MWCNT/V_2O_5 Core/Shell Sponge for High Areal Capacity and Power Density Li-ion Cathodes

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Supplemental Figures:

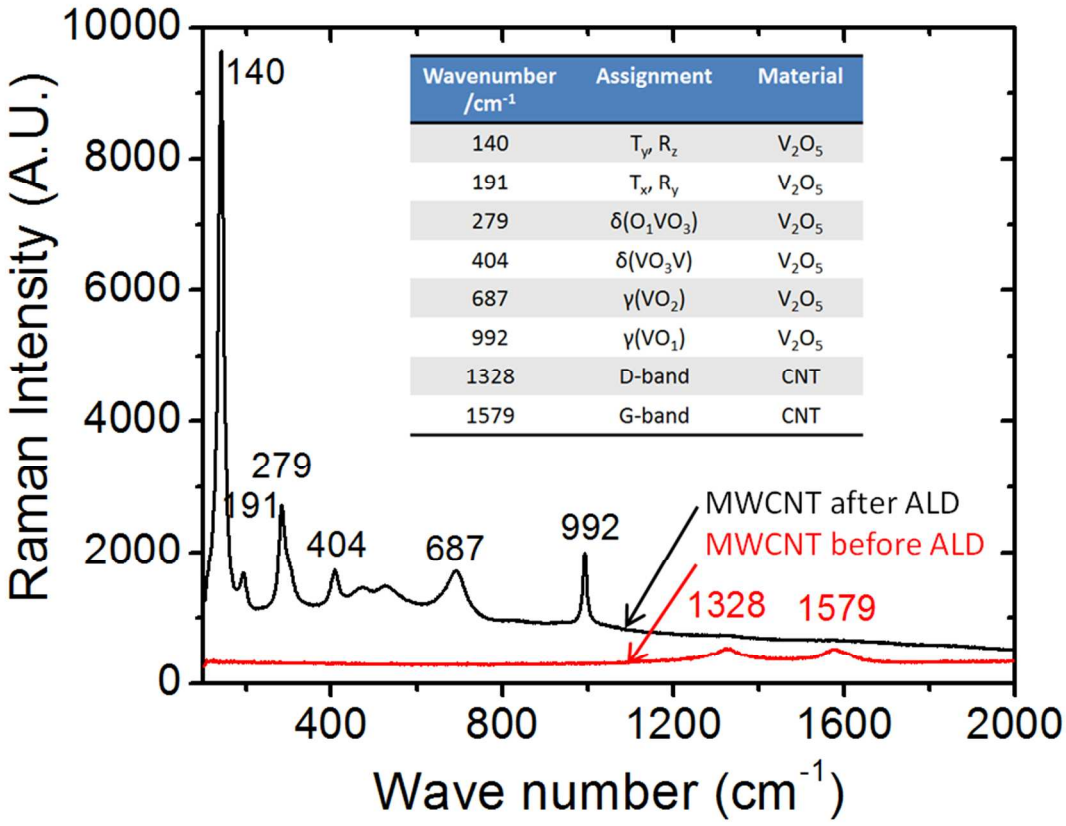


Figure 1S: Raman spectrum of MWCNT sponge before and after ALD of V_2O_5 with representative peaks marked and noted in the table inset.

Supplemental texts for Figure 1S:

The fresh MWCNT showed characteristic D-band peak at 1328 $cm^{-1}$and G-band peak at 1579 cm^{-1}.[1] After ALD V_2O_5 coating, the peaks from MWCNT were barely visible while other peaks emerged, which are in agree with that of V_2O_5 reported in the literature.[2] The detailed peak assignment are listed in the inset of Figure 1S. Typically, the peaks at 140 and 992 cm^{-1} correspond to the characteristic extension of the V_2O_5 unit cell and V=O stretching vibration modes, respectively.

