

Supporting Information

Non-aqueous semi-solid flow battery based on Na-ion chemistry. P2-type $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2 - \text{NaTi}_2(\text{PO}_4)_3$

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Synthesis of P2-type $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ (NaNCM)

The $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ (NaNCM) was synthesized by a solid-state reaction of sodium hydroxide (NaOH, Aldrich, >98%) and a manganese-nickel-cobalt hydroxide precursor.^[21-26] The latter was prepared by co-precipitating an aqueous solution of the three metal acetate salts (Mn, Ni and Co; Aldrich, >98%, stoichiometric ratio of 66:22:11, respectively) with sodium hydroxide (50% excess). After extensive rinsing with distilled water, the precipitate was dried at 120 °C overnight. The dried material was then dispersed in an aqueous solution of sodium hydroxide (0.76 *eq.* of NaOH per mole of $\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}(\text{OH})_2$) and the water was slowly removed by rotary evaporator. After drying and grinding, the mixture was annealed in air at 500 °C for 5 h, and then at 850 °C for 6 h, using an open-air muffle furnace. For the water treatment, about 1 g of the as-prepared material was stirred in 20 mL of distilled water (at room temperature) for 5 min. The suspension was then filtered and washed with 80 mL of distilled water, dried at 120 °C in air for 24 h. Afterwards, the material was ground by hand in a mortar, screened over a 45 μm sieve and finally stored under inert atmosphere.

Synthesis of carbon-coated $\text{NaTi}_2(\text{PO}_4)_3$ (NaTP)

NaTP was synthesized based on a modified protocol of Park et al.^[27] Ti(IV) isopropoxide (>97 %) was purchased from Sigma-Aldrich; hydrogen peroxide, ammonia (ACS grade), citric acid monohydrate and ammonium dihydrogen phosphate (ACS, >98%) was purchased from J.T. Baker. Sodium carbonate anhydr. (Ph.Eur. 99,8%) came from VWR. NaTP was prepared following a procedure reported by Park.^[27] 60 mmol of Ti(IV) isopropoxide was slowly dissolved in a mixture of 240 mL 30% H_2O_2 as oxidant and 90 mL 25% NH_3 ammonia as complexing agent to yield a clear yellow solution. 120 mmol citric acid monohydrate, 90 mmol ammonium dihydrogen phosphate and 15 mmol sodium carbonate were subsequently added. Adjusting the pH value to 6-7 using nitric acid resulted in heat generation and foaming while the solution turned orange. 120 mmol ethylene glycol was added as crosslinker. Raising the temperature to 80 °C resulted in the formation of a viscous orange gel and a further increase of the temperature resulted in the exothermic formation of a sticky brown resin indicating crosslinking of citrate and ethylene glycol. The resin was pyrolysed in air at 350 °C for 2 h, reground and calcined again at 800 °C (5 °C/min) in air for 8 h. The resulting white, crystallized NaTP powder was carbon-coated to increase conductivity by heat treatment with 10 wt.-% of glucose in Ar-flow for 6 h at 700 °C using a tubular Quartz oven. The resulting black powder contained ca. 2 wt.-% elemental carbon as determined by elemental analysis.

Structural characterization.

For NaNCM, X-ray powder diffraction (XRD) was performed using the Cu K_α radiation on the Bruker D8 Advance diffractometer (Germany) in the 2θ range from 10° to 90°. The Rietveld refinement of structures was performed using the TOPAS software. For $\text{C}/\text{NaTi}_2(\text{PO}_4)_3$, a Bruker ACS Advance diffractometer (Cu K_α , 2θ from 10° to 60°) was used.

