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Superior electrochemical performance of Li_3VO_4/N-doped C as anode for Li-ion batteries

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Experimental section

Sample preparation

The chemicals were analytical grade and purchased from Shanghai Chemical Reagents. In a typical procedure, 1 mmol V_2O_5, 3 mmol Li_2CO_3 and 5 mmol hexamethylenetetramine were dissolved in 30 ml distilled water. After stirring for 20 minutes, the homogeneous yellowy suspension was transferred into a 50 ml teflonlined autoclave, distilled water was subsequently added to 80% of its capacity. The autoclave was at last sealed and placed in an oven, heated at 120 ^{o}C for 24 h. The final transparent solution was transferred in a culture dish, and 0.5 mmol hexamethylenetetramine was added into the solution. After stirring for 2h, the homogeneous solution was dried in an oven at 50 °C. At last, the precipitates were collected and sintered in N_2 atmosphere at 550 °C for 5 h.

Structure and morphology characterization

The structure and morphology of the resulting products were characterized by X-Ray powder diffraction (Rigaku Ultima IV Cu Kα □radiation λ=1.5406 Å), field-emission scanning electron microscopy (FE-SEM JSM 7500F, JEOL) equipped with Energy Disperse Spectroscopy (EDS), and transmission electron microscopy (TEM, FEI, Tecnai G2 F30) equipped with selected area electron diffraction (SAED).

Electrochemical characterization

For fabricating of lithium ion battery, a mixture of 80 wt% of active material, 10 wt% of acetylene black, and 10 wt% of polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidine (NMP) solution (0.02 g mL^{-1}) were coated on copper foil and cut into disc electrodes with a diameter of 14 mm using a punch. The mass of active material on a disk electrode is about 1~1.5 mg. Coin-type cells (2025) of Li/1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/Li_3VO_4 disc electrode were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, $H_2O<1.0$ ppm, $O_2<1.0$ ppm). A Celgard 2400 microporous polypropylene was used as the separator membrane. The cells were tested in the voltage range between 0.02 and 3 V with a multichannel battery test system (LAND CT2001A). The Cyclic voltammetry (CV) measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of 0.2 mV s^{-1} between 0 and 3 V. Electrochemical impedance spectroscopy (EIS) measurements were performed on CHI660C electrochemical workstation under open circuit conditions over a frequency range from 0.01 Hz to 100 kHz by applying an AC signal of 5 mV in amplitude throughout the tests.

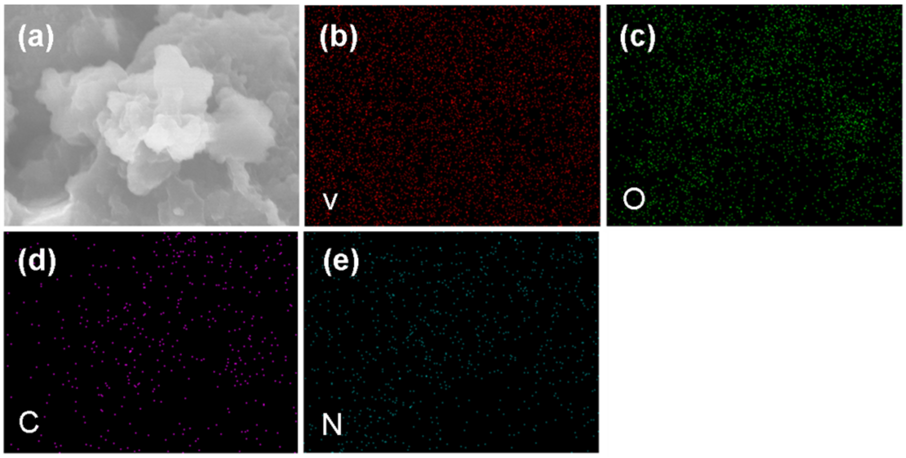

Fig. s1 SEM image (a) and EDS elemental mapping images (b), (c), (d), (e) of the as-prepared Li_3VO_4/N-C.

Fig. s1 is the EDS elemental mapping images of the products, which exhibits clearly the presence of V, O, C and N, demonstrating the successful preparation of Li_3VO_4/N-C.

