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$NaAlNb(PO_4)_3$ NASICON-type phosphate with the $Nb^{5+}/Nb^{4+}/Nb^{3+}$ multielectron redox activity on sodium intercalation

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Synthesis of $NaAlNb(PO_4)_3$. In the typical synthetic procedure 0.008 mol (0.9203 g) of $NH_4H_2PO_4$ (RusChim), 0.004 mol (0.4800 g) of NaH_2PO_4, 0.004 mol (1.3565 g), $Al(NO_3)_3 \cdot 7H_2O$ (Sigma-Aldrich) and 0.004 mol (1.7886 g) of $NH_4[NbO(C_2O_4)_2] \cdot 8H_2O$ (Sigma-Aldrich) were dissolved separately in deionized water (25 ml for each reagent). To form a chelating polymer matrix, 10 g of citric acid monohydrate $C_6H_8O_7 \cdot H_2O$ were melted upon heating and mixed with the 10 ml of 5% water suspension of polyvinyl alcohol $(C_2H_4O)_n$. The gel obtained after water evaporation on heating was carbonized by calcination in an open cup. The resulted black amorphous powder was pre-heated in air (13 h at 450 ºC) to oxidize residual carbon and after that ball-milled (2 h at 350 min^{-1}), and then annealed in air at 675 ºC during 20 h. At T > 675 ºC the melting of the sample was observed, lower temperature leads to poor crystallinity of the phase. EDX analysis showed us, that Na : Al : Nb : P ratio is 1.00(2) : 1.05(2) : 1.05(5) : 2.85(2), which correlates with the $NaAlNb(PO_4)_3$ formula.

Crystal structure refinement resulted in reasonable *R*-factors ($R_I = 0.038$, $R_p = 0.0136$, $R_{wp} = 0.0171$, GOF = 1.71) with an acceptable fit of the experimental data [Figure 1(*a*)], and the reliable structural parameters and interatomic distances typical for all elements were achieved (Tables S1, S2). $NaAlNb(PO_4)_3$ adopts a NASICON-type 3D framework. MO_6 octahedra are almost regular with d(M–O) = 1.91–1.90 Å. Na atoms occupy a trigonal-antiprismatic Na1 site (6*b*), while Na2 position (18*c*) with 8-fold coordination was found to be empty according to the Fourier analysis. The deviation of Na1 site occupancy from 1 apparently arises from high mobility of Na^+ ions within the NASICON framework,[S1] so about 20% of sodium are disordered among low-occupied positions and hardly detectable by X-ray powder diffraction.

Table S1 Structural parameters obtained from Rietveld refinement for the pristine $NaAlNb(PO_4)_3$ structure.

Atom	Position	Occupancy	x/a	y/b	z/c	U_{iso}, Å^2	BVS
Na1	6*b*	1	0	0	0	0.055(2)	1.03
Al1/Nb1	12*c*	0.5Al/0.5Nb	0	0	0.14504(8)	0.034(7)	Al/Nb 2.95/5.75
P1	18*e*	1	0.2852(4)	0.2852(4)	0.25	0.011(1)	4.87
O1	36*f*	1	0.4722(3)	0.3035(7)	0.2440(3)	0.008(1)	2.06
O2	36*f*	1	0.2028(5)	0.1758(5)	0.3081(2)	0.008(1)	2.00

Table S2 Selected interatomic distances for the $NaAlNb(PO_4)_3$ structures.

Distance/Å	
Na(1) – O(1)	6 × 2.767(2)
Nb(1)/Al(1) – O(1)	3 × 1.914(2)
Nb(1)/Al(1) – O(2)	3 × 1.904(2)
P(1) – O(1)	2 × 1.55(2)
P(1) – O(2)	2 × 1.54(2)

$NaAlNb(PO_4)_3$/C synthesis. A mixture of pure $NaAlNb(PO_4)_3$ sample and PAN (13 wt%) was treated with dimethylformamide (DMFA) and then rinsed with ethanol to eliminate DMFA excess. The obtained slurry was dried at 75 °C in air and annealed in high-pure argon flow (2 h ramping, 2 h at 650 °C) followed by quenching. Residual carbon content was estimated as 7% by TG measurements.

