Supplementary Information

Active formation protocols for extending the life-time of a sodium ion battery

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1. Experimental section

The sodium ion full cell consisted of a mixed P2-O3 type oxide material Na[Ni,Mn,Mg,Ti]O_2[1] cathode and a commercial hard carbon anode [2], separated by a polypropylene separator (Celgard2325, 18 mm dia.) with Na electrolyte (Flurochem, 1 M $NaPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) with 5 wt% fluorinated ethylene carbonate (FEC) as an electrolyte additive). The positive electrode (cathode) and negative electrode (anode) contained 92 wt% and 88 wt% of active materials, respectively. Conductive additives were 5 wt% and 3 wt% in cathode and anode, respectively, and rest PVDF binder. The cathode and anode slurries were prepared in NMP (N-methyl-2-pyrrolidone) and coated on carbon coated aluminium current collector. Both electrodes were dried on a hotplate at 80 ˚C with final drying carried out in a vacuum oven at 120 °C overnight. The cathode and anode of 14.8 and 15.0 mm diameter respectively were punched out from the electrode coatings. The specific capacities of cathode and anode was balanced such that the anode had 10 %

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excess capacity compared to the cathode.[3] The mass balancing of positive and negative electrode were calculated based on the $(N/P)_Q$ capacity ratio 1.1:1. The electrochemical performance of the full cells were evaluated in 2032-type coin cell, with cathode (12 mg cm^{-2}), hard carbon anode (5 mg/cm^{-2}), separated by Celgard polymer containing enough electrolyte to wet the components (~75µl). Each electrochemical test was performed using three independently produced cells to show standard deviations. Na-ion full cells were assembled in a coin cell configuration CR2032 in an argon-filled glove box (Mbraun, H_2O < 0.1 ppm and O_2 < 0.1 ppm). All electrochemical measurements were carried out using Biologic multi-channel potentiostat/galvanostat models VMP3 and BCS at 25 ± 1 °C. Electrochemical impedance spectroscopy (EIS) measurements were carried out on the full cells using a.c. current between 10 mHz – 100 kHz and d.c. amplitude of 10 mV.

