Supplementary Information (SI) for ChemComm.

Supplementary Information

In Situ Mössbauer Spectroscopy Confirms Fluoroethylene Carbonate Stabilizes Fe^{4+} in Charged $NaFeO_2$

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Experimental Methods

Materials preparation and characterization: The α-$NaFeO_2$ powder was prepared by solid-state reactions. A typical synthesis starts with mixing 15.2 mg Na_2O_2 (with 5 % excess compared with stoichiometric quantity) and 24.8 mg Fe_2O_3 via a high energy ball milling (SPEX Mill) for one hour. The milled powders were collected and pelleted and calcined at 650°C for 12 hours in air with a ramp rate of 3°C/minute. The calcined pellet was quickly transferred to a glove box and grounded into fine powder using a mortar and a pestle while inside glove box.

X-ray diffraction analysis was carried out on a Rigaku MiniFlex X-ray diffractometer operating at 30 kV and 15 mA using Cu Kα radiation (λ=0.15405 nm). Scanning electron microscope (SEM) analysis were collected using a Zeiss Merlin FE-SEM microscope; and EDS spectra were collected using a Bruker energy dispersive X-ray detector.

Electrochemical tests: cathodes were prepared by mixing $NaFeO_2$ powder with super P carbon black and polytetrafluoroethylene (PTFE) in the ratio 8:1:1 and rolling as a free-standing film. These electrodes were vacuum dried overnight and then cut into 12mm diameter discs. Typical mass loading of $NaFeO_2$ was ~20 mg/cm^{-2}. The electrolytes employed include $NaPF_6$ in propylene carbonate (with and without 5% FEC additive) and $NaClO_4$ in propylene carbonate (with and without 5% FEC additive). The propylene carbonate (PC) solvent was dried over a molecular sieve prior to electrolyte preparation. The separator was glass fiber disc, and the anode was a piece of sodium metal foil. Batteries were assembled both as standard coin cells and as homemade in-situ cells suitable for Mössbauer spectroscopy analysis. All cell assembly was performed inside an Ar filled glove box.

^{57}Fe Mössbauer spectra were recorded by a Kr proportional counter in transmission mode using a $^{57}Co/Rh$ radiation source mounted on a drive where the velocity varied sinusoidally. The isomer shifts were given relative to α-Fe and the velocity was calibrated using α-Fe foil. All spectra were measured under ambient with a velocity range of ± 8.0mm s^{-1}. The data were fitted to Lorentzian functions using a least square fitting route to find the Mössbauer parameter values regarding the isomer shift (IS) and the quadrupole splitting (QS).

Galvanostatic battery charge-discharge tests were performed using a Neware battery analyzer at 10 mA/g at room temperature. The voltage window was 2.0-3.8V.

Supplemental Tables

Table S1: Rietveld refinement parameters for the XRD of $NaFeO_2$ powders synthesized in this work.

$NaFeO_2$		
Space group	Unit cell parameter	Parameter value
R-3m	a	3.027392Å
	b	3.027392Å
	c	16.104240Å
	cell volume	127.823Å^3
	α	90.000º
	β	90.000º
	γ	120.000º
	R-factor (R_p)%	1.81
	R-factor (R_{wp})%	3.05

atom	Wyckoff	x	y	z	Occ.
Na	3a	0	0	0	0.17882
Fe	3b	0	0	0.500	0.08275
O	6c	0	0	0.223	0.08208

Table S2: Mössbauer parameters of Fe sites in pristine $NaFeO_2$ and its electrodes charged to the respective voltages in the 1.0M $NaPF_6$ in PC electrolyte, before and after a 24-hour resting at the open circuit.