Materials characterization. The phase composition of the samples and the electrodes (*ex situ*) was analyzed using X-ray powder diffraction (XRPD) data collected on a Huber Guinier camera G670 (transmission mode, Image Plate detector, CuKα_1 radiation λ = 1.54051 Å, curved Ge (111) monochromator, 3–100º 2θ angular range, 0.03º s^{-1} scanning rate).

The morphology of the samples was investigated in scanning electron microscope JEOL JSM – 6390- LA with built-in X-ray analyzer EX-230. The samples were glued on a metal table using a conductive carbon adhesive tape. The accelerating voltage of the electron gun was 5–20 kV. Images were obtained in primary electrons. Thermogravimetric (TG) study was performed by Netzsch STA 449C thermal analyzer in the 25–800 ºC range in the artificial air [20% $O_2(g)$ + 80% Ar(g)] atmosphere with the heating rate of 5 ºC min^{-1}.

The electrical conductivity of the electrodes was measured by the four-probe method using a Loresta GP MCP T610 resistivity meter (Mitsubishi Chemical, Tokyo, Japan). The electrode films for the conductivity measurement were prepared from the electrode slurries obtained as described above.

XANES measurements. Nb *K*-edge X-ray absorption near-edge spectroscopy (XANES) data was registered in the *ex situ* mode on a laboratory spectrometer of the Department of Radiochemistry, Moscow State University (Moscow, Russia). The spectrometer is based on the geometry of Rowland circle (0.5 m) and is equipped by an X-ray tube with a silver anode and a silicon drift detector (SDD; Amptek Inc.).[S2] To monochromatize and focus the spherical beam (2.5 mm radius), a bent Ge crystal was applied to scan the energy range 18900−19100 eV for niobium (reflections 12 12 0) *K*-edge. Data were collected in the reflection mode; each spectrum represents ten combined spectra that were merged and normalized with the IFEFFIT programme.[S3]

Electrochemical measurements. The electrochemical measurements were carried out using Swagelok-type two electrode cells with Al and stainless steel current collectors, glass-fiber separators and sodium metal as a counter electrode. 1 M $NaPF_6$ solution in 1 : 1 vol. ethylene carbonate (EC) : diethyl carbonate (DEC) (Kishida Chemicals) was employed as electrolyte. The working electrodes were prepared by mixing the carbon-coated $NaAlNb(PO_4)_3/C$ material, Super P carbon black, and polyvinylidene difluoride (PVDF, Solef 5130, Solvay S.A.) in a weight ratio of 75 : 15 : 10 with N-methyl-2-pyrrolidone (NMP, Acros Organics) as a solvent. The homogenous slurry was then casted on aluminum foil by Doctor Blade technique and dried overnight. Then it was rolled and punched into 16 mm discs, that were dried overnight at 100 °C under dynamic vacuum ($p < 10^{-2}$ atm).

For extended cycling, the $NaAlNb(PO_4)_3$-based composite electrodes was prepared by adding 2% of single-walled carbon nanotubes TuballTM (SWCNT, OCSiAl, length > 5 μm, G/D ratio > 40) to the carbon-coated $NaAlNb(PO_4)_3/C$ material. In this case the required amount of SWCNT was mixed with a 1 wt% aqueous solution of Carboxymethyl cellulose (CMC), which was applied as a stabilizer and as a binder. The resulting mixture was dispersed using an ultrasonic disperser with an immersion probe (Vibra-Cell VCX 750, Sonics Materials Inc., 20 kHz) for 10 min, mixed with the active material ($NaAlNb(PO_4)_3/C$) and stirred for 12 h. Then, the obtained viscous dispersion was casted on the graphitized aluminum foil (Gelon, China), with an active $NaAlNb(PO_4)_3$ content around 85%.