2. Supplementary figures

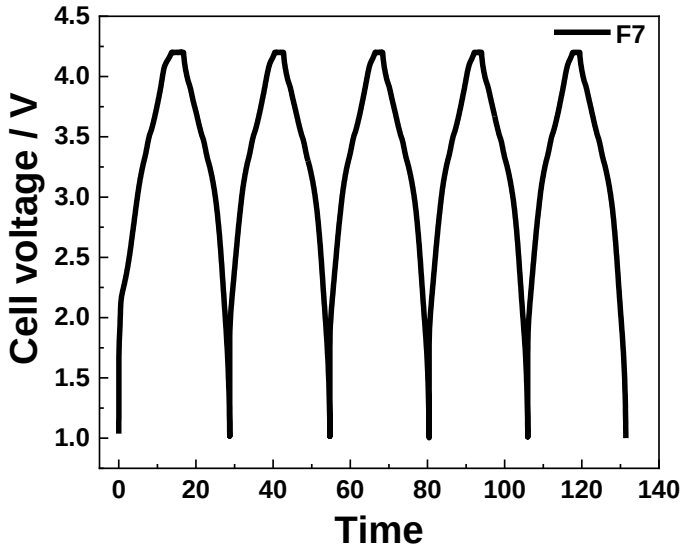

Figure S1 Voltage profile of F7 formation protocol

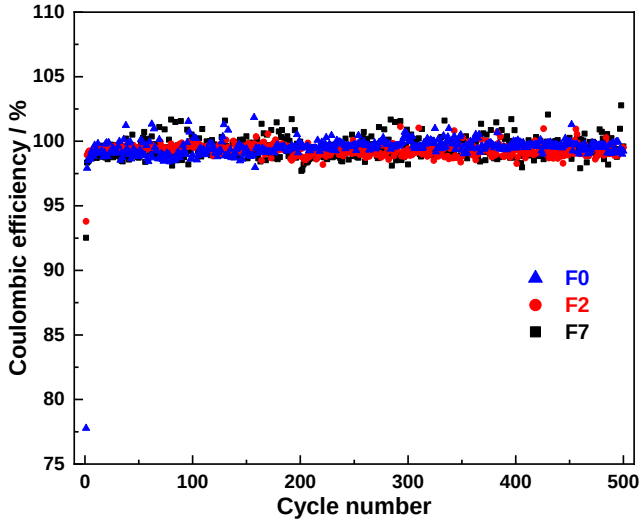

Figure S2 Coulombic efficiency over 500 charge-discharge cycles

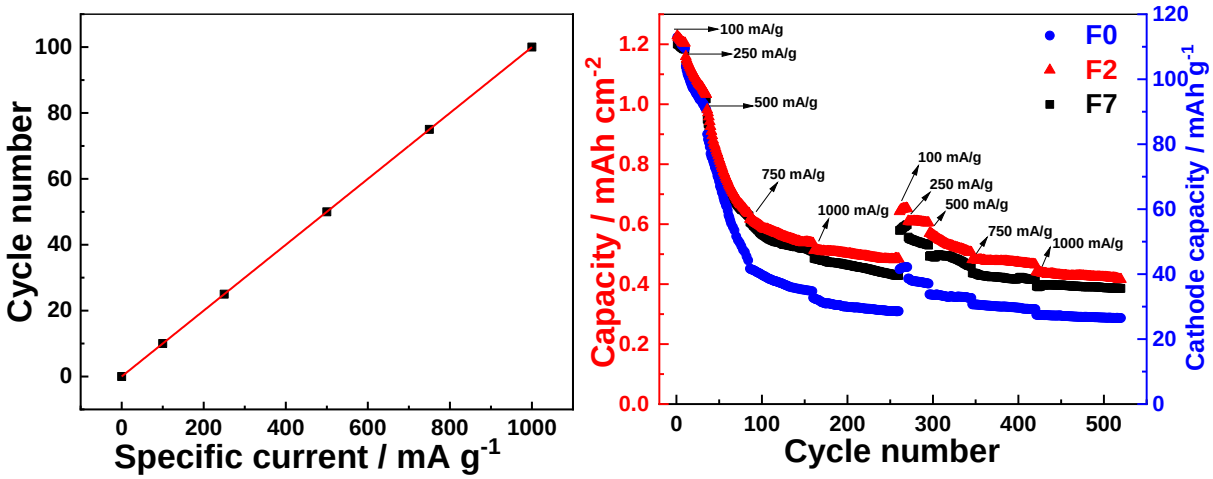

Figure S3 Linear fit of specific current vs cycle number (left) and faster accelerated ageing test for cells after F0, F2 and F7 formations (right).

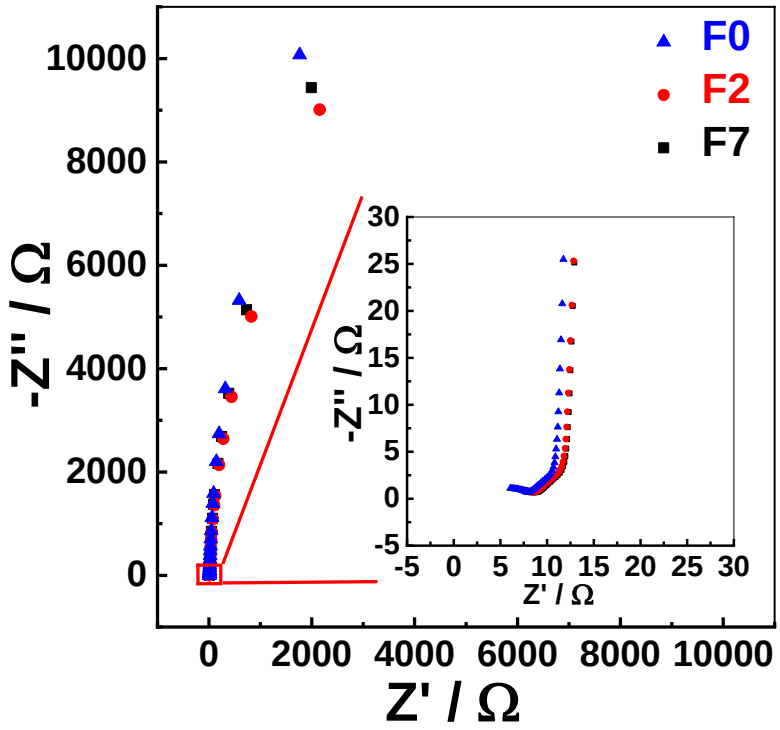

Figure S4 Electrochemical impedance spectra of fresh cells (inset is magnified high frequency region).