Tab. s1 The summarization of discharge capacity versus cycle number of various Li_3VO_4 electrodes (the referees number is in accordance with that in the manuscript).

material	current (mA/g) 1C≈394 mA/g	discharge/charge capacities mAh g^{-1}/cycle no.	ref.
Li_3VO_4	20 mA/g	~283, 283/25	1
Li_3VO_4/G	20 mA/g	~?, 378/50	2
Li_3VO_4/C	0.8 C	~366, 363/40	3
Li_3VO_4	0.25 C	398, 396/100	11
Li_3VO_4/C	1 C	394, 394/100	21
Li_3VO_4	0.5 C	250, 245/100	22
Li_3VO_4	0.2 C	164, 164/100 198, 197/100	23
Li_3VO_4/Ni	0.3 C	379, 378/100	24

Li_3VO_4/N-C	150 mA/g	462, 460/100	this work

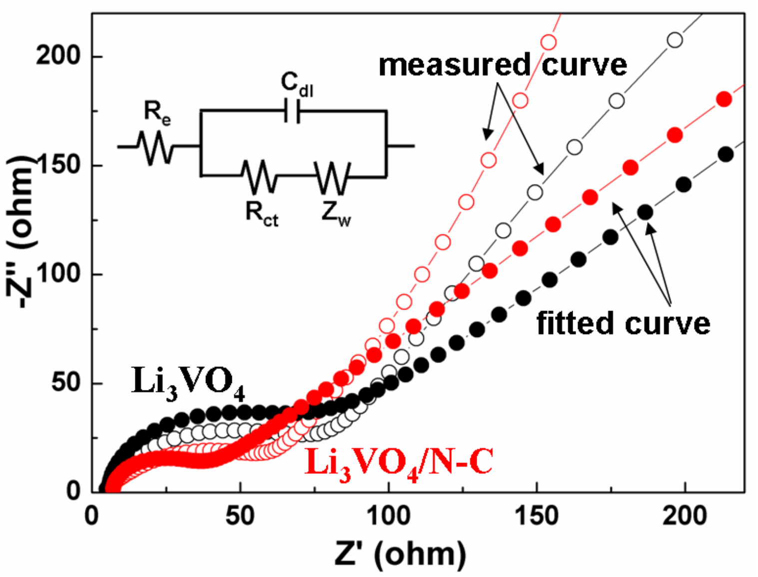

Fig. s2 EIS spectra of pristine Li_3VO_4 and N-doped Li_3VO_4/C electrodes.

Fig. s2 is the electrochemical impedance spectra (EIS) of fresh pristine Li_3VO_4 and Li_3VO_4/N-C electrodes. The intercept in high-frequency can be attributed to the SEI film and/or contact resistance, the medium-frequency semicircle is due to the charge-transfer impedance on electrode/electrolyte interface, and the inclined line in low-frequency corresponds to the Li-ion diffusion process within electrodes [s1]. The Nyquist plots were fitted via an R(C(RW)) equivalent circuit, and the contact and charge-transfer resistances of the electrode (Re and Rct) were obtained from the fitting results (tab. s2). As seen, under fresh state, Li_3VO_4/N-C electrode shows lower Rct than pristine Li_3VO_4 electrode, which suggests improved electronic conductivity owing to the presence of the N-C layer.

Tab. s2 The electrochemical kinetic parameters obtained from equivalent circuit fitting of Nyquist plots of pristine Li_3VO_4 and N-doped Li_3VO_4/C electrodes.

fresh electrode	Re (Ω)	R_{ct} (Ω)
pristine Li_3VO_4	5.68	58.79
Li_3VO_4/N-C	6.99	26.73

