Supporting information

of

NaCrO₂ cathode for high rate sodium-ion batteries

by

Chan-Yeop Yu^a, Jae-Sang Park^a, Hun-Gi Jung^b, Kyung-Yoon Chung^b, Doron Aurbach^{d,*}, Yang-Kook Sun^{c,*} and Seung-Taek Myung^{a,*}

^aDepartment of Nano Science and Technology, Sejong University 98 Gunja-dong, Gwangjin-gu, Seoul, 143-747, South Korea

^bCenter for Energy Convergence, Korea Institute of Science and Technology, Seoul 136-791, South Korea

^cDepartment of Energy Engineering, Hanyang university, Seoul 133-791, South Korea ^dDepartment of Chemistry, Bar Ilan University, Ramat-Gan, 5290000, Israel.

*Corresponding authors: <u>smyung@sejong.ac.kr</u>, <u>yksun@hanyang.ac.kr</u>, Doron.Aurbach@biu.ac.il

Experimental details:

To confirm the presence of NaOH and Na₂CO₃ in the cathode materials, pristine and cycled active materials were examined using a time-of-flight secondary ion mass spectroscope (ToF-SIMS, UNVAC-PHI TFS2000, PerkinElmer, USA) surface analyzer operated at 10^{-9} Torr and equipped with a liquid Bi ion source and pulse electron flooding. During the analysis, the targets were bombarded by 10 keV Bi beams with a pulsed primary ion current varying from 0.3 to 0.5 pA. The total collection time was 100s and was over a 200 μ m × 200 μ m area.



Figure S1. XRD patterns of the series of samples produced in the course of NaCrO₂ synthesis.



Figure S2. SEM images of (a) bare and (b) C-NaCrO₂ (3.4 wt. %) powders.



Figure S3. XRD patterns and TEM images with various carbon contents with (a) 1.4 wt.%, (b) 3.4 wt.%, (c) 7.3 wt.%, and (d) 14.6 wt.% pitch added. The scale bars in the TEM images correspond to 5 nm.

Table S1. Lattice parameters, carbon content and electric conductivity as a function of the amount of pitch added. The lattice parameter results are based on the Rietveld refinement method. The quantity of carbon was measured by a CHN analyzer and the conductivity was determined by the four-point probe method.

	Lattice parameters			Contrar contents (set 0/	Electric conductivity / S cm-1	
	a-axis / Å	c-axis / Å	<i>R</i> wp / %	Carbon content [®] / wt. %	Electric conductivity / S cill ·	
NaCrO ₂ (0 wt. %) ^a	2.9753(1)	15.9656(5)	11.1	-	2.6 ×10 ⁻⁶	
NaCrO ₂ (2 wt. %) ^a	2.9752(1)	15.9656(5)	12.2	1.4	4.4 ×10 ⁻³	
NaCrO ₂ (5 wt. %) ^a	2.9752(1)	15.9655(5)	13.7	3.4	1.4 ×10-2	
NaCrO ₂ (10 wt. %) ^a	2.9752(1)	15.9655(5)	13.9	7.3	1.1 ×10 ⁻¹	
NaCrO ₂ (20 wt. %) ^a	2.9752(1)	15.9655(5)	14.2	14.6	4.7 ×10 ⁻¹	

a: added amount of pitch

b: analyzed amount of carbon by CHN analyzer



Figure S4. (a) Comparison of the XRD patterns of the bare and carbon-coated $NaCrO_2$ after exposure to ambient air during 2 days and (b) the resulting ToF-SIMS spectra after exposure of bare $NaCrO_2$ to air during 2 hours, etched with Bi⁺ for 100s. After the exposure to air, the surface is composed of two layers, Na_2CO_3 layer (outermost) and NaOH layer (inner), as demonstrated by the increase of the relative intensity of NaOH⁺ fragment (m= 39.99) while decrease of that of NaC⁺ fragment (m=34.98) with Bi⁺ etching.



Figure S5. Voltage profiles and corresponding differential curves of (a) bare and (b) C-NaCrO₂ during charge and discharge.



Figure S6. Continuous charge and discharge profiles obtained at 20 mA g⁻¹; (a) conducting agent (C.A.)-free bare NaCrO₂ (top) and C.A.-free C-coated NaCrO₂ (with 3.4 wt.% of residual carbon as carbon coating layers) (bottom); (b) 4.4 wt. % of C.A. (KS-6 and Super-P with 1:1 in weight)-added bare NaCrO₂ (top) and 1 wt. % of C.A.-added C-coated NaCrO₂ with 3.4 wt.% of residual carbon (bottom), in which total amount of carbon was fixed to 4.4 wt.% for both composite electrodes; (c) rate capability of 4.4 wt. % of C.A.-added bare NaCrO₂ and (d) 1 wt. % of C.A.-added C-coated NaCrO₂ with 3.4 wt.% of residual carbon. For the rate test, the cells were first cycled at 20 mA g⁻¹ and then charged at 20 mA g⁻¹ prior to discharge at various currents.

