Supporting Information

New Insight into Structural Evolution in Layered $NaCrO_2$ during Electrochemical Sodium Extraction

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Table S1 Structural parameters of $NaCrO_2$ obtained from EAXFS measurements at Mn and Ni *K*-edges: interatomic distance (*R*), and Debye-Waller factor (σ^2), and phase correction (ΔE) were refined. Coordination number (CN) was fixed based on the structural model.

Sample	Shell Number	X-Y Pair	CN	***R*** / Å	σ^2/ Å^2	ΔE / eV	***k***-range	R-factor / %
pristine	Cr 1	Cr-O	6	2.008(9)	0.0018 (12)	2.0(15)	2.65-12.15	2.3
	Cr 2	Cr-Cr	6	2.986(8)	0.0016(13)			
3.6 V	Cr 1	Cr-O	4	1.92 (7)	0.002(9)	-0.3(111)	2.7-13.0	0.082
	Cr 2	Cr-O	2	2.03(7)	0.0007(116)			
	Cr3	Cr-Na	2	2.8(14)	0.0009(6355)			
	Cr4	Cr-Cr	2	2.8(23)	0.0005(2313)			
	Cr5	Cr-Cr	4	2.9(4)	0.002(28)			
2.5 V after 3.6 V	Cr 1	Cr-O	6	1.994(12)	0.0007(17)	-0.6(12)	2.65-12.15	2.98
	Cr 2	Cr-Cr	6	2.976(10)	0.0009(11)			

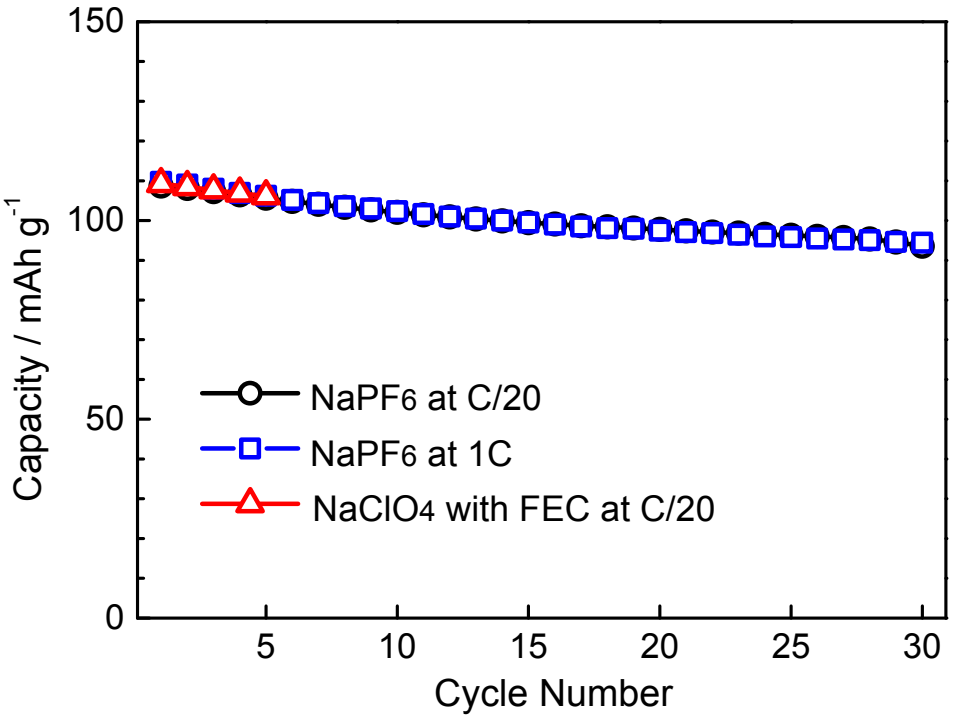

Fig. S1 Discharge capacity retention of Na//$NaCrO_2$ cells with 1.0 mol dm^{-3} $NaPF_6$/PC electrolyte solution at C/20 and 1C rate (1C = 250 mA g^{-1}) and 1.0 mol dm^{-3} $NaClO_4$/PC with 2 vol % FEC in the voltage ranges of 2.5 – 3.5 V.

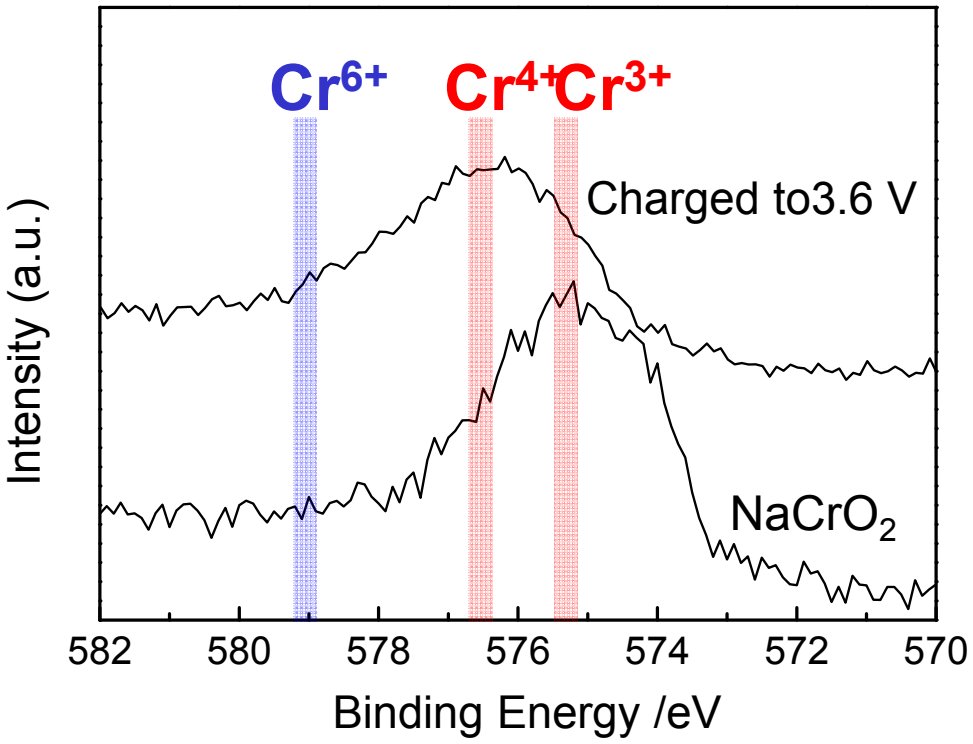

Fig. S2 Cr $2p_{3/2}$ XPS spectra of $NaCrO_2$ electrodes before and after charge to 3.6 V. Energy shift of a peak at about 575 eV was observed, whereas a peak attributed to Cr^{6+} at 579 eV was not seen.