Supporting Information

Generalized synthesis of NaCrO₂ particles for high-rate sodium ion batteries prepared by microfluidic synthesis in segmented flow

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Least-squares crystal structure refinements were carried out on the basis of the structure models of NaCrO₂,¹ NaFeO₂,² Na_{1-x}CoO₂,³ and NaAlO₂ ⁴ using TOPAS Academic 4.1⁵ and applying the fundamental parameter approach for reflections profiles in a window of $0.5 \le Q/Å \le 8.0$. The background (defined by a 20-30-parameter polynomial depending on the background) was refined always in the initial step. Background, cell parameters, zero-point, scale, peakwidth, shape and asymmetry, crystallite sizes, one overall displacement parameter and the positional parameters of the atoms were refined. Anisotropic pseudo-Voigtian peak broadening, modeled by using the Stephens peakshape macro,⁶ was applied to the peak shapes. Convergence was assumed to have been achieved when the parameter shifts in the final cycle of refinement were less than ten percent of the associated estimated standard deviation (e.s.d.). The results of the refinements are compiled in Table 1.

NaCrO₂

The crystal structure reported by Scheld and Hoppe¹ was used as starting point for the refinement. The starting value for the lattice constants were set at a = b = 2.9747 Å and c=15.9538 Å and refined. The scale factor was refined in the next step. Subsequently, the Stephens peakshape macro⁶ (4 parameters) and preferred orientation⁷ (8 parameters) were introduced and refined for the anisotropic peak shape. In the last step, all previous variables and the atom positions (those variables that are not fixed by symmetry, i.e. the z – parameter of O and one common isotropic thermal parameter of all atoms) were refined step by step until convergence.

NaFeO₂

The crystal structure reported by Grey, Hill and Hewat² was used as starting point for the refinements of β -NaFeO₂, because the structures of the other polymorphs could be excluded. The starting values for the lattice constants were set at *a* = 5.672 Å, *b* = 7.136 Å and *c* = 5.377 Å and refined. The scale factor was refined in the next step. Subsequently, preferred orientation⁷ (8 parameters) was introduced and refined for the anisotropic peak shape. In the final step all variables (including atom parameters, and thermal parameters which are not fixed by symmetry) were refined step by step.

Na_{0.74}CoO₂

The crystal structure reported by Suan et al.³ was used as starting point for the refinements of Na_{0.74}CoO₂. The starting values for the lattice constant a = b and c was set at 2.831 Å and 10.9 Å and refined. 15.96 Å. In the next step the scale factor was refined. The parameters for preferred orientation⁷ (8 parameters) were applied and refined for the anisotropic peak shape. In the last step,

all variables (that are not fixed by symmetry) including isotropic parameters and occupancies of the Na atoms were refined step by step. For $Na_{1-x}CrO_2$ (x = 0) the O3-type is preferred due to stochiometry, while the P2-type would be favored for lower Na contents (increasing x).

NaAlO₂

The crystal structure reported by Takeda et al.⁴ was used as starting point for the refinements of β -NaAlO₂, because the structures of the other polymorphs could be excluded The starting values for the lattice constants were set at *a* = 5.3871 Å, *b* = 7.032 Å and *c* = 5.218 Å and refined. The scale factor was refined in the next step Subsequently, the preferred orientation⁷ (8 Parameters) was introduced and refined for the anisotropic peak shape. In the last step, all variables (including atom parameters, and thermal parameters that are not fixed by symmetry) were refined step by step.

Table S1. Rietveld refinement results for NaCrO₂.

