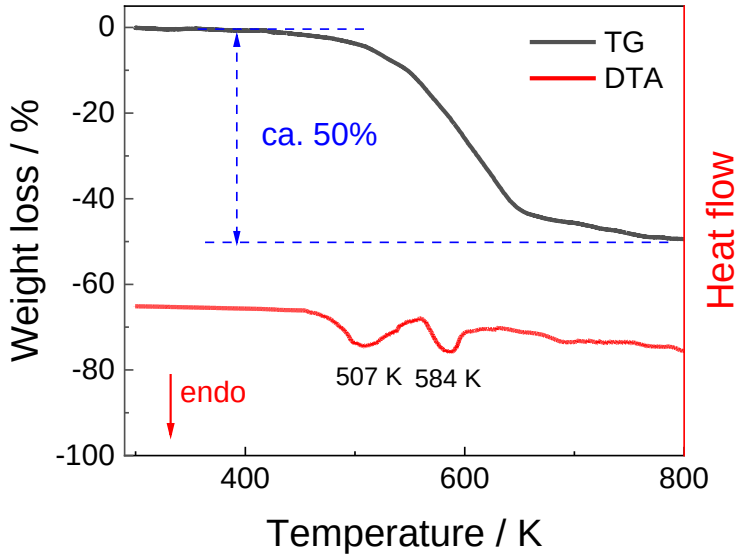

Fig. S2 The TG-DTA curves of NaDFP. Scan rate: 1 K min^{-1}. Atmosphere: dry Ar gas.

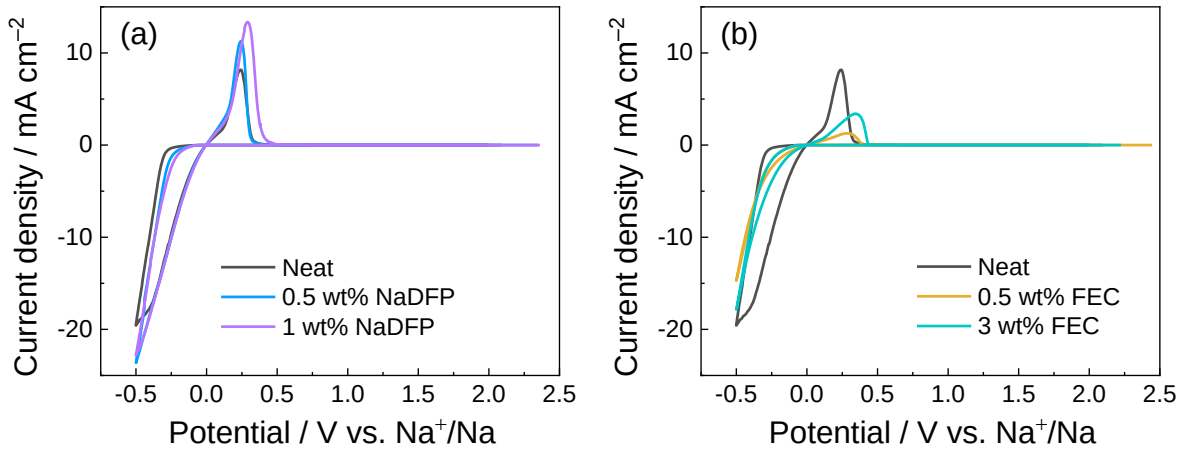

Fig. S3 Cyclic voltammograms of Al electrodes using 1 M $NaPF_6$-EC/DMC (1:1, v:v) with (a) NaDFP and (b) FEC at a scan rate of 5 mV s^{-1}. The voltammograms using the neat 1 M $NaPF_6$-EC/DMC (1:1, v:v) is shown for comparison. The cathodic and anodic peaks at 0 V vs. Na^+/Na correspond to the deposition and dissolution of Na metal, respectively.