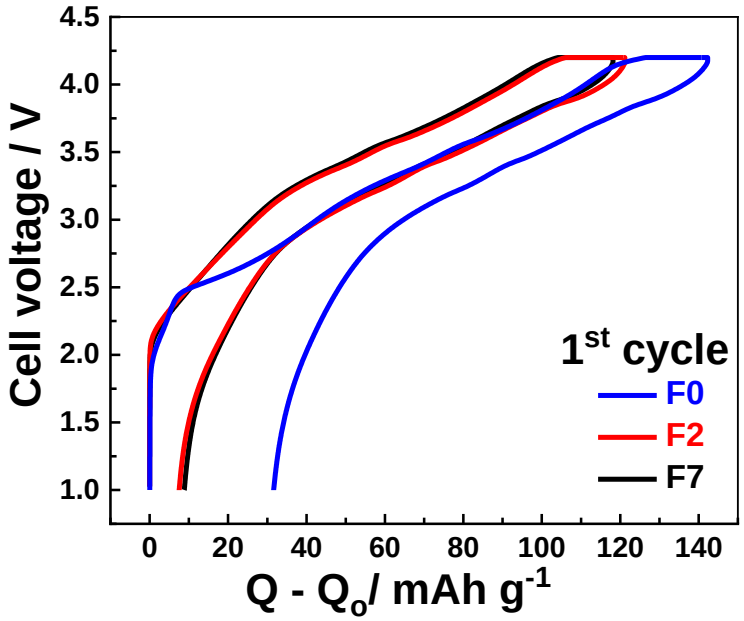

Figure S5 First charge-discharge cycle of cell after F0, F2 and F7 formation.

Table S1 Summary of the specific capacity and fade rates at higher cycling rates of the NIB cells after performing F0, F2 and F7 formation protocols.

Cycle no.	Rate	Specific Capacity ($mAhg^{-1}$ cat)			Fade Rate (% capacity $cycle^{-1}$)		
	mAg^{-1}	F7	F0	F2	F7	F0	F2
1	**100**	110.84	112.93	113.38	0.177	0.383	0.249
10		109.24	109.48	111.14			
11	**250**	104.34	103.99	107.02	0.433	0.556	0.486
35		93.95	90.64	95.35			
36	**500**	87.66	83.08	90.62	0.607	0.792	0.652
85		57.92	44.26	58.70			
86	**750**	56.01	41.68	56.91	0.122	0.121	0.101
160		46.99	32.71	49.46			
161	**1000**	44.90	32.60	47.35	0.054	0.041	0.026
260		39.56	28.58	44.77			
261	**100**	53.45	41.51	59.27	-0.196	-0.073	-0.105
270		55.21	42.17	60.21			
271	**250**	51.40	38.62	56.34	0.105	0.064	0.022
295		48.88	37.09	55.81			
296	**500**	45.49	33.77	52.56	0.063	0.022	0.120
345		42.38	32.67	46.67			
346	**750**	40.38	30.69	44.51	0.028	0.020	0.022
420		38.29	29.22	42.87			
421	**1000**	36.33	27.49	40.77	0.007	0.010	0.024
520		35.60	26.48	38.40			

Table S2 1 Impedance parameters for the cells after F7 and F2 formation and five charge/discharges cycles of cell without formation (F0) and after 500 charge-discharge cycles. The values in brackets represent the deviations.

	After formation cells			After 500 cycles cells		
	F0	**F2**	**F7**	**F0**	**F2**	**F7**
R_s (Ω)	10.3(1)	11.6(1)	11.7(1)	7.9 (1)	9.2(1)	12.1(1)
R_f (Ω)	1401(1)	2085(2)	1796(2)	180(3)	302(2)	312(1)
CPE1 (F s^{a-1})	0.0001	0.0001	0.0001	0.0005	0.0001	0.0004
a1	0.8(0.5)	0.7(0.5)	0.7(0.5)	0.6(0.5)	0.6 (0.6)	0.5(0.9)
R_{ct} (Ω)	--	--	--	227 (1)	52	68(2)
CPE2 (F s^{a-1})	--	--		0.0005	0.0003	0.0001
a2	--	--	--	0.5(0.5)	0.7(0.8)	0.8(0.9)

4. References

1 United States, US20150243983A1, 2015.

2 A. Bauer, J. Song, S. Vail, W. Pan, J. Barker and Y. Lu, *Adv. Energy Mater.*, 2018, **8**, 1702869.

3 J. Kasnatscheew, T. Placke, B. Streipert, S. Rothermel, R. Wagner, P. Meister, I. C. Laskovic and M. Winter, *J. Electrochem. Soc.*, 2017, **164**, A2479–A2486.