Figure S1 shows the XRD patterns of (a) $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ and (b) $\text{C}/\text{NaTi}_2(\text{PO}_4)_3$. The diffraction pattern of NaNCM confirms phase purity (space group $P6_3/mmc$) of the P2-type hexagonal layered structure. Calculated lattice parameters via Rietveld refinement are $a=2.8623(79)$ Å and $c=11.204(65)$ Å. The NaTP crystallizes in space group R-3c with a NASICON-type $\text{Ti}_2\text{P}_3\text{O}_{12}$ framework, in which the TiO_6 octahedra are linked by their corners to PO_4 tetrahedra. The dispersed background pattern indicates the presence of the amorphous carbon coating.

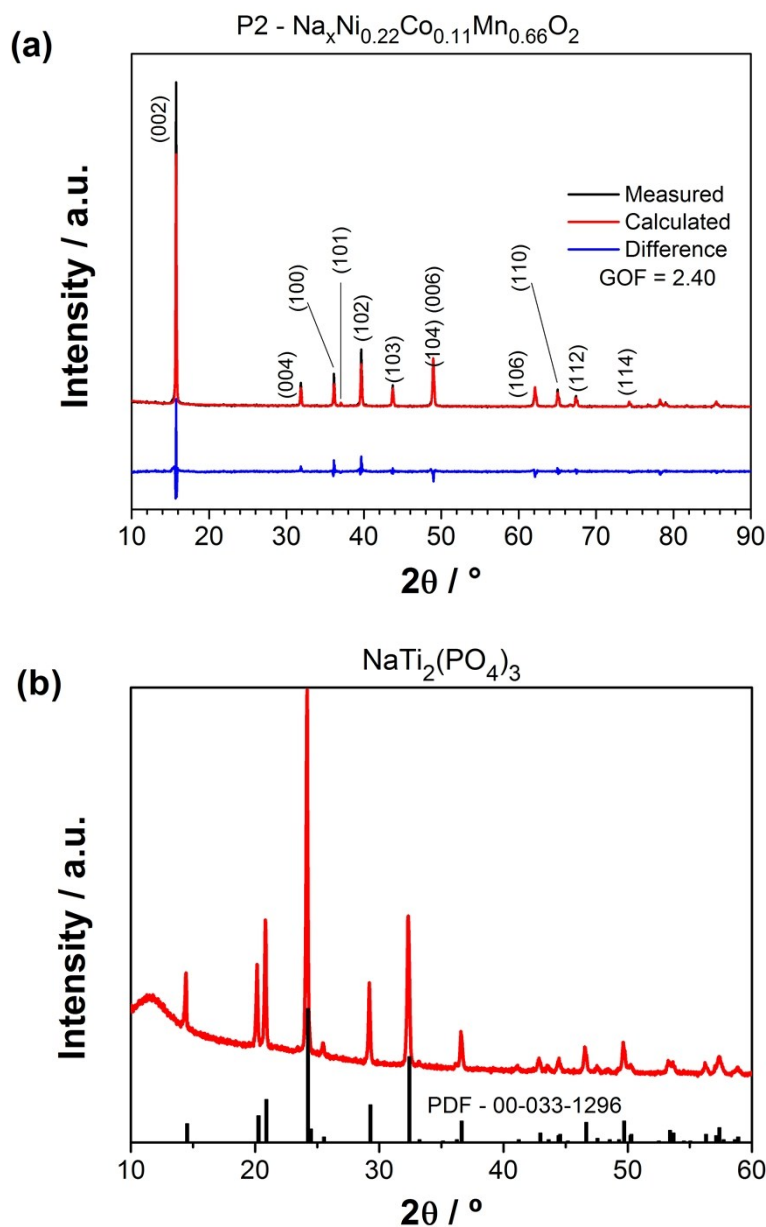


Figure S1. XRD patterns of (a) $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ and (b) $\text{C}/\text{NaTi}_2(\text{PO}_4)_3$.

Scanning electron microscopy images were taken with a high resolution scanning electron microscopy (FE-SEM, Zeiss Auriga) for NaNCM and a Quanta3D (FEI) in secondary electron mode for C/NaTi₂(PO₄)₃.