We tested the bare and the C-NaCrO₂ (3.4 wt. % of residual carbon contained) by reducing the amount of the C.A. to 0 and 4.4 wt. % for the bare NaCrO₂ and 0 and 1 wt. % for the C-NaCrO₂ to equalize the amount of carbon in both electrodes (Figure S6). The C.A.-free NaCrO₂ did not show capacity (Figure S6a), while the C-NaCrO₂ without C.A. could deliver a discharge capacity approximately 102 mAh (g-oxide)⁻¹ with good

capacity retention. Addition of the CA 4.4 wt. % obviously improved the capacity delivery compared to that of C.A.-free bare NaCrO₂ (Figure S6b). However, the cycling performance was very disappointing for the bare NaCrO₂. Meanwhile, the C-NaCrO₂ was able to maintain the high capacity approximately 120 mAh g⁻¹ during cycling. For the rate test, the cells were first cycled at 20 mA g⁻¹ and then charged at 20 mA g⁻¹ prior to discharge at various currents. The bare NaCrO₂ cell was inactive at the rates higher than 3C (Figure S6-c), whereas the C-NaCrO₂ could deliver the discharge capacity approximately 106 mAh g⁻¹ at 20 C-rate (Figure S6-d). These data reflect that the carbon coating layers give significant improvement in the electric conductivity of the active mass up to 10^{-1} S cm⁻¹, which affects the high capacity retention during prolonged cycling and enabled to obtain high capacity at high rates though the added amount of C.A. was lowered to 1 wt. % for the composite electrode comprising the C-NaCrO₂.



Figure S7. Continuous charge and discharge profile of C-NaCrO₂ tested in FEC-free electrolyte at 20 mA g^{-1} (top); and the resulting rate performance (bottom). For the rate test, the cells were first cycled at 20 mA g^{-1} and then charged at 20 mA g^{-1} prior to discharge at various currents.



Figure S8. Rate capabilities of (top) bare $NaCrO_2$ and (bottom) C-NaCrO₂ electrodes presented by voltage profiles. For the rate test, the cells were first cycled at 20 mA g⁻¹ and then charged at 20 mA g⁻¹ prior to discharge at various currents.

Electrode Materials	Space group	Voltage range	Initial Capacity (mAh g ⁻¹)	Cycle retention @ 10 th cycle	Rate capability @ 1 C-rate	Refer ence
O3-NaCrO ₂	R-3m	2.0 V - 3.6 V	121	≥99%	≥99%	Ours
O3-NaMnO ₂	C2/m	2.0 V - 3.8 V	180	80%	No Info.	12
P2-Na _{0.6} MnO ₂	P6 ₃ /mmc	2.0 V - 3.8 V	160	40%	No Info.	13
O3-NaVO ₂	R-3m	1.2 V – 2.4 V	120	\geq 99%	No Info.	14
P2-Na _{0.6} VO ₂	P6 ₃ /mmc	1.2 V – 2.4 V	100	\geq 99%	No Info.	14
O3-NaNi _{0.5} Mn _{0.5} O ₂	R-3m	2.0 V - 3.8 V	125	95%	84%	15
$O3-NaFe_{0.5}Mn_{0.5}O_2$	R-3m	1.5 V – 4.3 V	190	$\geq 80\%$	70%	16
P2- NaFe _{0.5} Mn _{0.5} O ₂	P6 ₃ /mmc	1.5 V – 4.3 V	120	$\geq 80\%$	No Info.	16
$O3\text{-}NaNi_{0.25}Fe_{0.5}Mn_{0.25}O_2$	R-3m	2.1 V – 3.9 V	140	$\geq 98\%$	$\geq 90\%$	17
$O3\text{-}NaNi_{0.33}Fe_{0.33}Mn_{0.33}O_2$	R-3m	2.0 V - 4.0 V	120	$\geq 99\%$	75%	18
O3- NaNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	R-3m	2.0 V - 3.75 V	120	$\geq 99\%$	75%	19

 Table S2. Comparison of the electrochemical performances of layered cathode materials for sodium ion batteries.