Pristine $NaFeO_2$				
site	δ (mm s^{-1})	ΔEQ (mm s^{-1})	area (%)	width
Fe^{3+}	0.364(1)	0.485(1)	100	0.288(1)

$NaFeO_2$ in 1.0M $NaPF_6$/PC					
voltage (V)	site	δ (mm s^{-1})	ΔEQ (mm s^{-1})	area (%)	width
3.4V	$Fe^{3+}O_6$ $Fe^{4+}O_6$	0.33(3) 0.00(2)	0.69(1) 0.51(2)	75.0 25.0	0.405(4) 0.366(9)
3.6V	$Fe^{3+}O_6$ $Fe^{4+}O_6$	0.34(2) 0.00(3)	0.73(4) 0.62(1)	64.1 35.9	0.410(5) 0.368(7)
3.8V	$Fe^{3+}O_6$ $Fe^{4+}O_6$	0.34(3) -0.01(2)	0.78(4) 0.63(2)	60.6 39.4	0.407(5) 0.390(7)
after 24 hours resting at open circuit					

3.4V	Fe^{3+}O$_6$ Fe^{4+}O$_6$	0.32(2) -0.05(3)	0.65(3) 0.42(2)	86.4 13.6	0.423(4) 0.28(1)
3.6V	Fe^{3+}O$_6$ Fe^{4+}O$_6$	0.33(3) 0.10(2)	0.74(5) 0.56(3)	73.3 26.7	0.407(4) 0.389(8)
3.8V	Fe^{3+}O$_6$ Fe^{4+}O$_6$	0.34(2) 0.01(5)	0.79(2) 0.64(3)	68.5 31.5	0.435(5) 0.391(9)

Table S3: Mössbauer parameters of Fe sites in NaFeO$_2$ electrodes charged to 3.8V in the 1.0M NaPF$_6$ in PC electrolyte with 5% FEC additive, before and after a 24-hour resting at the open circuit.

NaFeO$_2$ in 1.0M NaPF$_6$/PC + 5% FEC.					
voltage (V)	site	δ (mm s^{-1})	ΔEQ (mm s^{-1})	area (%)	width
3.8V	Fe^{3+}O$_6$ Fe^{4+}O$_6$	0.37(2) 0.06(3)	0.78(5) 0.65(3)	58.4 41.6	0.45(2) 0.49(2)
after 24 hours rest					
3.8V	Fe^{3+}O$_6$ Fe^{4+}O$_6$	0.36(4) 0.06(2)	0.76(5) 0.64(3)	59.1 40.9	0.47(2) 0.52(2)

Table S4: Mössbauer parameters of Fe sites in NaFeO$_2$ electrodes charged to 3.8V in the 1.0M NaClO$_4$ in PC electrolyte, before and after a 24-hour resting at the open circuit.

NaFeO$_2$ in 1.0M NaClO$_4$/PC					
voltage (V)	site	δ (mm s^{-1})	ΔEQ (mm s^{-1})	area (%)	width
3.8	Fe^{3+}O$_6$ Fe^{4+}O$_6$	0.35(1) 0.00(3)	0.79(3) 0.67(3)	61.8 38.2	0.405(5) 0.357(6)
after 24 hours rest					
3.8	Fe^{3+}O$_6$ Fe^{4+}O$_6$	0.31(3) 0.35(5)	0.88(2) 0.47(2)	50.4 49.6	0.503(2) 0.278(5)

Table S5: Mössbauer parameters of Fe sites in NaFeO$_2$ electrodes charged to the respective voltages in the 1.0M NaClO$_4$ in PC electrolyte with 5% FEC electrolyte, before and after a 24-hour resting at the open circuit. 1.

$NaFeO_2$ in 1.0M $NaClO_4$/PC + 5% FEC					
voltage (V)	site	δ (mm s^{-1})	ΔEQ (mm s^{-1})	area (%)	width
3.4	$Fe^{3+}O_6$	0.33(4)	0.80(4)	73.4	0.494(7)
	$Fe^{4+}O_6$	-0.01(2)	0.66(3)	26.6	0.42(1)
3.6	$Fe^{3+}O_6$	0.34(3)	0.80(2)	68.7	0.480(7)
	$Fe^{4+}O_6$	0.00(1)	0.66(4)	31.3	0.43(1)
3.8	$Fe^{3+}O_6$	0.35(3)	0.79(3)	60.7	0.438(6)
	$Fe^{4+}O_6$	0.00(2)	0.66(3)	39.3	0.419(8)
after 24 hours rest					
3.4	$Fe^{3+}O_6$	0.33(2)	0.81(3)	75.1	0.502(7)
	$Fe^{4+}O_6$	0.00(1)	0.67(2)	24.9	0.402(7)
3.6	$Fe^{3+}O_6$	0.34(1)	0.81(3)	69.6	0.471(6)
	$Fe^{4+}O_6$	-0.01(2)	0.68(3)	30.4	0.42(1)
3.8	$Fe^{3+}O_6$	0.34(3)	0.79(2)	61.8	0.451(7)
	$Fe^{4+}O_6$	0.01(2)	0.65(3)	38.2	0.43(1)

