Supporting Information

Hollow carbon nanofiber as stabilizer for in-situ TiO$_2$/VO$_2$ co-impregnation with high power rate and ultra-long cyclinglife as lithium-ion Battery anode

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EXPERIMENTAL SECTION

Synthesis of TiO$_2$/VO$_2$ co-impregnated HCNFs. Self-supported TiO$_2$/VO$_2$ co-impregnated HCNFs were synthesized using an improved method based on one of our previous report. In a typical synthesis, 0.3g Polyvinylpyrrolidone (PVP, M.w.=1300000, Sigma) was dissolved into 5 ml deioned ethanol (previously removed water using 5Åsieves, sigma) followed with 3.2 ml titanium isopropoxide (Ti(OiPr)$_4$, Alfa) and 2 ml acidic acid (previously removed water using 5Å sieves, sigma). After stirring for 10 min, the PVP/Ti(OiPr)$_4$ solution was naturally cooled to room temperature. 0.3g vanadium (IV)oxyacetylacetonate (VO(acac)$_2$, Alfa) was involved in the solution and ultrasonic dispersed to form the PVP/Ti(OiPr)$_4$/VO(acac)$_2$ as the shell solution for the following electrospinning process. By applying liquid paraffin as the core solution, hollow nanofiber was electrospun-synthesized under the voltage of 1.8 kVcm^{-1}. The flow rates of core and shell solution sustained at 0.09 mlh^{-1} and 0.6 mlh^{-1}, respectively. The as-spun nanofiber membrane was left over night to remove the possible residue solvent, then washed several times using water and dried naturally. The electrospun nanofiber membrane was post-annealed in H$_2$/Ar atmosphere and maintained at 800°C for 2h with a 2°C.min^{-1} heating rate.

Material characterization. The samples were characterized using X-Ray diffraction (XRD, Panalytical,X'Pert PRO α-1 diffractometer, Cu-Kα), transmission electron microscopy (TEM, JEOL,JEM-2100F), energy dispersive X-ray spectroscopy (EDS,FEI, MLA 250), field-emission scanning electron microscope (FESEM, JEOL,JEM2100) and X-Ray photoelectron spectroscopy(XPS, VG Scientific ESCALAB220IXL).The electrochemical properties were evaluated using two

