Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPORTING INFORMATION: Effect of Aging and Hydrothermal Treatment on Electrochemical Performance of Chemically Pre-Intercalated Na-V-O Nanowires for Na-Ion Batteries

Mallory Clites, Bryan W. Byles, and Ekaterina Pomerantseva

Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104

Investigating kinetics of the aging step

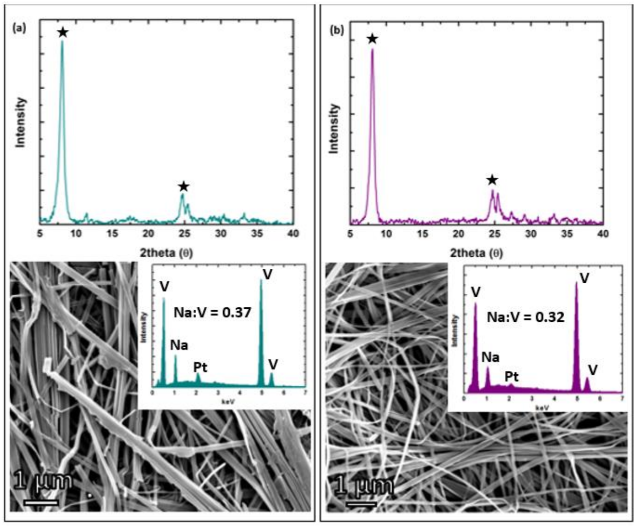

Figure S1. XRD patterns, SEM micrographs, and EDX spectra for (a) sample dried in hood for 4 days before hydrothermal treatment (sample S4) and (b) sample dried in oven for less than 1 hour before hydrothermal treatment. Stars denote the $Na_xV_2O_5$ phase.

The aging step is accompanied by the slow removal of water from the crystal structure of the material which allows more Na^+ ions to be absorbed into the sponge-like gel and for restructuring of the vanadium-oxygen matrix around Na^+ ions to allow for a more favorable accommodation of the Na^+ ions. We believe this removal of water is key to the formation of the bilayered phase. To test this hypothesis, we attempted to dry samples in an oven to the same consistency as those dried by aging in a fume hood. Samples were synthesized alongside each other. One sample was then placed in the fume hood to age for 4 days as per the methods in our manuscript. The second sample was then placed in an oven heated to 95°C with the fan set to high. The sample dried in the oven took less than 1 hour to reach the consistency and moisture of samples aged for 4 days. Once proper consistencies were reached, samples were hydrothermally treated following the procedures from our manuscript. The XRD patterns, SEM micrographs, and EDX spectra for both samples can be seen below in **Figure S1**. Both samples showed the formation of the bilayered phase. From this result, we can conclude that the formation of the bilayered phase is not time dependent or kinetically limited in our synthesis but rather relies on the evaporation of a significant amount of water in our sample prior to hydrothermal treating. This water loss occurs through extended aging but can also be achieved through aging at raised temperatures for shortened periods of time.

Water content and its affect in synthesized samples:

We have evaluated water content in our samples through thermogravimetric analysis (TGA); the TGA data for samples S1 and S4 can be seen below in **Figure S2**. The most significant mass loss is seen below 110°C, similar to previous studies on Na-containing bilayered materials.[1] This mass loss is attributed to physically absorbed water molecules. The inclusion of a drying step at 100°C in our synthesis is included in order to remove this physically adsorbed water. TGA shows that mass loss continues to occur above 110°C to ~500°C, which is attributed to crystallographically bound water. This water remains in our samples during cycling, and may improve the electrochemical performance, as discussed above. Above 500°C, TGA analysis shows a large mass loss for sample S4, which is determined to be due to a phase transformation from the bilayered $Na_xV_2O_5$ phase to a β-NaV_6O_{15} (PDF# 00-024-1155), an open-structured, bronze phase.

