

Electronic Supplementary Information

"Redox Properties of Alluaudite Sodium Cobalt Manganese Sulfates as High-Voltage Electrodes for Rechargeable Batteries"

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Analytical methods

X-ray powder diffraction: The XRD data were carried out on Bruker D8 Advance diffractometer with CuK α radiation in the range from 5.3° to 80° 2 θ with a scanning step of 2 θ = 0.02° and counting time 1s/step.

The Rietveld refinement procedure includes several steps. Initially, the structure is refined by soft constraints consisting of all S-O bond lengths and thereafter they are released in the final cycles without causing any substantial structural distortions before reaching convergence. All the atoms are refined isotropically. Due to the expectation of some similar U_{iso} values for the O atoms, they are refined in a group. The same approach is selected for the Na atoms as well as for the Mn and Co atoms (in the primitive lattice case). The ratio between Co and Mn atoms occupying single 8f position is fixed at that determined from chemical analysis (i.e. Co/Mn=0.63/0.37). Neutral atomic scattering factors, as these are stored in GSAS, were used for all atoms. No corrections were made for absorption.

Electrochemical experiments: The electrochemical Li⁺ intercalation into investigated compound was accomplished by using two-electrode cells type Swagelok consisting of Li|LiPF₆(EC:DMC)|Na₂(Co_{0.63}Mn_{0.37})₂(SO₄)₃. The positive electrodes, supported onto an aluminum foil with high purity, were a mixture containing 80% of the active compositions, 5% poly(vinylidene fluoride) (PVDF), 7.5% C-ENERGY KS 6 L graphite (TIMCAL) and 7.5% Super C65 (TIMCAL). The loaded mass of active materials on Al collectors was about ~3.5 mg. 1 M LiPF₆ solution in ethylene carbonate–dimethyl carbonate (1:1 by volume) was used like electrolyte with less than 20 ppm of water. The lithium electrodes consisted of a pure lithium metal disk with diameter of 10 mm. The cells were assembled in a dry box under argon atmosphere. The Arbin BT2000 system with eight-channels in galvanostatic mode was used for electrochemical tests. The charge and discharge rates were expressed as C/h, where h is the time interval in hours, needed for the insertion of one lithium ion per formula unit at the applied current intensity. The model lithium cells were cycled between 5.0 and 1.8 V at C/50 rate. The electrochemical cells were disassembled inside a dry box.

Electron Paramagnetic Resonance: The coordination of Mn ions inside double sulfate salts was determined by a Bruker EMXplus EPR spectrometer operating in the X-band (i.e. at 9.4 GHz) and in the temperature range of 120–295 K.

Thermal analysis: The DTA/TG curves for the sample were measured using LABSYS™ EVO (Setaram, France) apparatus in the temperature range of 30–400 °C at a heating rate of 5 °C min⁻¹ in air atmosphere.

Scanning electron microscopy/Energy dispersive X-ray spectroscopy: SEM experiments of the tested materials were conducted on JSM 6390 electron microscope (Japan) in conjunction with EDS (Oxford INCA Energy 350) in regimes of secondary electron image (SEI). The accelerating voltage was 20 kV. The specimens were coated with gold before the analysis for less than one minute.

Figure S1. XRD pattern of mixed cobalt-manganese hydrated salt with blödite-type structure $\text{Na}_2\text{Co}_{0.63}\text{Mn}_{0.37}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