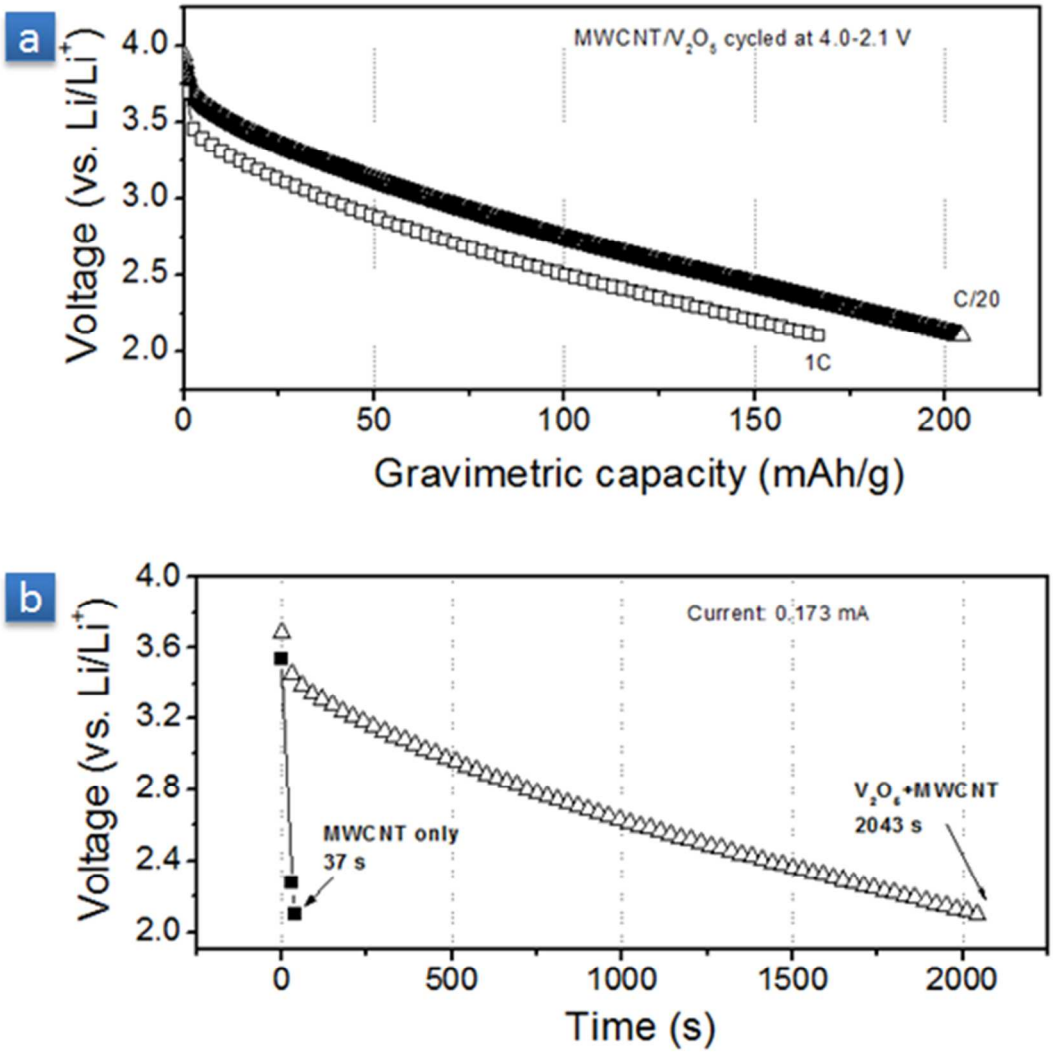


Figure 2S: (a) Gravimetric discharge curves for the cells with MWCNT/V_2O_5 sponge cathodes for 2Li/V_2O_5 (4.0-2.1 V) at C/20 and 1C rate. (b) Discharge curves for V_2O_5 coated MWCNT and equal amount of MWCNT only with same current.

Supplemental texts for Figure 2S:

As shown in Figure 2Sa, the C/20 discharge gave an expected higher capacity of 204 mAh/g than that at 1C rate (167 mAh/g, 82% of 204 mAh/g). We noted that the capacity difference at 1C and C/20 is small because the thin V_2O_5 layer and the high conductivity of MWCNT provide fast kinetics. Therefore, we concentrate on the 1C rate to represent the results of our composite. In addition, testing at 1C rate is 20X faster than that at C/20, significantly shortening experiment time for 100 cycle life time testing.

Shown in Figure 2Sb, the MWCNT sample coated with ALD V_2O_5 took 2043 s to discharge to 2.1V, while that with MWCNT only took 37 s. This result means that MWCNT only stored a tiny amount of charge compared to V_2O_5. The portion of charge stored by MWCNT is less than 2% (37/2043 = 1.8%). Since most capacity is from V_2O_5, the cell performs more like a battery than a carbon supercapacitor.