Figure S2 depicts the SEM images of (a) Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O₂ and (b) C/NaTi₂(PO₄)₃. The NaNCM material is composed of micro-sized particles with a well-defined shape and quite homogeneous size distribution, ranging from 1 to 3 μm. The resulting NaTP consists of sub-micron sized primary particles which formed larger agglomerates in the order of several micrometers.

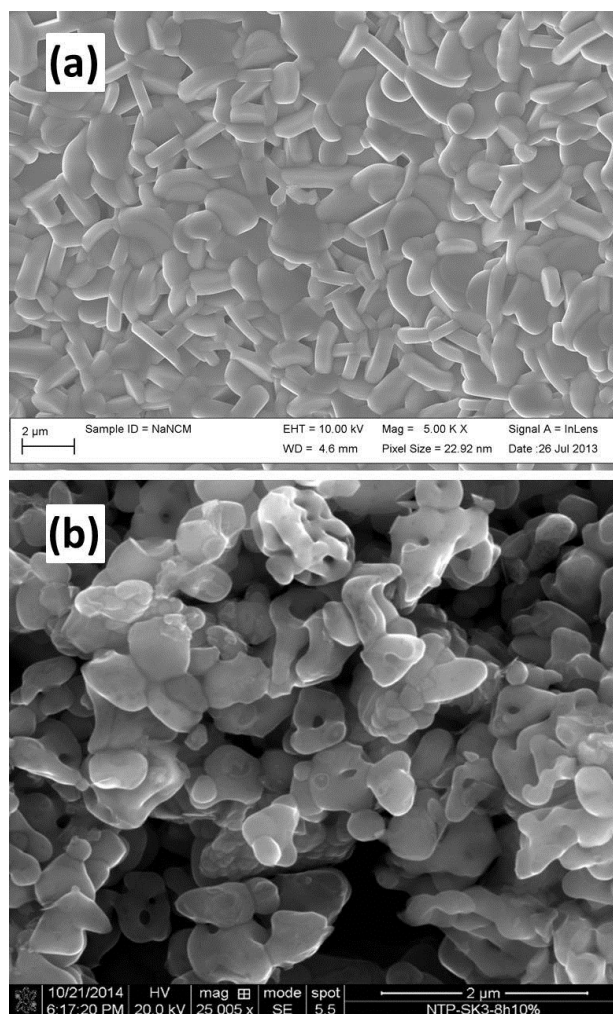


Figure S2. SEM images of (a) P2-type Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O₂ and (b) NaTi₂(PO₄)₃.

Elemental analysis of $\text{NaTi}_2(\text{PO}_4)_3$ was performed in the central analysis facilities of the Ruhr-University Bochum using an AAS 6 vario (Analytik Jena) for Na and Ti determination and an vario EL (Elementar Hanau) for determination of carbon content. The Na:Ti was found to be 1.05:1.

The stoichiometry of several samples of the P2-NaNCM were checked via Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with a Spectro ARCOS ICP-OES (Spectro Analytical Instruments, Kleve, Germany) instrument with axial plasma viewing in some previous works. The ratio of the transition metals was in accordance with previous works and confirmed the formula $\text{Na}_x\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$, whereas the Na content slightly varied in the range of $0.40 \leq x \leq 0.46$.^{23,26}

Electrode preparation

The solid electrodes were prepared by mixing the active material, the conductive additive (Super C65, SFG6, Timcal) and the binder (PVdF, Solef S5130, Solvay) in NMP at a weight ratio of 85:10:5 (NaNCM:C65:PVdF) and 80:7:5:8 (NaTP:C65:SFG6:PVdF). The mixture was cast onto aluminum foil using Doctor-Blade technique. The solvent was evaporated at 80 °C, disc electrodes were cut (12 mm diameter), pressed (NaNCM) and then dried at 120 °C under vacuum overnight. The electrode loading was 2.5 - 2.75 mg cm⁻² for NaNCM and 2.76 mg cm⁻² for NaTP.