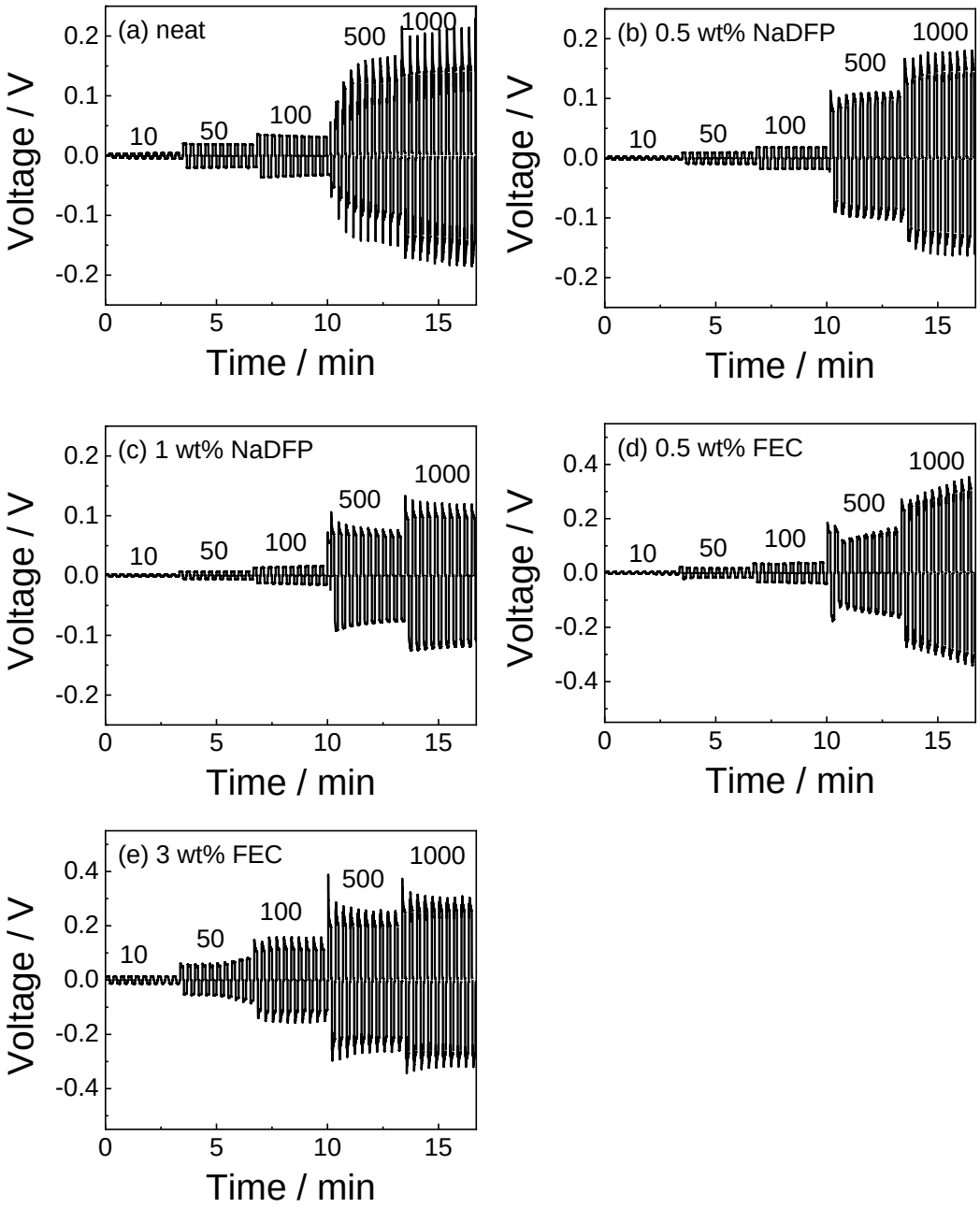

Fig. S4 Voltage profiles of the Na/Na symmetric cells during galvanostatic Na metal deposition/dissolution using 1 M $NaPF_6$-EC/DMC (1:1, v:v) (a) in neat and with (b) 0.5 wt% NaDFP, (c) 1 wt% NaDFP, (d) 0.5 wt% FEC, and (e) 3 wt% FEC. Current densities shown in each panel are in the unit of μA cm^{-2}.