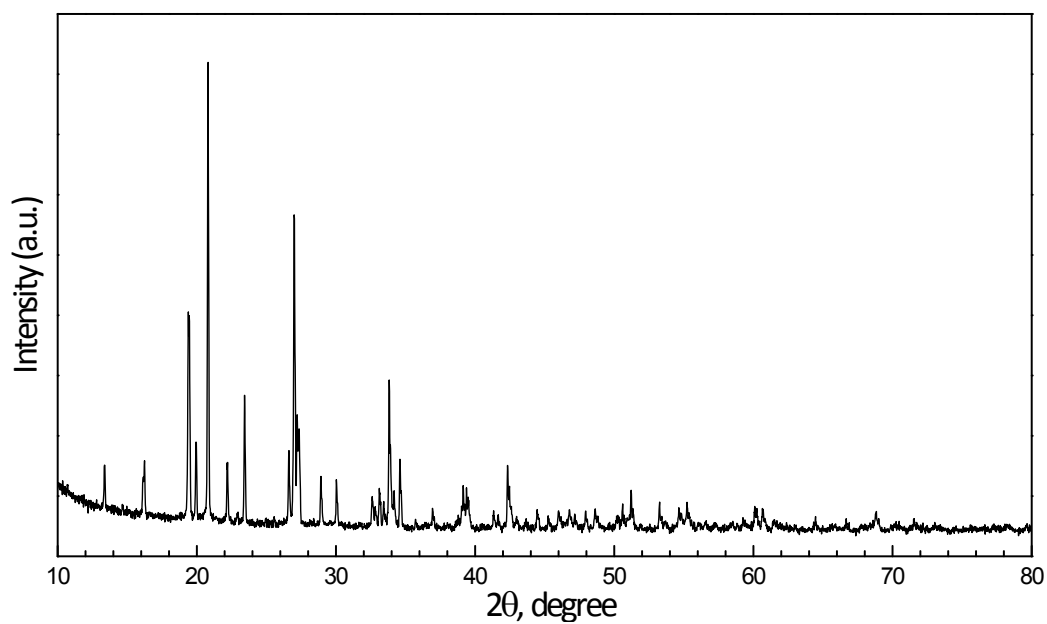


Figure S2. DTA and TG curves of mixed cobalt-manganese hydrated salt with blödite-type structure $\text{Na}_2\text{Co}_{0.63}\text{Mn}_{0.37}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

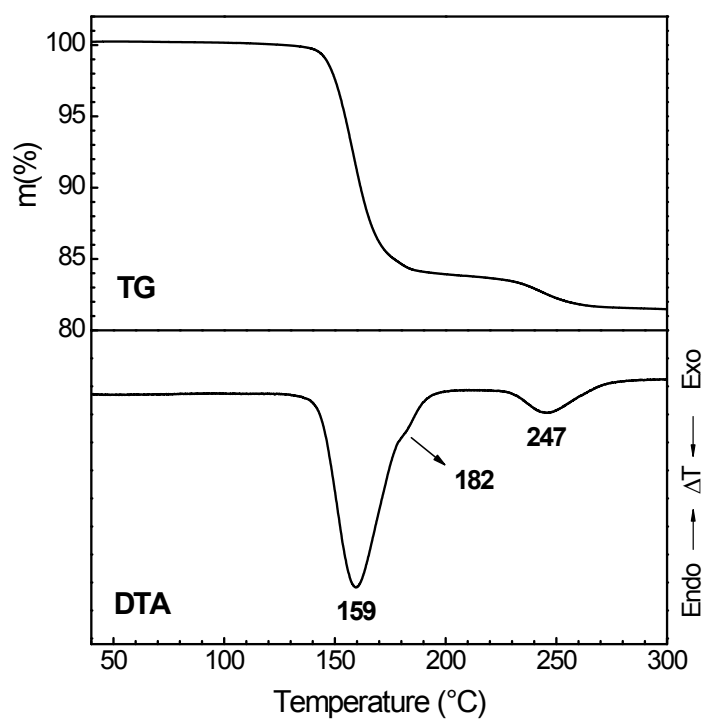
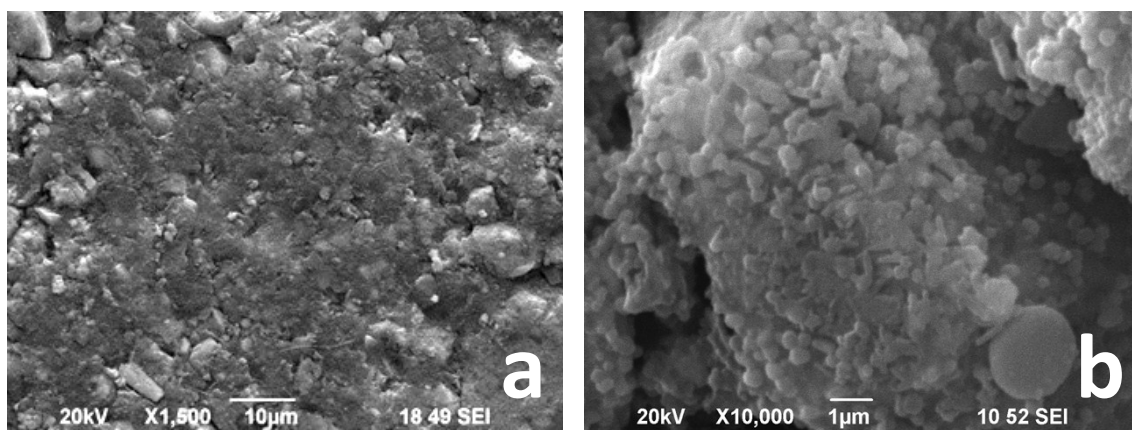