The suspensions were prepared by mixing active material and conductive additive in 0.5 M NaPF_6 in EC:DMC (Sigma-Aldrich) by magnetic stirring overnight. For the positive fluid electrode, 1.25 g of NaNCM and 0.12 g of Ketjenblack EC-600 (AkzoNovel) were mixed in 6 mL of electrolyte. For the negative fluid electrode, 1.25 g of NaTP and 0.10 g of Ketjenblack EC-600 were mixed in 6 mL of electrolyte. Less amount of carbon additive was added in the negative electrode suspension since NaTP was already carbon-coated.

Cell assembly and electrochemical characterization.

For the evaluation of the solid electrode, three-electrode Swagelok cell was assembled in Ar-filled glovebox ($O_2 < 2$ ppm and $H_2O < 1$ ppm). Sodium metal was used as counter and reference electrodes. Whatman GF/D glass fiber filters served as separators. The electrolyte was 1 M $NaPF_6$ (Sigma-Aldrich) in propylene carbonate (UBE) for NaNCM and 1 M $NaClO_4$ (Sigma-Aldrich) in propylene carbonate (Merck) for the NaTP. Electrochemical measurements were performed with a Maccor series 4000 battery tester (USA) for the NaNCM and, for the NaTP, a Bio-Logic VMP-3 (Bio Logic SAS, Claix, France) at charge rate of 0.1 C, being 1 C equivalent to 123 mA g^{-1} and 117 mAh g^{-1} for NaNCM and NaTP, respectively. Potential window was 4.3 – 2.1 V and 2.5 – 1.5 V vs. Na metal for NaNCM and NaTP, respectively

For the evaluation of the fluid electrodes, a filter-press cell (Figure S1) was used. The cell was assembled inside an Ar-filled glove-box (O_2 and $H_2O < 1$ ppm). The filter press-cell configuration consists of several independent elements sandwiched (e.g. current collector, gaskets, channel frames) to define reaction zones (negative suspension and positive suspension compartments) separated by a Celgard 2500 film. Between each element, several gaskets must be introduced to avoid slurry leakages. Finally, the whole system is closed by metallic end-plates to give consistency to the system. Figure S3 illustrates the three electrode configuration cell used in this study. The semi-solid suspension containing solvents (alkyl carbonates), conductive salt ($NaPF_6$), conductive agent (carbon black) and electroactive particles is pumped through a Teflon plate, an Ethylene Propylene Diene Monomer (EPDM) gasket, and the positive (titanium plate) or negative (titanium plate) current collector until reaching the channel frame. The channel frame consists of a 0.5 mm thick Teflon frame, sandwiched by two 0.5 mm thick gaskets made of expanded Teflon (ePTFE). Together they form a 75 mm long x 4 mm wide x 1 mm (approximately 0.3 mL slurry and 3 cm^2) deep channel. The working electrode zone is limited by the separator (Celgard

2500). The sodium coated nickel wire of 0.25 mm of diameter (Sigma-Aldrich) was placed between the positive and negative compartments and employed as reference electrode.