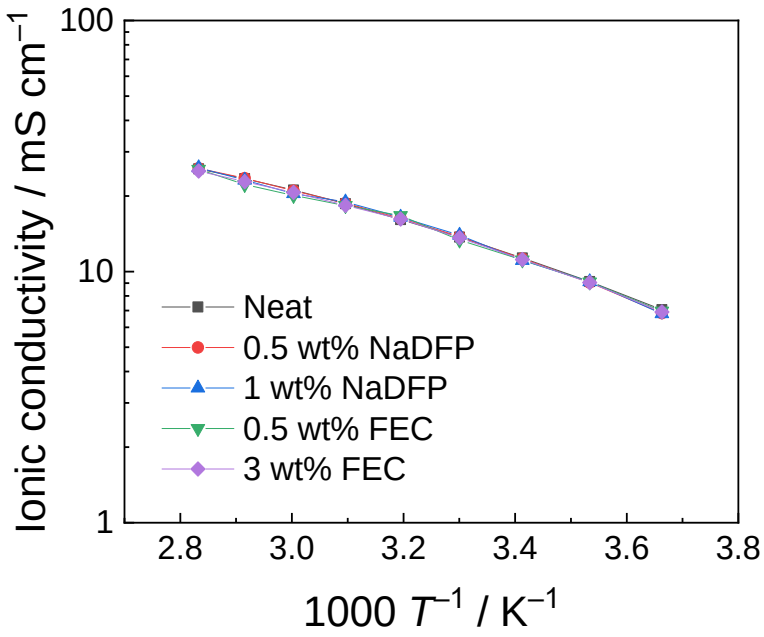

Fig. S5 Temperature dependence of ionic conductivity for 1 M $NaPF_6$-EC/DMC (1:1, v:v) in neat and with 0.5 wt% NaDFP, 1 wt% NaDFP, 0.5 wt % FEC, and 3 wt % FEC additives in the temperature range between 273 and 353 K.

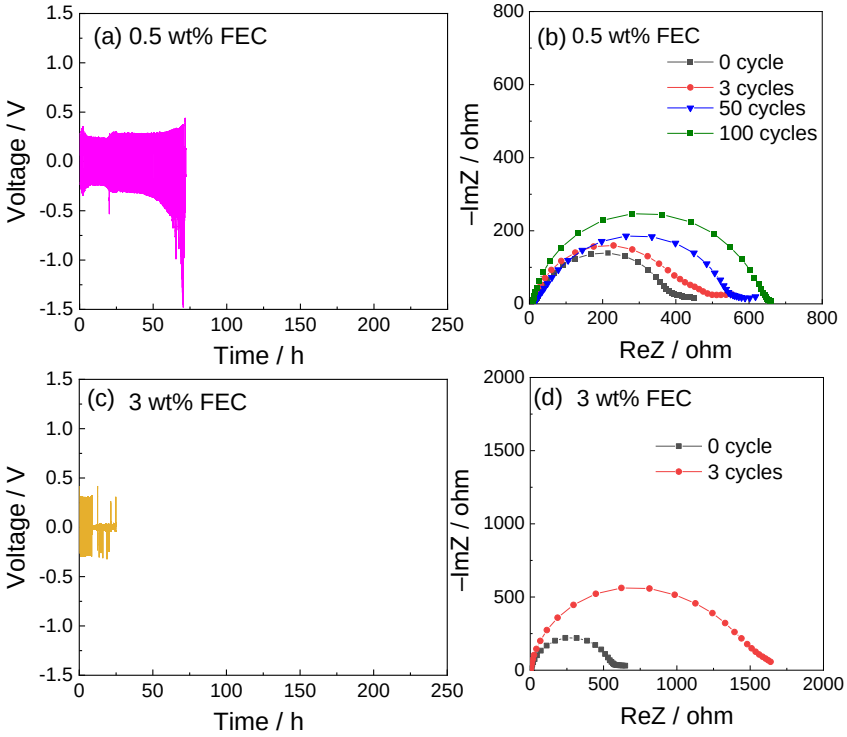

Fig. S6 Voltage profiles and Nyquist plots of the Na/Na symmetric cells during galvanostatic Na metal deposition/dissolution cycles with (a, b) 0.5 wt% FEC and (c, d) 3 wt% FEC.