Supplemental Figures

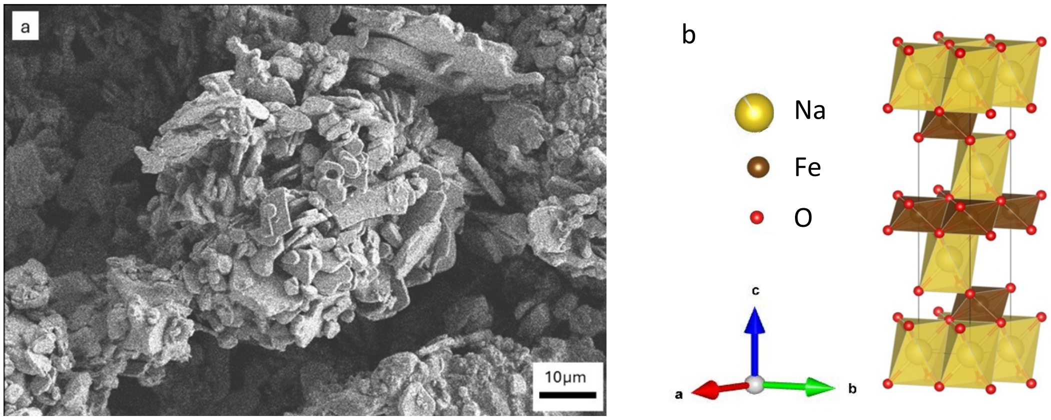
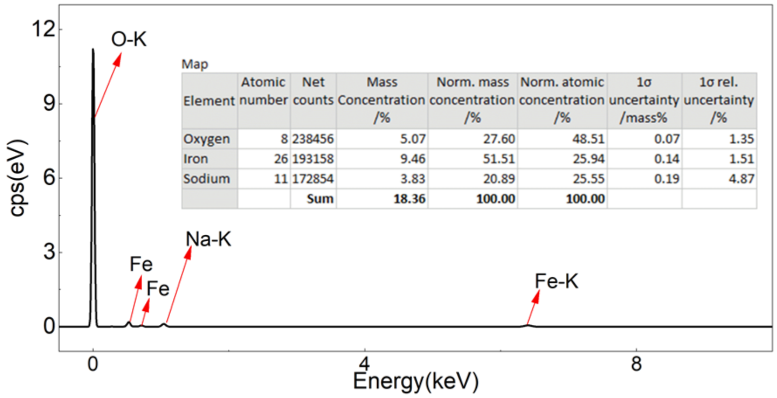


Figure S1: a) SEM image of the $NaFeO_2$ powders, b) graphic representation of its crystal structure derived from the refinement results.



Element	Atomic number	Net counts	Mass Concentration /%	Norm. mass concentration /%	Norm. atomic concentration /%	1σ uncertainty /mass%	1σ rel. uncertainty /%
Oxygen	8	238456	5.07	27.60	48.51	0.07	1.35
Iron	26	193158	9.46	51.51	25.94	0.14	1.51
Sodium	11	172854	3.83	20.89	25.55	0.19	4.87
		Sum	**18.36**	**100.00**	**100.00**		

Figure S2: EDS spectrum and atomic ratio quantification of the $NaFeO_2$ powders employed in this work.