Crystal data:

		NaCrO ₂	β-NaFeO ₂	Na _{0.74} CoO ₂	β-NaAlO ₂
Space group		R-3m(166)	Pna2 ₁ (33)	P6 ₃ /mmc(194)	Pna2 ₁ (33)
<i>a</i> (Å)		2.9719(8)	5.6709(2)	2.8259(1)	5.3777(3)
$b(\mathbf{A})$		2.9719(8)	71416(4)	2.8259(1)	7.0324(5)
$c(\dot{A})$		15.971(2)	5.3835(2)	10.955(5)	5.2186(3)
$V(Å^3)$		122.17(7)	218.03(3)	75.41(3)	197.36(3)
Structure type		03	b-NaFeO ₂	P2	b-NaFeO ₂
Crystal size (nm ³)		100 (10)	500(30)	7705 (200)	900 (60)
21920		ref. 1	ref. 2	ref. 3	ref. 4
Atom	ic coordinates	and B(Å ²) val	lues:		
Na1	x	0	0.0673(2)	0	0.06637
1141	V	Ő	0.0079(2) 0.1250(2)	ů 0	0.62415
	J Z	Ő	0.0373(3)	05	0.0485
	B	0.30(2)	0.0575(5) 0.76(7)	1	0.63(4)
	Occ	1	0.70(7)	0.5(1)	0.05(1)
Na2	x			0.6667	
1142	V			0.3333	
	Z			0.25	
	B			1.00(3)	
	Occ			0.24(8)	
М	Х	0	0.3830(1)	0	0.06101
	v	0	0.1671(9)	0	0.12513
	Z	0.5	0.1152(8)	0	0.067
	В	0.30(2)	0.66(2)	0.88(9)	0.08(7)
01	х	0	0.4269(6)	0.4269(6)	0.0306
	у	0	0.1173(7)	0.1173(7)	0.079
	Z	0.2325	0.5642(6)	0.5642(6)	0.3969
	В	0.30(2)	0.53(5)	0.48(7)	1.00(3)
O2	х		-0.0393(13)		0.3763
	y		-0.0908(9)		0.1747
	Z		0.1980(9)		0
	В		0.97(9)		0.61(4)
Agree	ement indices:				
R _{wm} (%)		5.45	7.60	9.45	3.26
R_{ovn} (%)		3.35	2.96	3.25	3.09
Variables		79	57	70	46
Bkg. Terms		30	21	30	20
0					

Particle	diameter
1	58 392
2	83.824
3	93.971
4	94.234
5	98.830
6	104.392
7	106.216
8	113.396
9	233.608
10	340.052

 Table S2. Size evaluation for selected NaCrO2 crystallites in the reaction product.



Figure S1. Preliminary test for the formation of an emulsion by ultrasonication.



Figure S2. XRPD pattern of the synthesis with an annealing temperature of 300° C. Ticks shows the calculated values of the reflections for NaCrO₂.



Figure S3. (A) SEM image of an annealed NaCrO₂ sample with the corresponding elemental EDX mapping of (B) Cr and (C) Na (green and red dots) and an (D) overview spectra.



Figure S4. HRTEM image of NaCrO₂ crystallites with plate-like "hexagonal" morphology. Some particles are aligned so that the layer direction is perpendicular to the viewing direction, while other particles (on the edge) are rotated by 90° so that individual layers can be seen.



Figure S5. Laser scanning microscopy images of pre-annealed NaNO₃ and $Cr(NO_3)_3$ inside Tween "nanoreactors" with (A) low and (B) high magnification.



radii $R_{\rm H}$.



Figure S7. ²³Na-NMR spectra of (A) the preannealed sample measured at a frequency of 20 (black) and 25 kHz (red) and (B) the annealed sample measured at a frequency of 20 (black), 25 (red) and 28 kHz (blue), to determine the satellite signals. The sharp signal at -267 ppm is a spinning sideband.



Figure S8. ¹H-NMR before (black) and after annealing (red). The signal with low intensity in the red spectrum arises from background



Figure S9. IR spectra of $NaCrO_2$ sample after annealing at temperatures between 400 and 800°C. The spectra show no vibrational bands of nitrate, nitrate or peroxide anions or organic groups. Thus, the samples are free of crystalline or amorphous molecular impurities.

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