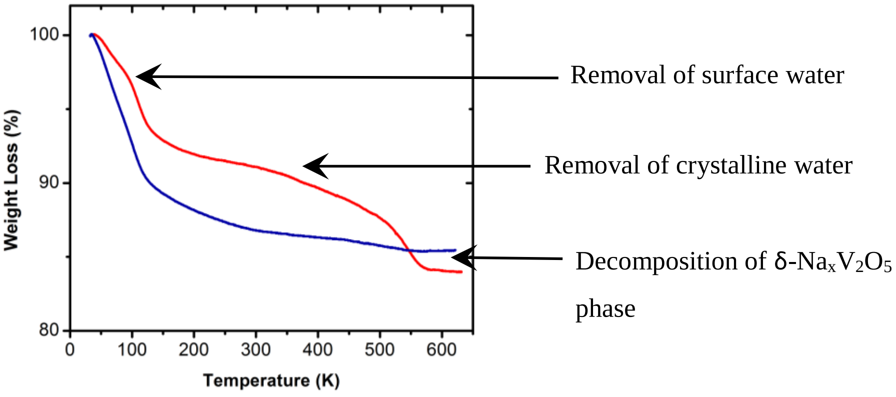

Figure S2. TGA analysis of samples S1 (blue) and S4 (red) under a Nitrogen rich atmosphere from ambient temperatures to 600°C.

Electrochemical life cycle performanc:

The cycle life results for samples S2 and S3 are added to the results **Figure 4(e)** of the original manuscript and shown below in **Figure S3.** Sample S4 out performs all other hydrothermally treated samples. This is in agreement with the inclusion of NaV_3O_8, , which has an interlayer spacing of ~8 Å, in samples S2 and S3, which has a specific capacity 172 mAh/g, discussed in our manuscript. These results initially confirm that the bilayered phase, which has an interlayer spacing of ~11.4 Å, is advantageous for the reversible cycling of large Na^+ ions. We speculate that such advanced electrochemical performance is achieved by the large interlayer spacing typical for the bilayered phase. This structural feature combined with chemical preintercalation may facilitate ion diffusion, increasing the electrochemical performance in sample S4. We believe that because these mixed-phase samples show lower initial capacities, poor cycle life performance, and were not the desired phase in this work, it is not necessary to include their cycle life capacities in the manuscript.

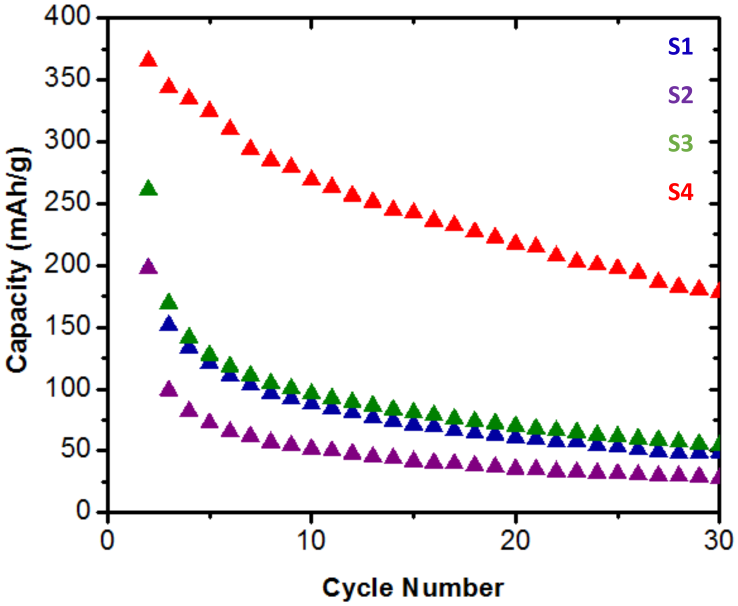

Figure S3. Cycle life results for samples S1-S4 at 20 mA/g for 30 cycles in Na-ion cells.