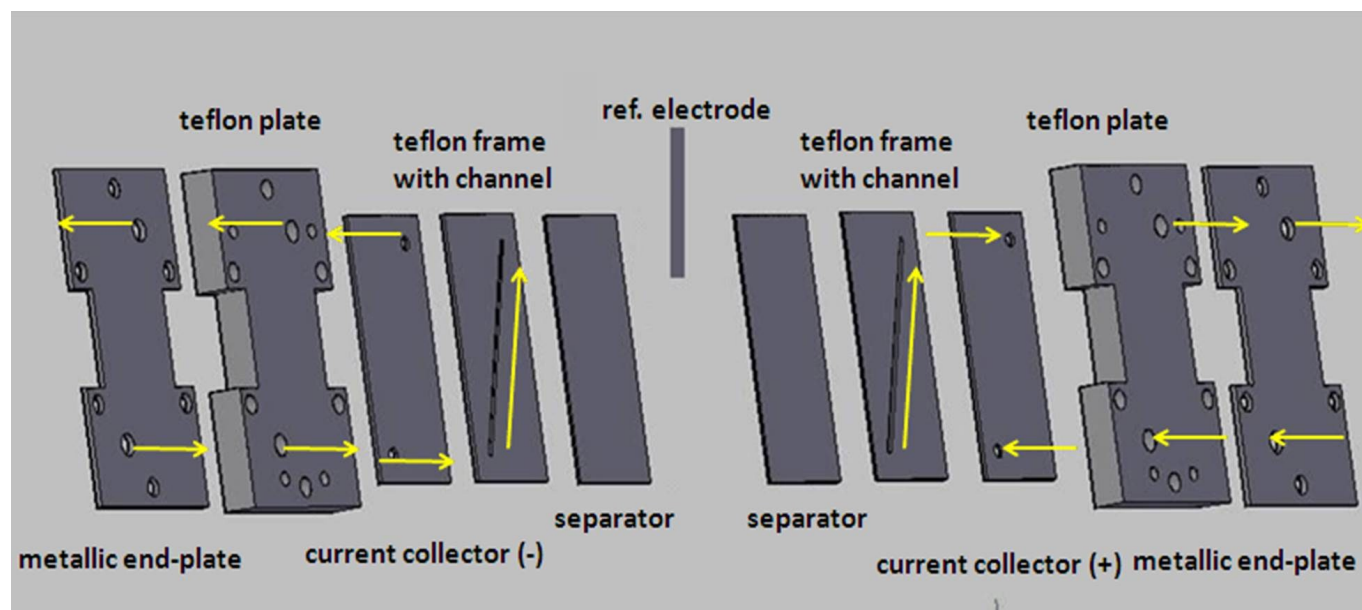


Figure S3. Schematic representation of the electrochemical flow cell

Electrochemical impedance spectroscopy (200 KHz – 50 mHz and 10 mV amplitude) was carried out in two-electrode configuration (suspensions of NaNCM - NaTP) before starting the measurements shown in Figure 3 of the manuscript. The Nyquist plot (Figure S4) reveals a large resistance to the electron transfer (the semi-arc at middle frequencies). The electrolyte resistance obtained at high frequencies was ca. 7 Ohm.

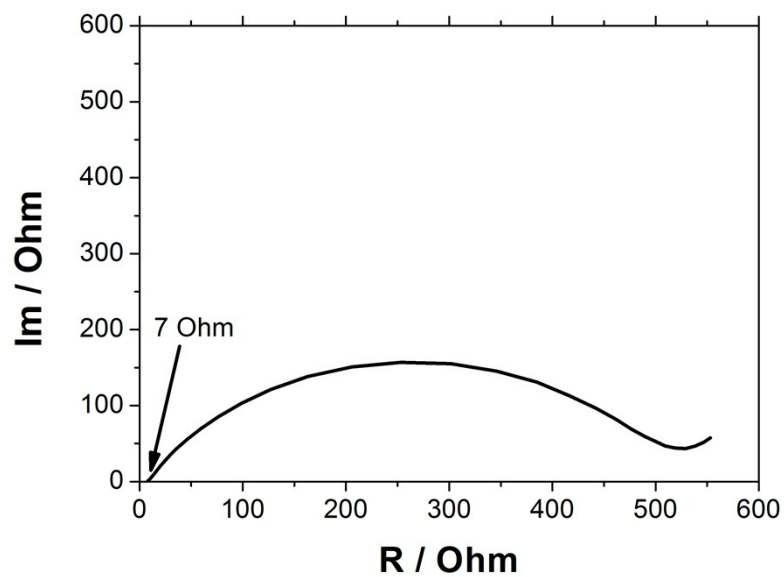


Figure S4. Nyquist plot of the cell consisting of NaNCM – NaTP suspensions.