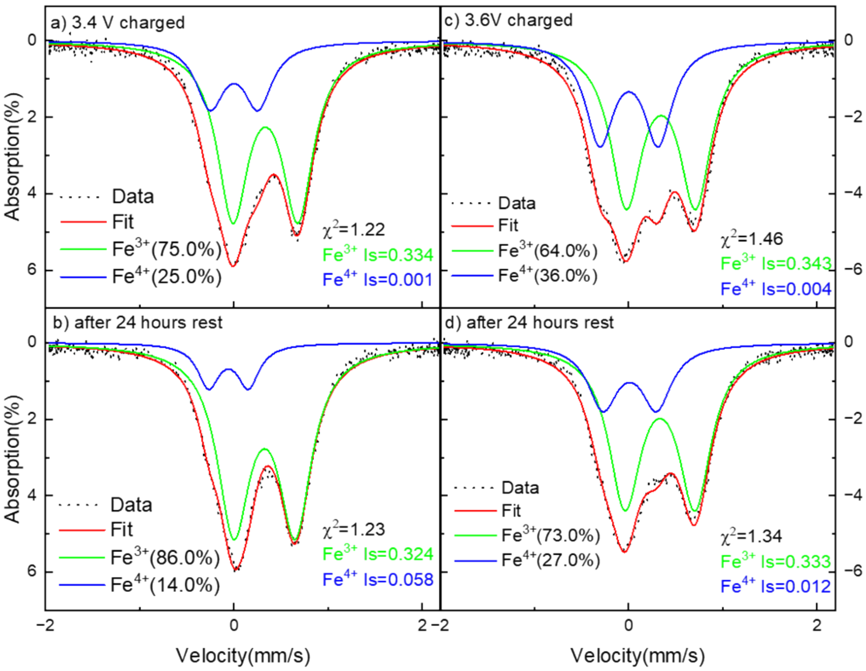


Figure S3: In situ Mössbauer spectra and the fitting results of $NaFeO_2$ cathodes acquired at a) holding at 3.4V and b) after resting for 24 hours at open circuit after charging to 3.4V; c) holding at 3.6V and d) after resting for 24 hours at open circuit, after charging to 3.6V. The electrolyte was 1.0M NaPF6 in PC without FEC additive.