electrodes 2025 coin cell with lithium metal disks as the counter and reference electrode, respectively. TiO_2/VO_2 co-impregnated HCNFs were directly assembled as cathode electrode without any additives and conducting agent. Polypropylene membrane (Celgard, 2400) was cut into ϕ 20 and was used as separator. The electrolyte used was1M $LiPF_6$ dissolved in 1:1 V/V ethylene carbonate/dimethyl carbonate (EC/DMC) solvent.Cyclic voltammetry (CV) tests and electrochemical impedance spectroscopy (EIS) were carried out with ModuLab (Solartron) and the galvanostatic method was used tomeasure the electrochemical capacity of the electrodes at roomtemperature (LAND-CT2001A instrument).
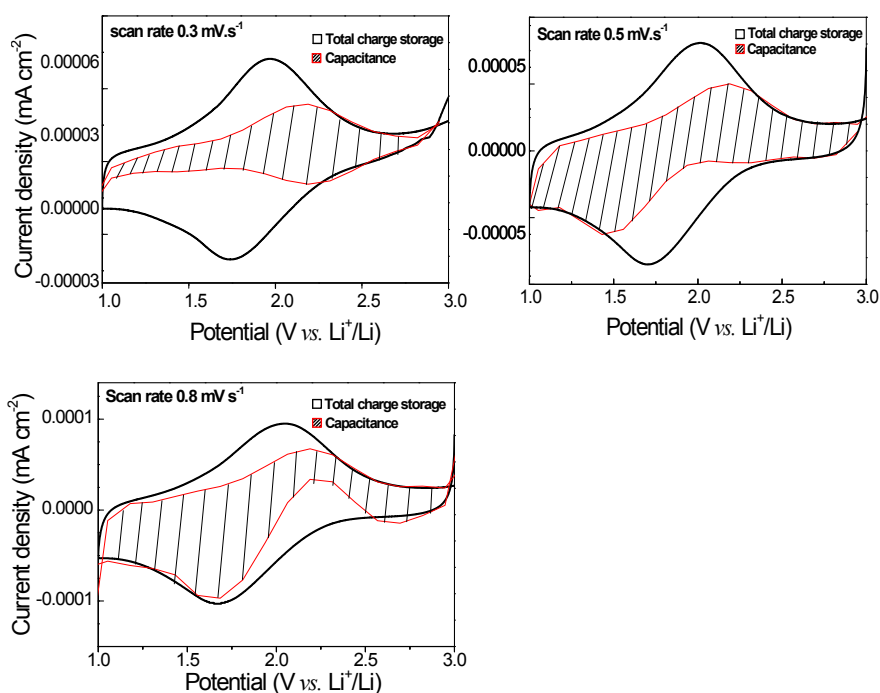
Figure S1 Contribution ratio of capacitance and intercalation capacity of theTiO$_2$/VO$_2$ co-impregnated HCNFs under 0.3, 0.5 and 0.8 mV s^{-1} scan rate.
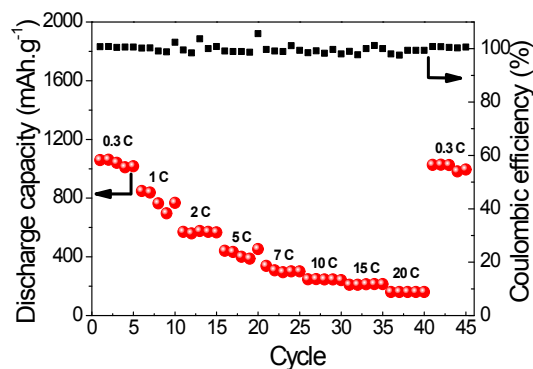
Figure S2 The high power rate performance and good retention ability of TiO_2/VO_2 co-impregnated HCNFs from 0.3 C to 20 C with potential window of 0-3 V.
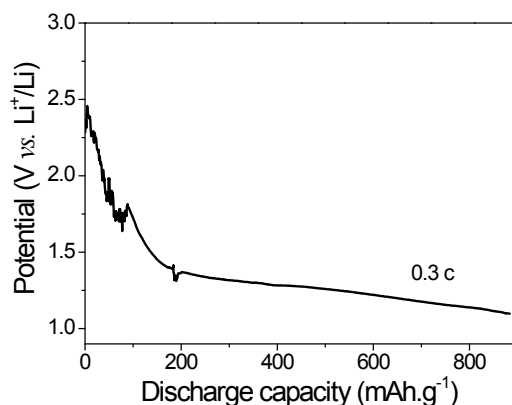
Figure S3 The initial discharge profile from open circuit voltage to 1.0 V of the rate performance.

Intercalation capacity and surface capacitive calculation:

These two mechanisms can be expressed in terms of scan rate υ as:

$$i(V) = k_1\upsilon + k_2\upsilon^{1/2} \text{ or } i(V)/\upsilon^{1/2} = k_1\upsilon^{1/2} + k_2 \qquad \textbf{Equation S1}$$

where $k_1\upsilon$ and $k_2\upsilon^{1/2}$ correspond to the current contribution from the surface capacitive effects and the diffusion-controlled intercalation process, respectively. k_1 and k_2 are quantitatively determined from the slope and the y-axis intercept point of the linear line fitted by the $\upsilon^{1/2} \sim i/\upsilon^{1/2}$ curve at each fixed potential.

Warburg coefficient σ_w calculation: The EIS spectrum is composed of a semicircle at high frequency and a linear line within the low frequency. The diameter of the semicircle represents the resistance of the charge transfer process and the slope of the linear line corresponds with the lithium ions diffusion into the bulk of the electrode, the Warburg diffusion. The Warburg coefficient σ_w can be obtained by Equation (2):

$$Z_{re} = R_e + R_{ct} + \sigma_w \omega^{-0.5}$$ **Equation S2**

where R_e is the electrolyte resistance, R_{ct} is the electron transfer resistance and ω is the angular frequency which is quantitatively calculated by the frequency within the measurement range of 0.1 Hz to 100 kHz. Therefore, σ_w is the slope for the Z_{re} vs. $\omega^{-0.5}$ plot.

Diffusion coefficient D calculation:

$$D = 0.5(\frac{RT}{AF^2\sigma_w C})$$ **Equation S3**

where R is the gas constant, T is the measurement temperature, A is the area of the electrode surface, F is the Faraday's constant and C is the concentration of lithium ions.

Exchange current density i_o calculation:

$$i_0 = \frac{RT}{nFR_{ct}}$$ **Equation S4**

Where R is the gas constant, T is the measurement temperature, n is the exchanged electron number, F is the Faraday's constant and R_{ct} is the electron transfer resistance, calculated from EIS measurement.