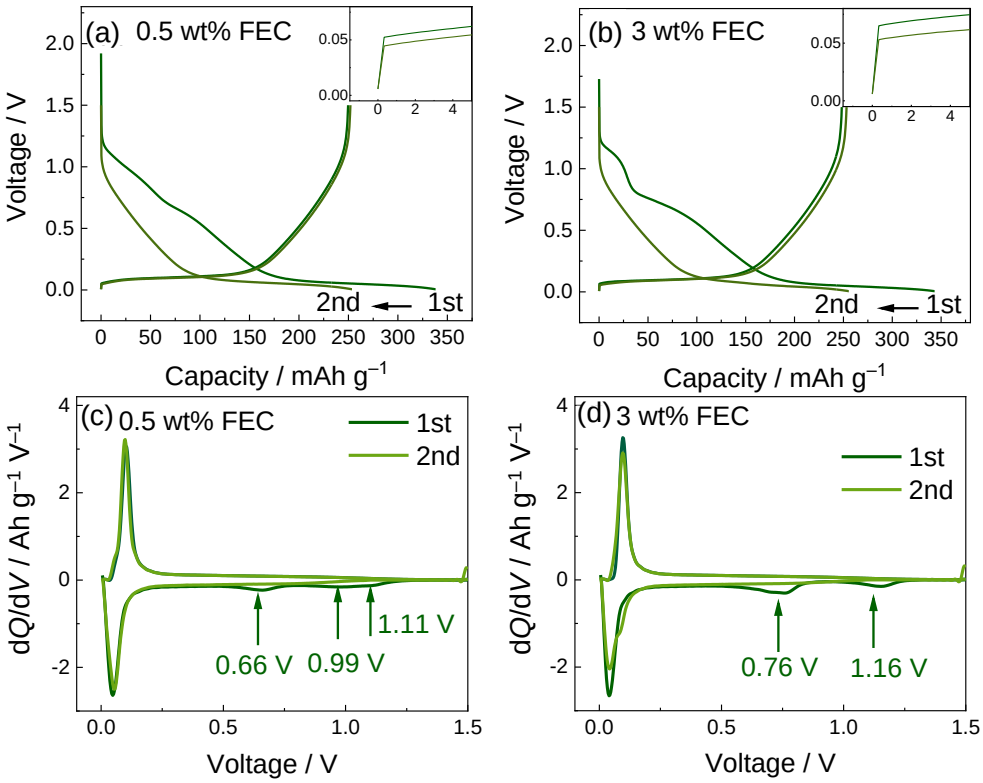

Fig. S7 Charge-discharge curves and the corresponding dQ/dV plots of the Na/HC cells using 1 M $NaPF_6$-EC/DMC with the (a, c) 0.5 wt% FEC and (b, d) 3 wt% FEC. Current density: 25 mA g^{-1}. Cut-off voltage: 0.005–1.5 V.

