Supporting Information

Reaction Pathway and Wiring Network Dependent Li/Na Storage of Micro-Sized Conversion Anode with Mesoporosity and Metallic Conductivity

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Experimental Section

Sample Preparation: Zn₃V₂O₈ was prepared by a solid state reaction of the stoichiometric mixture of powders ZnO (99.99 %, Sigma Aldrich) and V₂O₅ (99.6%, Alfa Aesar). The powders were ground together and heated at 500 ºC for 4 h, and then subsequently increased to 750 ºC for 40 h. A few grams of the oxide were placed in an alumina boat. The boat was then placed in a stainless steel tube with air tight stainless steel end caps that had welded valves and connections to input and output gaslines. All gases were purified to remove trace amounts of oxygen or water using pellet copper, nickel, palladium and platinum with zeolites as support. The stainless steel tube was then placed in a split tube furnace and the appropriate connections to gas sources were made. Argon gas was passed over the sample for 15 min to expel air before establishing a flow of ammonia gas (Anhydrous, Air Gas). The sample was then heated to 700 ºC at 200 ºC/h. After 6 h, the furnace power was turned off and the product was cooled to room temperature in about 4 h under an ammonia flow. Before the
stainless steel tube was taken out of the split tube furnace, argon gas was used to purge the tube and expel the ammonia gas. The stainless steel tube was left in lab for 24 h with one valve open in order to expose the ammonolyzed product to air slowly.

Material Characterization: The morphology, structure and crystallinity of pristine and cycled samples were observed through scanning electron microscopy (SEM, Carl Zeiss Leo 1530 VP Gemini) and X-ray diffraction (XRD, Philips X’Pert MRD Pro diffractometer). Crystal structure of the resulting nitride was confirmed by powder XRD (PXRD) profile using the GSAS package. The reaction products and their microstructures of pristine and discharged samples were further investigated by high-resolution transmission electron microscopy (HR-TEM, JEOL JSM-6700F) and selected area electron diffraction (SAED) measurements. Ex-situ measurement of X-ray absorption fine structure (XAFS) was carried out for the VN anodes with different cycled stages at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF) in the fluorescence mode. Si (111) double crystal monochromator was employed to monochromatize the beam. The XAFS data was further analyzed using the IFEFFIT program [B. Ravel, M. Newville, J. Synchrotron Rad. 2005,12, 537]. Nitrogen adsorption/desorption isotherms were measured at -196 °C using a Micromeritcs ASAP 2020 system. The samples were degassed at 200 °C for 24 h on a vacuum line. Elemental analyses of nitrogen and oxygen contents of the nitride samples were done with a LECO TC-600 analyzer using the inert gas fusion method. Nitrogen was detected as N₂ by thermal conductivity, and oxygen was detected as CO₂ by infrared detection. The apparatus was calibrated using Leco standard oxides; Si₂N₂O and TaN were used as nitrogen standards [W. Gruner, B. Wollein, W. Lengauer, Microchim. Acta 2004,146, 1].

Electrochemical Test: Two-electrode coin-type cells were assembled with VN samples as working electrodes and high-purity lithium foil or sodium foil (Aldrich) as counter electrode. The working electrodes were prepared by mixing nitride, super P and poly (vinyl difluoride) (PVDF) with a weight ratio of 80:10:10, which were then pasted on pure Copper foil (>99%,
United copper foils (Huizhou) Ltd.) followed by drying in vacuum at 80 °C for 20 h. The loading mass of electrode materials is ~2mg/cm². For comparison, some electrodes were also prepared by directly mixing nitride and PVDF with a weight ratio of 90:10 without the addition of super P. Glass fiber (GF/B) from Whatman was employed as the separator. For LIBs, 1 M LiPF₆ in a non-aqueous mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1 was used as electrolyte. For NIBs, the electrolyte was composed by dissolving 1M NaClO₄ in a non-aqueous mixture of ethylene carbonate (EC), propylene carbonate (PC) and fluoroethylene carbonate (FEC) with a weight ratio of 9.5:9.5:1. All the electrolyte-related chemicals were purchased from Sigma Aldrich. Before use, the salts were baked at 80°C in vacuum for 24h and the solvents were purified with fresh activated molecular sieve for more than one week. The final water content in solvent (measured by a Metrohm 831 KF Coulometer) was below 4 ppm. The cells were assembled in an Ar-filled glove box. Charge-discharge measurements were performed at room temperature under different rates from 0.1C to 10C (1C denotes the current density to theoretically achieve three-electron transfer within 1 h) in a voltage range of 0.01-3.0 V on an Arbin MSTAT battery test system. Cyclic voltammetry (CV) was carried out at a scan rate of 0.1 mV/s in a voltage range of 0.1−3 V by electrochemical workstation (700D, CHI Instrument). For the ex-situ characterizations (such as XAFS and XRD), the discharged or charged electrodes were taken out from the cells in the Ar-filled glove box, washed by anhydrous dimethyl carbonate (DMC), and protected by Mylar film wrapping or Be window encapsulation.
**Figure S1.** Scheme of the synthesis procedure of mesoporous VN by ammonolyzing bulk Zn-based ternary oxide based on template-free solid-solid phase separation. At a temperature above 500°C with different flow atmospheres, Zn$_3$V$_2$O$_8$ is firstly formed through solid-state reaction, then Zn components sublime out of the product to create mesopores and meanwhile three O$^-$ anions are displaced by two N$^+$ anions.