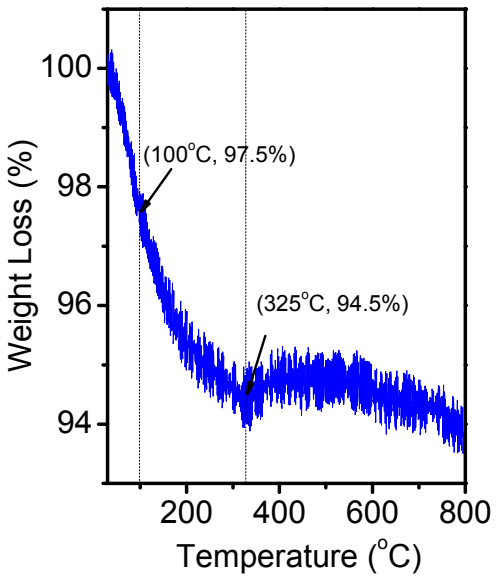


Figure 3S: TGA curve for V_2O_5 deposited with H_2O-based process, showing H_2O-related residual in the film.

Supplemental texts for Figure 3S:

The method for TGA measurement is the same as what we reported in our previous paper.[3] Briefly speaking, in order to deposit a detectable amount of V_2O_5 for TGA analysis, the inorganic AAO template (200-300 nm diameter, 60 um thick, from Whatman) with high surface area was used as the substrate. The weight loss from the AAO template has been subtracted to present the results from V_2O_5 films. The weight loss from room temperature to 325 ^oC can be attributed to water loss. While our V_2O_5 electrode was baked at 100 ^oC before assembled in a cell, the total amount of H_2O residual should correspond to the weight loss between 100 and 325 ^oC, which is about 3%. The chemical formula of the film can be written as $V_2O_5(H_2O)_{0.3}$. This amount of protons can contribute to a capacity of 88mAh/g (0.6Li per V_2O_5), higher than what we see in the first five cycles (~40 mAh/g, see Figure 4Sb below). In addition, we found from another report a similar behavior that showed the "warm-up" is more obvious with hydrous

materials.[4] The hydrous NaV_3O_8 took about 10 cycles before reaching its maximum capacity while the anhydrous counterpart reached the highest capacity in the second cycle.

