Electronic Supplementary Information for

Redox Processes in Sodium Vanadium Phosphate Cathode – Insights from operando Magnetometry

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Voltage profiles of the NVP cathode at different C-rates (see Fig. 1b)

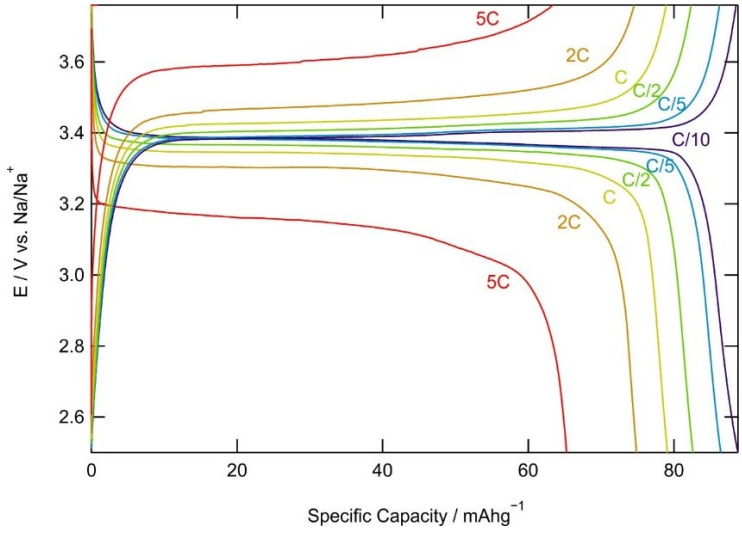

Figure S1. Charge and discharge profiles at the C-rates used to characterize the NVP material.

Elemental analysis with Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

A Microwave heated pressurized autoclave digestion system - Ultraclave IV, MLS and a ICPMS 7700x from Agilent Technologies were used to determine concentrations of the elements Na, V and P. Sample preparation was done by dissolving the NVP/C sample in 10% HNO_3. He was used as cell gas and Be (m/z 9) and Ge (m/z 74) were used as internal standards. The results are shown in Table S1 together with the relative *n* values in mol of Na, V and P which were calculated by setting *n* of P to 3 as it is in $Na_3V_2(PO_4)_3$. Based on this *n* of Na and

V were calculated. It can be seen that the values fit to the desired stoichiometric NVP within the measurement uncertainties. An additional screening of elements did not show any conspicuous elements present in the sample.

Table S1: Results of ICP-MS as concentrations *c* of Na, V and P in g of element per kg sample. From these results the relative amount of substance *n* in mol have been calculated by setting *n* of P to 3 mol.

	Na	**V**	**P**
***c* in g/kg**	117(4)	182(6)	162(7)
***n* in mol**	2.9(1)	2.05(7)	3.0(1)

Cyclic voltammetry

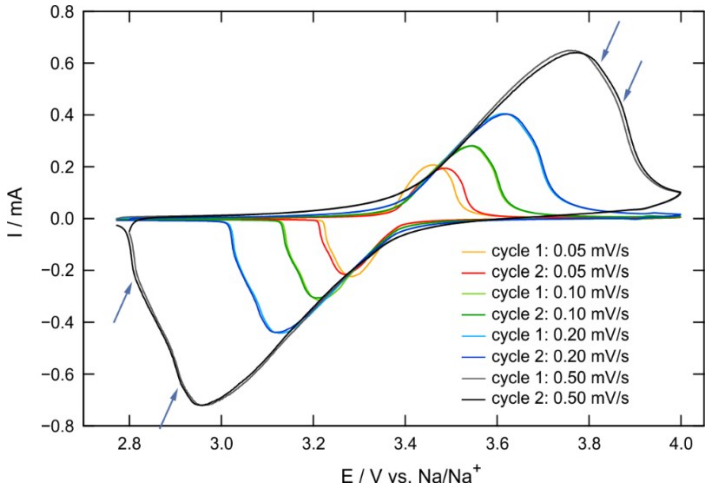

Figure S2. Cyclic voltammetry of NVP/C with different cycling rates of 0.05, 0.10, 0.20 and 0.50 mV/s.

Ex-situ magnetic susceptibility measurement

Ex-situ magnetic susceptibility measurements on $Na_2V_2(PO_4)_3$ were performed at an applied magnetic field of 5000 Oe in the temperature range between 300 and 8 K.

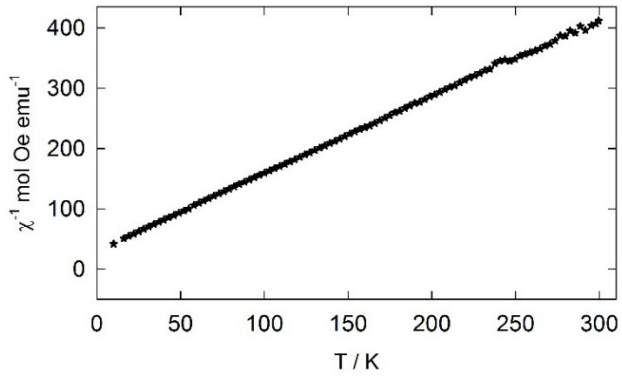

Figure S3. Inverse of the magnetic susceptibility χ as a function of temperature *T* (field cooling measurement).

X-ray powder diffraction (XRD)

The synthesized NVP carbon composite (NVP/C) material was characterized by X-ray diffractometry using a Bruker D8-Advance X-ray powder diffractometer equipped with a Lynxeye detector in Bragg-Brentano geometry with Cu-Kα radiation. The diffraction angle was varied by 0.02° (counting time 2-4 s per step) between 10 and 100°. The pattern obtained from NVP/C after the synthesis is compared to a reference spectra from Inorganic Crystal Structure Database.[1]

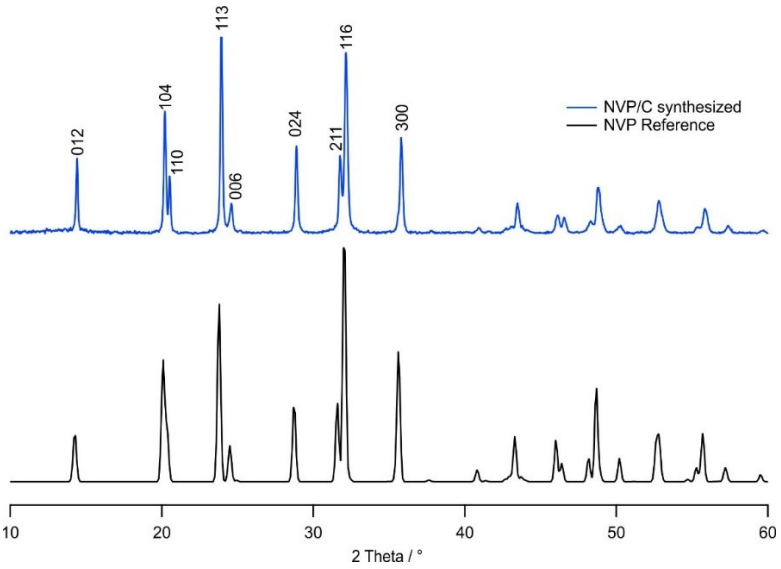

Figure S4. XRD pattern of NVP/C (blue) in comparison with a reference taken from the Inorganic Crystal Structure Database (ICSD) (black). No crystalline impurities were identified in the synthesized NVP material.

References

(1) Zatovsky, I. V. NASICON-Type Na3V2(PO4)3. *Acta Crystallogr. Sect. E Struct. Reports Online* **2010**, *66* (2), 0–5. https://doi.org/10.1107/S1600536810002801.