**Figure S2.** Barrett-Joyner-Halenda (BJH) pore size distribution of mesoporous VN microparticles from the adsorption branch. The average pore sizes range from 20 nm to 40 nm.
Figure S3. (a,b) HRTEM images and (c) SAED patterns of the pristine VN sample. The mesoporous and polycrystalline features of VN are indicated from the distribution of lattice stripes and diffraction rings assigned to VN.

Figure S4. Capacity and coulombic efficiency of VN anodes as a function of cycle number for (a) Li-storage and (b) Na-storage at different rates from 0.1C to 10C. For Li-storage, the reversible capacity at 0.1C is stabilized at ~700 mAh/g even after long-term (100 cycles) and high-rate (10C) cycling. Under much higher rates of 1C, 2C, 5C and 10C, the capacities of 600, 550, 500 and 400 mAh/g are still able to preserve respectively with high reversibility and CE (100%). In the Na-storage case, the highly reversible capacities are achieved at 250, 200, 150 and 100 mAh/g at much higher rates of 0.5C, 1C, 2C, and 5C respectively, all with a CE close to 100%.
Figure S5. CV curves of VN as anodes for (a) LIB and (b) NIB during the first three cycles under a voltage range from 0.1 V to 3 V with a scan rate of 0.1 mV/s. During the first lithiation VN displays four cathodic peaks locating at 2.5 V, 1.3 V, 0.75 V and near 0 V. Most the peaks disappear during the following cycles apart from the reversible ones around 2 V and 0 V. For the first sodiation, the curve becomes smoother with less intensity of current, which gradually increases from 1.25 V to 0 V. Similarly, the following cycles for NIB are also highly reversible but with a more pseudocapacitive behavior. For both the cases, a larger current area for the first cathodic process is in accordance with the first irreversible capacity observed in the galvanostatic measurement (Figure 2a and b).

Figure S6. SAED patterns of (a) lithiated and (b) sodiated VN samples after discharging to 0.01V. After deep lithiation, VN is converted into nanocrystalline Li$_3$N and V. The existence of unreacted VN nanodomains cannot be ruled out in view of the difficult propagation of reaction frontiers or conversion interfaces in some thick regions. In contrast, a deep sodiation
of VN results in the formation of N-deficient VN$_{0.35}$ (JCPDS 06-0624) rather than metal V with substantially residual V-N bonds in the discharge products. The Na-contained products cannot be identified due to their amorphous structure or instability under e-beam irradiation.

Figure S7. PXRD pattern of lithiated and sodiated VN sample after discharge to 0.1 V. The nanocrystalline Li$_3$N phase can be detected from XRD, whereas the peaks for other phases (VN$_{0.35}$, V or residual VN) are almost invisible owing to their nanodomain characteristics. Other standard XRD peaks of Be, BeO and Cu as encapsulation or current collector materials are also listed as reference.

Figure S8. Overview SEM images of (a) lithiated and (b) sodiated VN samples after discharge to 0.1 V. It is seen that the internal mesoporosity is still well kept owing to the integrity of micro-sized framework, although the evolution of pore size and geometry is unavoidable due to conversion-driven volume expansion and SEI formation. Note that the
shrinkage of pore spaces is more evident for sodiation than for lithiation due to larger volume expansion and/or thicker SEI formation.

**Figure S9.** Overview TEM images of (a) lithiated and (b) sodiated VN samples after discharge to 0.1 V. As shown, for both the cases the self-reconstructed local framework appears to quite uniform in component distribution from the color contrast.

**Figure S10.** Capacity of carbon additive free VN anodes as a function of cycle number at 0.1C in a potential range of 0.1-3V. The electrochemical activity degrades seriously due to electrical contact loss of external conductive networks. The capacity for Na-storage is almost negligible, whereas a gradual capacity increase is observed for Li-storage. The latter indicates a self-optimization or self-activation capability of internal conductive network.