Supplementary Information to

Operando monitoring the redox activity of sodium vanadium titanium phosphate electrodes in organic and aqueous electrolytes by magnetometry

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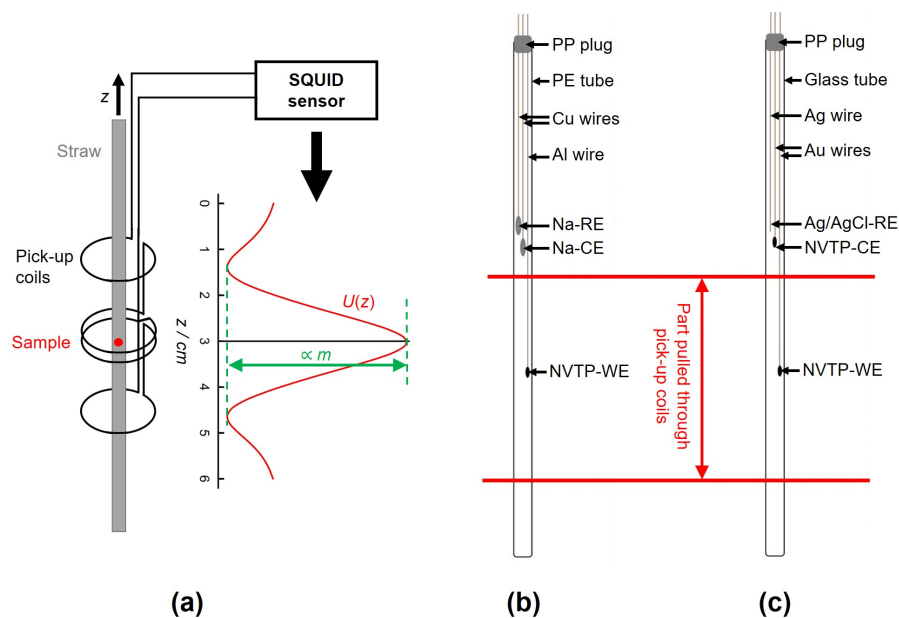[‡] These authors contributed equally to this work.

Fig. S1 (a) Schematic of the general measurement principle of a SQUID magnetometer. (b),(c) Sketch of the electrochemical cell design used for the operando SQUID magnetometry measurements on NVTP@C electrodes in (b) organic and (c) aqueous electrolyte. Note that the polyethylene tubes which were put around the wires to prevent short circuits in the cells are not shown.

S1 General measurement principle of SQUID magnetometer and design of electrochemical cells for operando magnetometry measurements

Figure S1(a) depicts the general measurement principle of the SQUID magnetometer. A sample is mounted in a plastic straw, which is pulled in z-direction trough a set of superconducting pick-up coils (second-order gradiometer). In this way the sample induces a magnetic flux change, which is converted into a voltage signal $U(z)$ by the SQUID sensor. The amplitude of this voltage signal is proportional to the magnetic moment m of the sample.

To perform operando magnetometry studies on the working electrode of an electrochemical cell, a cell design is required, where the detected magnetic flux change arises solely from this electrode. We developed such a cell design first for the in-situ electrodeposition of magnetic thin films[1] and adapted it later for measurements on Li-[2,3] and Na-ion battery electrodes[4]. Figures S1(b) and S1(c) show sketches of the cell design that was used in the current work for the organic and the aqueous electrolyte, respectively. The main advantage of this design is that only the magnetic flux change of the working electrode is detected. This is achieved because
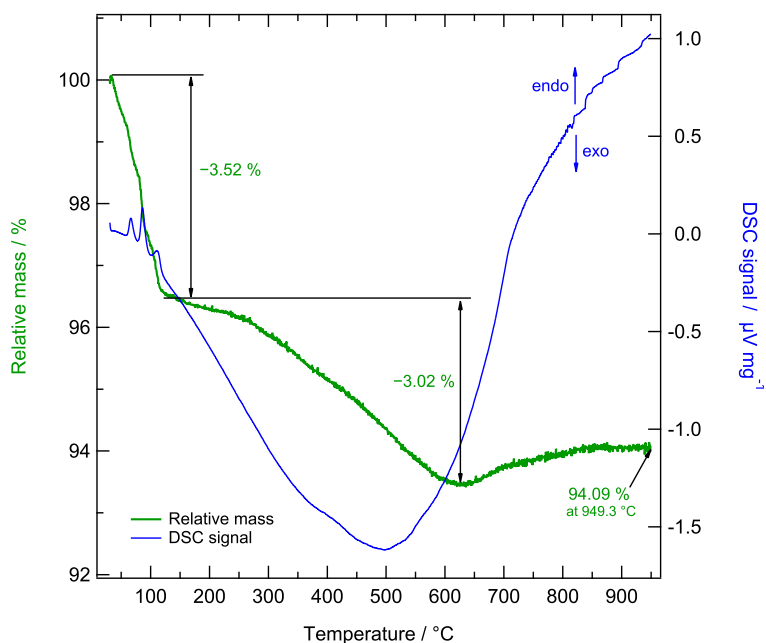
Fig. S2 Thermogravimetric analysis curves of pristine NVTP@C powder measured under air atmosphere.

the other cell components are either outside of the pick-up coils during the whole sample scan (e.g. the counter and reference electrodes), or they are homogeneous and within the pick-up coils during the scan (e.g. the cell compartment). In both cases these parts of the cell will not induce a magnetic flux changes into the pick-up coils.

S2 Thermogravmetric analysis

Thermogravimetric analysis (TGA) was carried out in synthetic air atmosphere to determine the carbon content in the pristine NVTP@C powder. As shown in Figure S2, an initial mass loss of about 3.5 wt% occurred below 100 °C, which can be attributed to the drying of the sample. The second mass loss can be explained by carbon combustion in air and decomposition of sodium carbonate, which may have formed in very small quantities during the sample storage at air. This mass loss is superimposed by a mass gain, most likely due to the oxidation of V^{3+} to V^{4+} in air. Considering this reaction, the mass gain due to vanadium oxide formation (oxygen uptake) can be estimated to be about 1.8 wt%. Adding this mass gain to the observed mass loss, the carbon content in the pristine NVTP@C powder is most likely close to 5 wt%. Considering this carbon content and the water content of about 3.5 wt%, the weight fraction of NVTP in the pristine powder is about 91.5 %.

S3 Formal oxidation states and theoretical slopes of susceptibility variations of operando measurements

As discussed in the Section 3.3 of the article, the fact that the observed susceptibility variations in our operando measurements can be well described by the theoretical slopes assuming the formal oxidation states and the corresponding values of μ_i, indicates that only small deviations, if any, from the formal oxidation states occur. However, theoretically, a case could be constructed where the same slope expected from the formal oxidation states is obtained for different values of μ_i in the case that two redox reactions occur simultaneously. The existence of exactly this combination alone is in itself quite unlikely. In addition, the fact that the slopes in our measurements are constant over the whole potential regime, would imply that the fraction of the two simultaneous redox reactions must be constant over the whole regime, which in itself is unlikely too. Furthermore, these two already unlikely cases would have to occur simultaneously not only once, but even twice, namely for the high and the low voltage regime. All this together makes it highly unlikely that this theoretically possible case actually occurs.

References

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