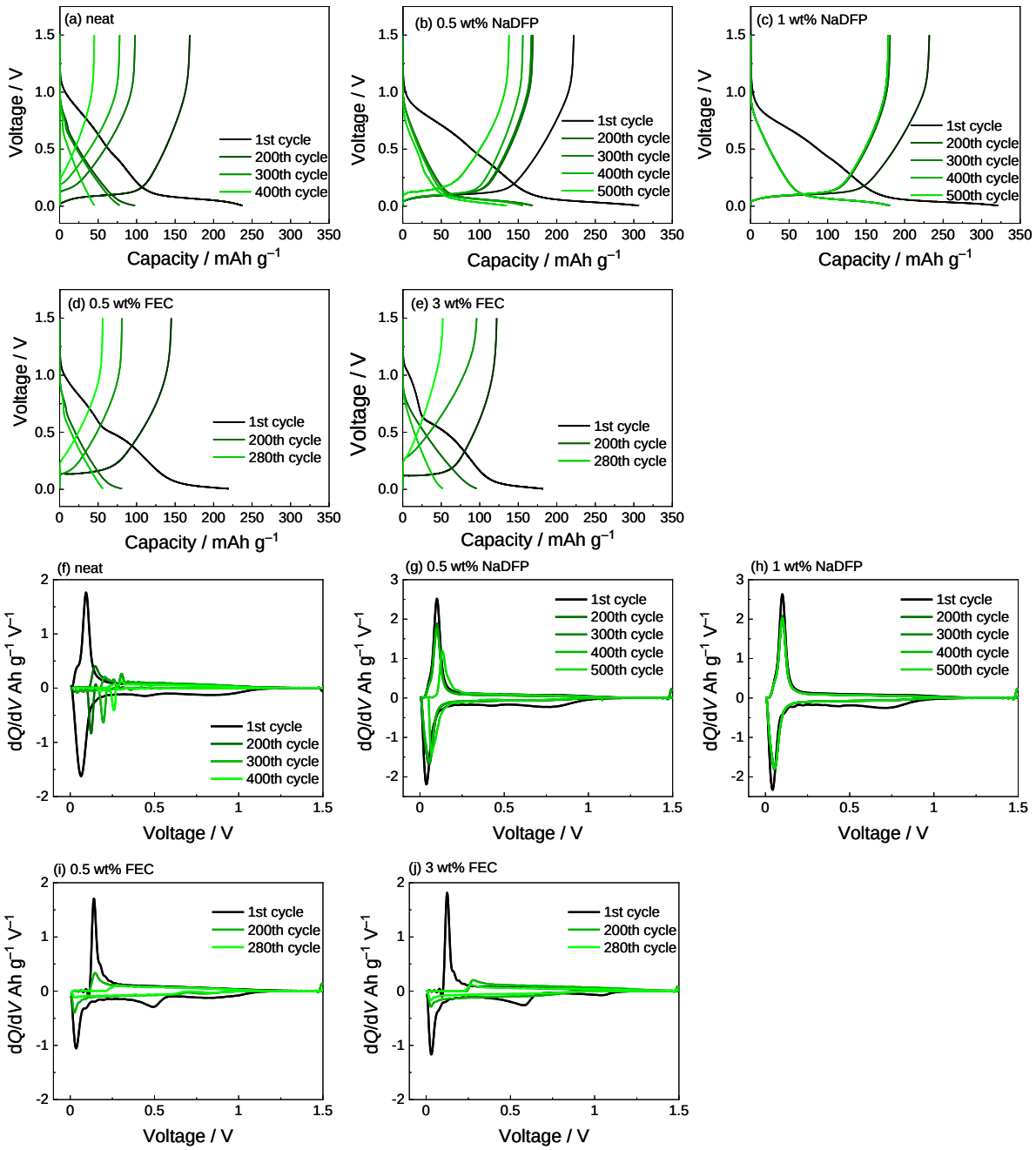

Fig. S8. Charge-discharge curves and the corresponding d*Q*/d*V* plots of the Na/HC cells in 1 M $NaPF_6$-EC/DMC (1:1, v:v) with (a, f) 0 wt% additive (neat), (b, g) 0.5 wt% NaDFP, (c,h) 1 wt% NaDFP, (d, i) 0.5 wt% FEC, and (e, j) 3 wt% FEC after cycles. Current density: 100 mA g^{-1}. Cut-off voltage: 0.005–1.5 V.