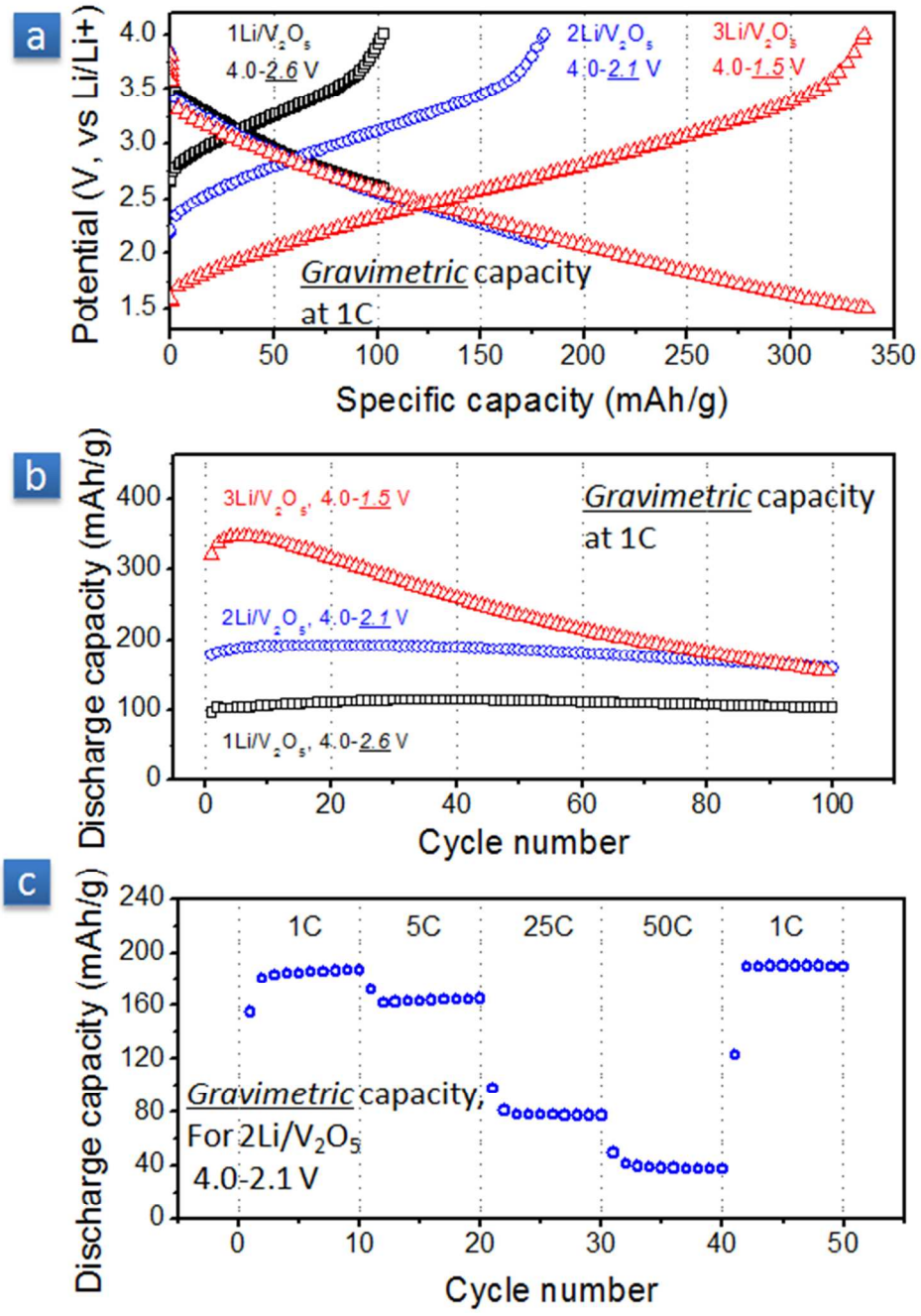


Figure 4S: (a) Gravimetric discharge and charge curves (second cycle) for the cells with MWCNT/V_2O_5 sponge cathodes in three different voltage ranges at 1C rate. (b) Cycling performance of the cells with MWCNT/V_2O_5 sponge cathodes in three different voltages at 1C rate. (c) Rate capability data for MWCNT/V_2O_5 sponge cathodes in the voltage range for 2Li/V_2O_5 (4.0-2.1 V) at different C-rates as indicated in the figure.

Supplemental texts for Figure 4s:

The gravimetric capacity data of the V_2O_5 in MWCNT/V_2O_5 nanostructured sponge are recorded in Figure 4Sa. The initial specific capacity of the V_2O_5 was 103, 181, and 336 mAh/g when the discharge cut off voltage was set for 3Li, 2Li, and 1Li transfer respectively. Taking the 2Li/V_2O_5 range (4.0-2.1 V) for example, the capacity of V_2O_5 on MWCNT is 181 mAh/g, which is not far away from the thin V_2O_5 on planar stainless steel disk (219 mAh/g, not shown here). This again indicates that most of V_2O_5 on MWCNT was accessible for (de)/lithiation. While a capacity of 181 mAh/g at 4.0-2.1 V is not among highest of the reported values for V_2O_5, it is comparable to that of the well-known $LiFePO_4$ cathode (166 mAh/g) cycled at similar conditions (4.5-2.0 V at 2 C rate).[5] When cycled for 3Li/V_2O_5 (4.0-1.5V) with 1C rate, the capacity of V_2O_5 on MWCNT (336 mAh/g) is lower than reported value (455 mAh/g) for amorphous ALD V_2O_5 film on planar Ti foil, which was tested at C/10 rate though.[6] For the 1Li/V_2O_5 (4.0-2.6 V), the capacity of 103 mAh/g reported here is lower than our previous report on crystalline V_2O_5 (130 mAh/g) at the same 1C rate, primarily due to the difference in crystallinity. This also indicates higher capacity would be expected with deposition of crystalline V_2O_5 on MWCNT.[3] The cycling performances for the gravimetric capacities (Figure 4Sb) are consistent with the areal ones discussed in Figure 4c. The rate performance data in Figure 4Sc show gravimetric capacities of 181, 163, 80, and 40 mAh/g at current of 1C, 5C, 25C, and 50C, respectively. The highest energy and power density from V_2O_5 delivered here are 453 Wh/kg, and 5000 W/kg.

Taking into account that the V_2O_5 mass is 54% of the whole sponge on average and that typical cathode mass is around 40% of a battery, one can make a full battery with energy density of 98 Wh/kg and power density of 1080 W/kg, which all surpasses the DOE goal for application in hybrid electric vehicles (HEV).[7] In all, these gravimetric results show MWCNT /V_2O_5 sponge is also promising for the applications in LIBs.

Reference for supplemental texts:

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