Table S1. Crystallographic data and results of the Rietveld refinement of $\text{Na}_2(\text{Co}_{0.63}\text{Mn}_{0.37})_2(\text{SO}_4)_3$ and $\text{Na}_6\text{Co}(\text{SO}_4)_4$

Powder data statistics/ Formula unit	$\text{Na}_{2.68}(\text{Co}_{0.63}\text{Mn}_{0.37})_{1.86}(\text{SO}_4)_3$	$\text{Na}_6\text{Co}(\text{SO}_4)_4^*$
1	2	3
Space group	<i>C2/c</i> (15)	<i>P2₁/c</i> (14)
Cell parameters:		
<i>a</i> (Å)	12.646(1)	9.719(0)
<i>b</i> (Å)	12.773(1)	9.236(1)
<i>c</i> (Å)	6.511(0)	8.264(0)
angles (°) α	90.000	90.000
angles (°) β	115.425(3)	113.529(20)
angles (°) γ	90.000	90.000
<i>V</i> (Å ³)	949.86(10)	680.06(28)
Calculated unit cell Fw	1826.762	1162.194
Z	4	4
P_{calc} (g cm ⁻³)	3.194	2.838
Wavelength (Å)	1.5419	1.5419
2 θ range (deg)	10-80	10-80
Step-scan increment (2 θ), deg	0.02	0.02
Step-scan time, s	35	35
No of data points	3487	3487
No of contributing reflections	1480	1480
No of varied parameters	79	79
Profile function	Pseudo-Voigt	Pseudo-Voigt
R_{wp}	0.0710	0.0710
R_{p}	0.0501	0.0501
R_{F}^2	0.1114	0.1114
χ^2	1.168	1.168
Wt. Frac. %	86	14

* The atomic parameters for phase $\text{Na}_6\text{Co}(\text{SO}_4)_4$ are not included in the refinement.

Figure S3. The SEM images at different magnifications (a – x1 500 and b – x10 000) of the electrode cycled 25 cycles between 2.0 and 5.0 V, followed by 10 cycles between 1.8 and 5.0 V.



EDS data (averaged values) for the electrode cycled 25 cycles between 2.0 and 5.0 V, followed by 10 cycles between 1.8 and 5.0 V

Element	Na	Mn	Co	S	O
At.%	13.62	3.56	5.64	15.70	61.48

Figure S4. The first derivatives of charge/discharge curves for $\text{Na}_{2+2\delta}(\text{Co}_{0.63}\text{Mn}_{0.37})_{2-\delta}(\text{SO}_4)_3$ cycled between 2.0 and 5.0 V (first 25 cycles), followed for the next 10 cycles between 1.8 and 5.0 V. The cell cycling starts with a charge using a C/50 rate.