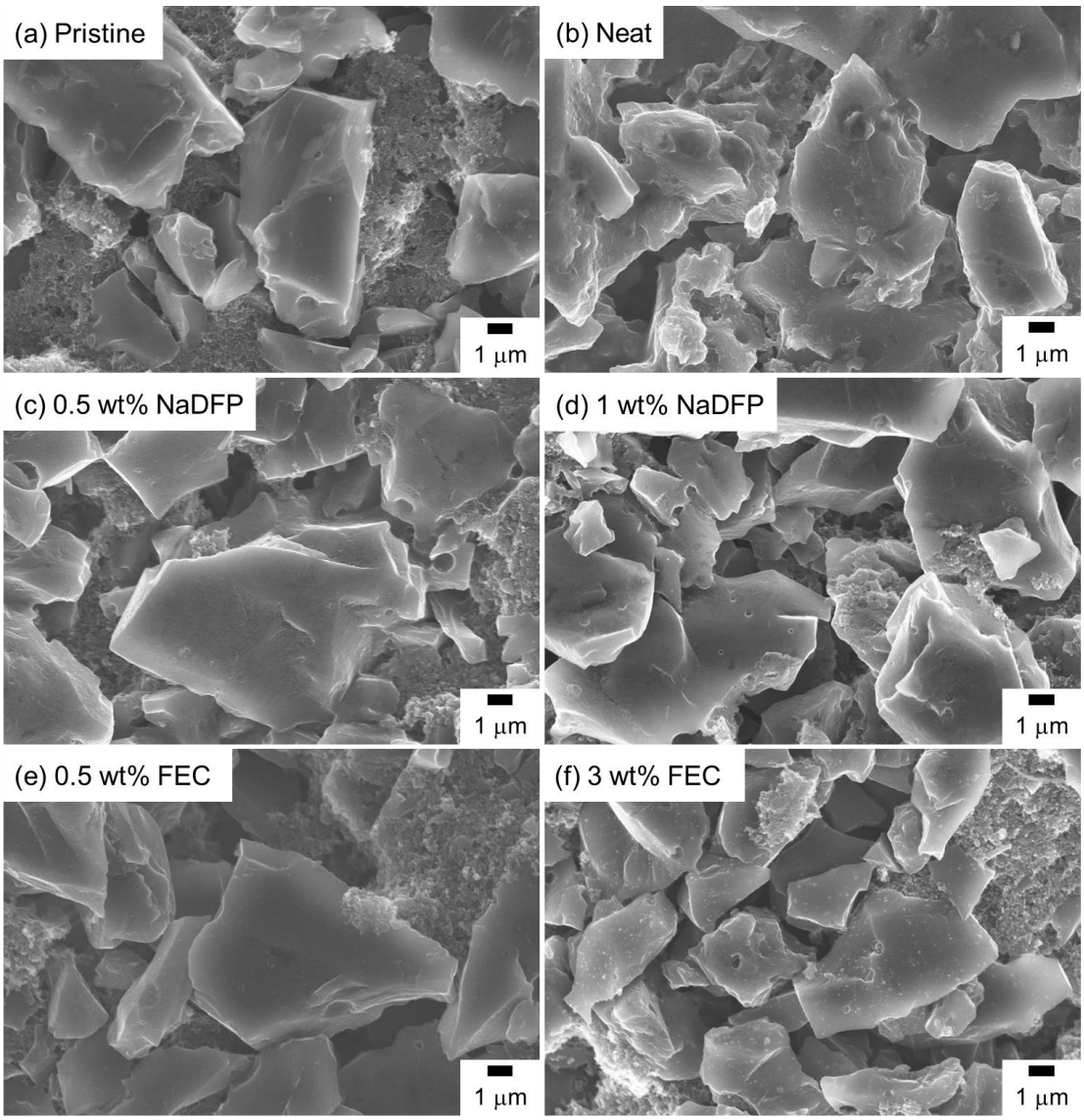

Fig. S9 Surface SEM images of the HC electrodes, (a) the pristine state and after 3 cycles in 1 M $NaPF_6$-EC/DMC (b) in neat and with (c) 0.5 wt% NaDFP, (d) 1 wt% NaDFP, (e) 0.5 wt% FEC, and (f) 3 wt% FEC.