Table S3 Electrical conductivity of $NaCrNb(PO_4)_3$-based electrode materials.

Sample	σ/S cm^{-1}
$NaAlNb(PO_4)_3$	$< 10^{-7\,a}$
$NaAlNb(PO_4)_3$/C	$7{\cdot}10^{-2}$
$NaAlNb(PO_4)_3$/C@SWCNT	1.5×10^{0}

[a] the value is located beyond the measurable range

The further procedure for electrode preparing was similar to that described above. The loading of the active material on the electrodes was about 1.5–2.0 mg cm^{-2}. The capacity values were calculated based on the mass of the active material, 1C refers to 123 mA g^{-1} based on two electron transfer.

Electrochemical cells were assembled in an Ar-filled glove box (MBraun, $pO_2 < 0.1$ ppm, $pH_2O < 0.1$ ppm). The galvanostatic cycling and cyclic voltammetry measurements were performed at room temperature using Elins P20x8 potentiostat-galvanostat.

Thermal stability investigations. Thermal stability of the electrode materials was explored by differential scanning calorimetry (DSC) using a Netzsch DSC 204 F1 Phoenix instrument within the temperature range 50–450 °C (5 °C min^{-1} heating rate) in argon atmosphere. Hard carbon (HC) was synthesised by Bobyleva according to the route described in the following article.[S4] Sodiated electrodes (fully charged on C/15 rate to 0.8 V and 10 mV *vs.* Na^+/Na for $NaAlNb(PO_4)_3$ and hard carbon respectively) were extracted from electrochemical cells, washed with dimethyl carbonate (DMC), dried under vacuum, and then electrode materials were scrapped from the current collector. The resulting powders (about 6 mg), either separately (‘dry’) or in the presence of an about 5µl electrolyte (‘wet’), were placed in sealed crucibles made of high-pressure Cr–Ni stainless steel in an Ar-filled glove box. The electrode powder: electrolyte mass ratio was chosen as 1 : 1 to ensure an excess of electrolyte during the experiment. To calculate the magnitude of the thermal effect, the area under the peak on the DSC curve was considered with subtraction of the background using the Netzsch Proteus program. All values were normalized per 1 g of ‘dry’ electrode material. Results are presented in table S4.

Table S4 DSC thermoanalytical data.

	Initial temperature/ °C	Peak temperature/ °C	Heat flow/ J g^{-1}
$NaAlNb(PO_4)_3$ 'dry'	116	160	61
$NaAlNb(PO_4)_3$ 'wet'	154	200, 258, 291	226
HC 'dry'	151	192, 273	610
HC 'wet'	85	114, 238	1205
Electrolyte (1M $NaPF_6$ EC : DEC)	274	290	268

References

S1 J. B. Goodenough, H. Y-P. Hong and J. A. Kafalas, *Mater. Res. Bull.*, 1976, **11**, 203; https://doi.org/10.1016/0025-5408(76)90077-5.

S2 D. Novichkov, A. Trigub, E. Gerber, I. Nevolin, A. Romanchuk, P. Matveev and S. Kalmykov, *J. Synchrotron Rad.*, 2023, **30**, 1114; https://doi.org/10.1107/S1600577523006926.

S3 B. Ravel and M. Newville, *J. Synchrotron Rad.*, 2005, **12**, 537; https://doi.org/10.1107/S0909049505012719.

S4 Z. V. Bobyleva, O. A. Drozhzhin, A. M. Alekseeva, K. A. Dosaev, G. S. Peters, G. P. Lakienko, T. I. Perfilyeva, N. A. Sobolev, K. I. Maslakov, S. V. Savilov, A. M. Abakumov and E. V. Antipov, *ACS Appl. Energy Mater.*, 2023, **6**, 181; https://doi.org/10.1021/acsaem.2c02716.