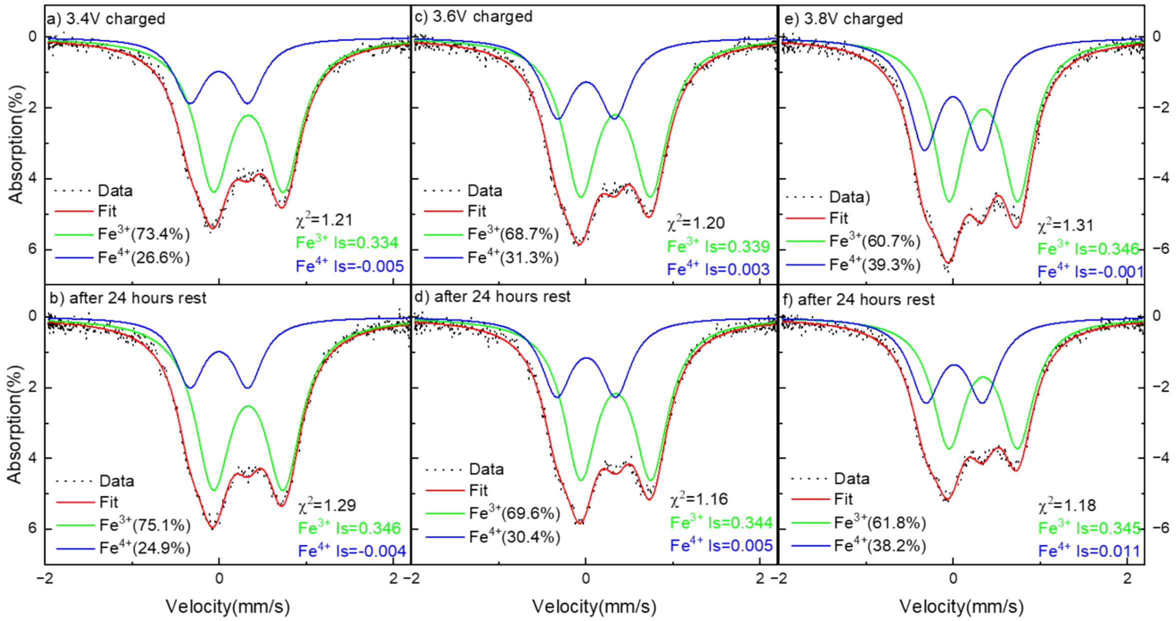


Figure S4: In situ Mössbauer spectra and the fitting results of $NaFeO_2$ cathodes acquired at a) holding at 3.4V and b) after resting for 24 hours at open circuit after charging to 3.4V; c) holding at 3.6V and d) after resting for 24 hours at open circuit, after charging to 3.6V; e) holding at 3.6V and f) after resting for 24 hours at open circuit, after charging to 3.8V;The electrolyte was 1.0M $NaClO_4$ in PC with 5% FEC additive.

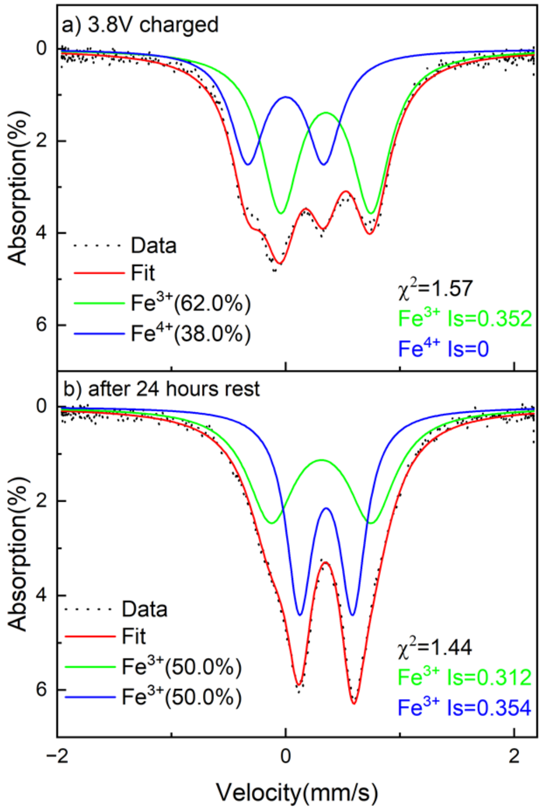


Figure S5: In situ Mössbauer spectra and the fitting results of $NaFeO_2$ cathodes acquired at a) holding at 3.8V and b) after resting for 24 hours at open circuit, after charging to 3.8V; The electrolyte was 1.0M $NaClO_4$ in PC without FEC additive. Two distinct Fe^{3+} species were observed after 24 hours, and the blue curve represents Fe^{3+} in small lattice distortion (low strain environment; small quadrupole splitting) while the green curve represents high strain environment (large lattice distortion; large quadrupole splitting).

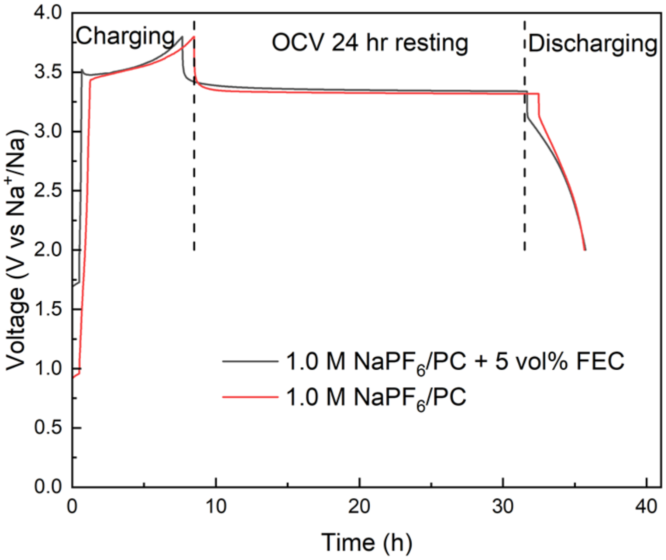


Figure S6: comparison of voltage profiles for $NaFeO_2$ in the 1.0M $NaPF_6$/PC electrolyte with and without FEC additive during charging, resting at OCV and subsequent discharging, the current density was 10 mA/g.