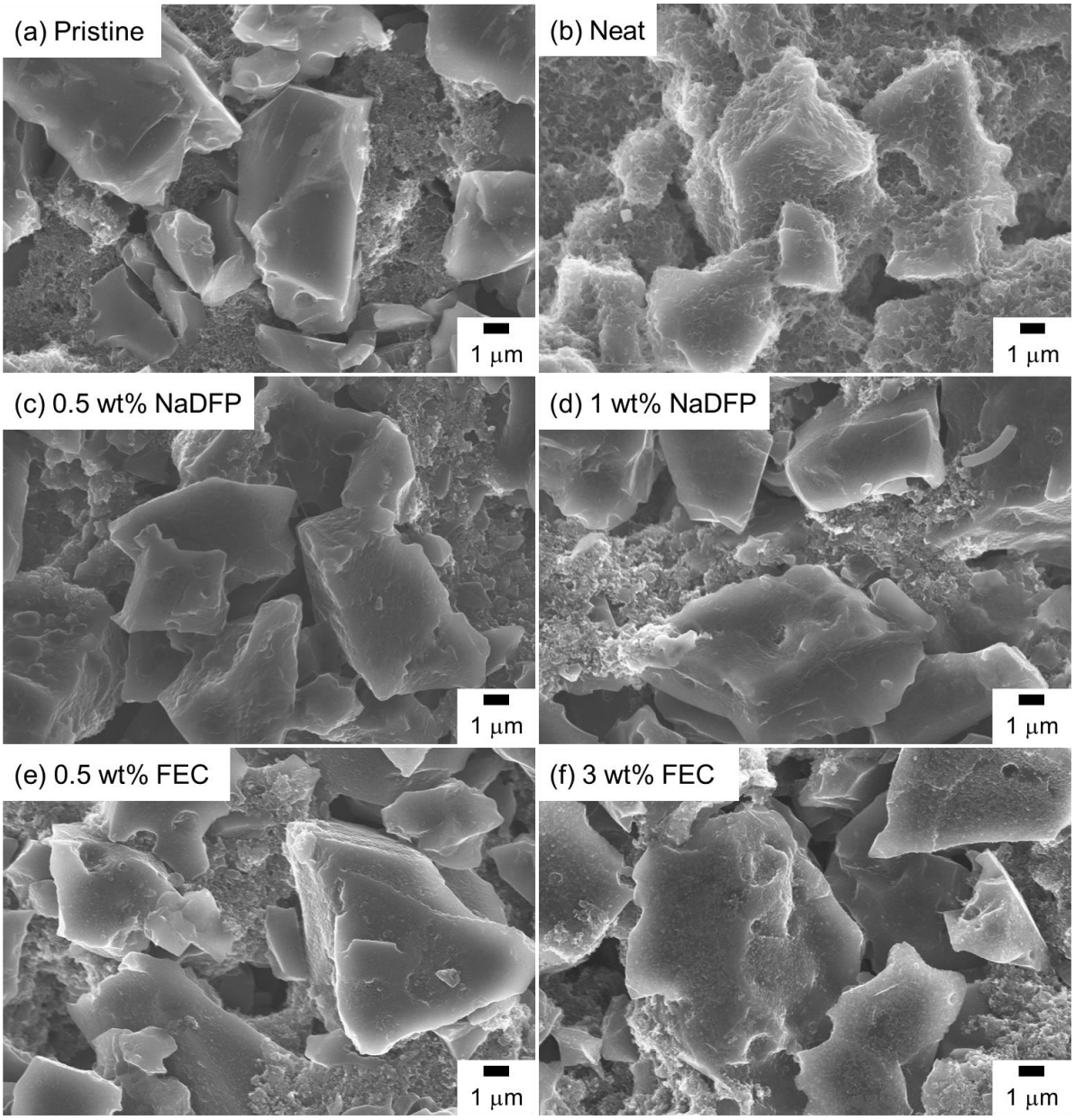

Fig. S10 Surface SEM images of the HC electrodes, (a) the pristine state and after 20 cycles in 1 M $NaPF_6$-EC/DMC (b) in neat and with (c) 0.5 wt% NaDFP, (d) 1 wt% NaDFP, (e) 0.5 wt% FEC, and (f) 3 wt% FEC.

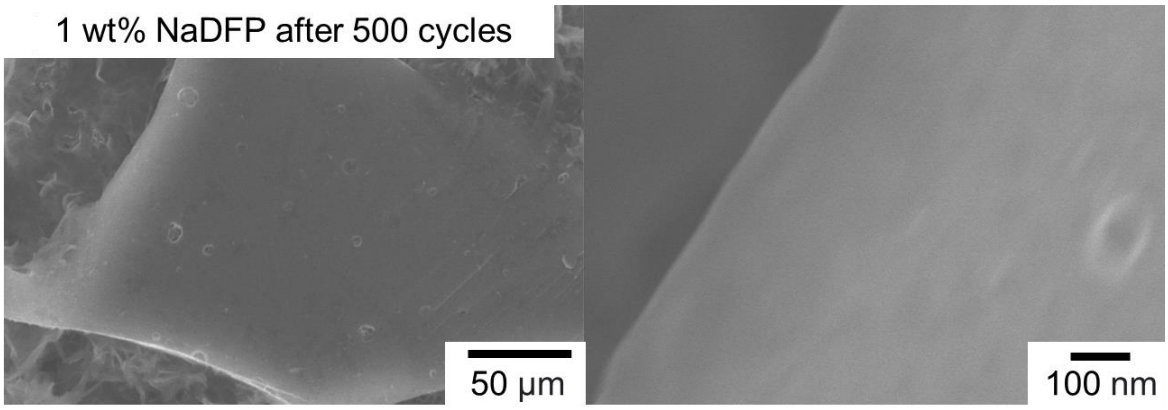

Fig. S11. Surface SEM images of the HC electrodes after 500 cycles in 1 M $NaPF_6$-EC/DMC (1:1, v:v) with 1 wt% NaDFP.

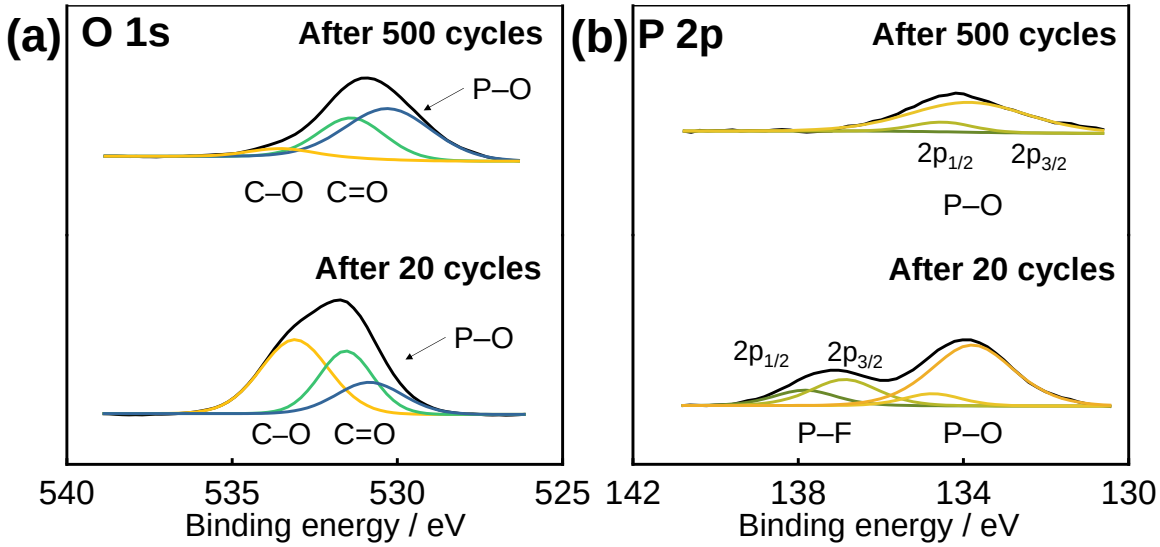

Fig. S12 Comparison of X-ray photoelectron spectra for the SEI layers formed on the HC electrodes after 20 and 500 cycles in 1 M $NaPF_6$-EC/DMC (1:1, v:v) electrolyte with 1 wt% NaDFP. (a) O1s, and (b) P 2p.