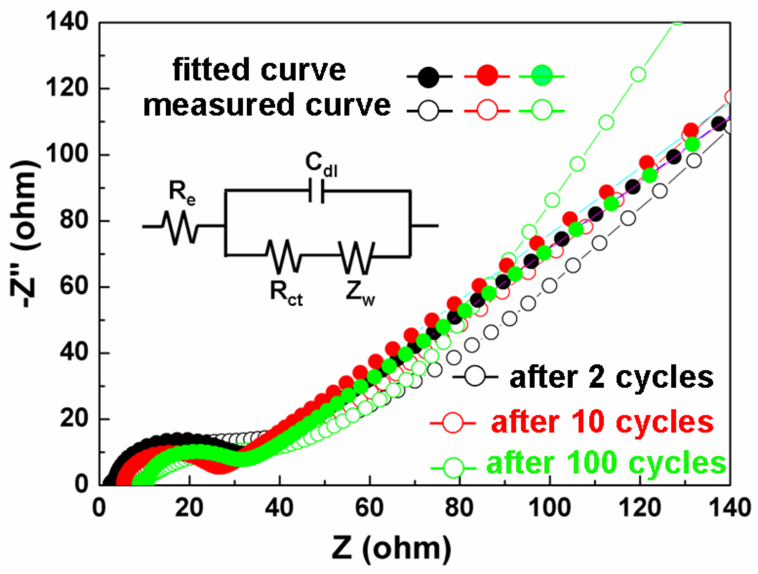

Fig. s3 EIS spectra of N-doped Li_3VO_4/C electrode after different cycles with charge state.

Fig. s3 is the EIS spectra of N-doped Li_3VO_4/C electrode after different cycles with charge state. The Nyquist plots were fitted via an R(C(RW)) equivalent circuit, and the contact and charge-transfer resistances of the electrode (Re and Rct) were obtained from the fitting results. As shown in Tab. s3, Re shows little increase along with the increasing of cycling number, which may be relevant to the gradually formation of SEI in cycling owing the activation process. In addition, Rct shows close value in cycling, which suggests highly stable charge transfer process owing to the good contact between Li_3VO_4 and electric N-doped carbon.

Tab. s3 The electrochemical kinetic parameters obtained from equivalent circuit fitting of Nyquist plots of N-doped Li_3VO_4/C electrode after different cycles with charge state.

Li_3VO_4/N-C electrode	Re(Ω)	R_{ct}(Ω)
after 2 cycles	3.40	25.22
after 10 cycles	5.40	18.70
after 100 cycles	10.46	17.72

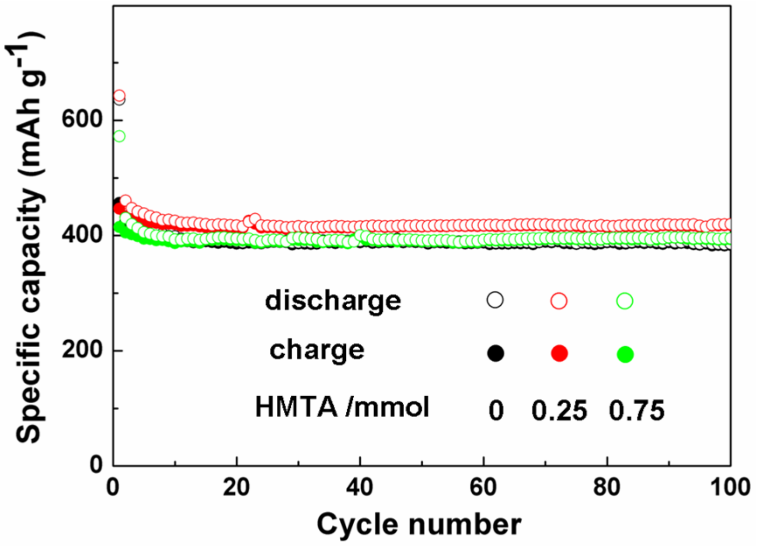

Fig. s4 Cycle performance of pristine Li_3VO_4 and Li_3VO_4/N-C electrodes obtained with different amount of hexamethylenetetramine (HMTA) at a specific current of 150 mA g^{-1}.

As shown in Fig. s4, both pristine Li_3VO_4 and Li_3VO_4/N-C electrodes show good cycle performance at a specific current of 150 mA g^{-1}. For pristine Li_3VO_4 electrode, the charge and discharge capacities are 384 and 386 mAh g^{-1} after 100 cycles. For Li_3VO_4/N-C electrode obtained with 0.25 and 0.75 mmol HMTA, the 100th charge and discharge capacities are 419 and 420, 394 and 395 mAh g^{-1}, respectively.

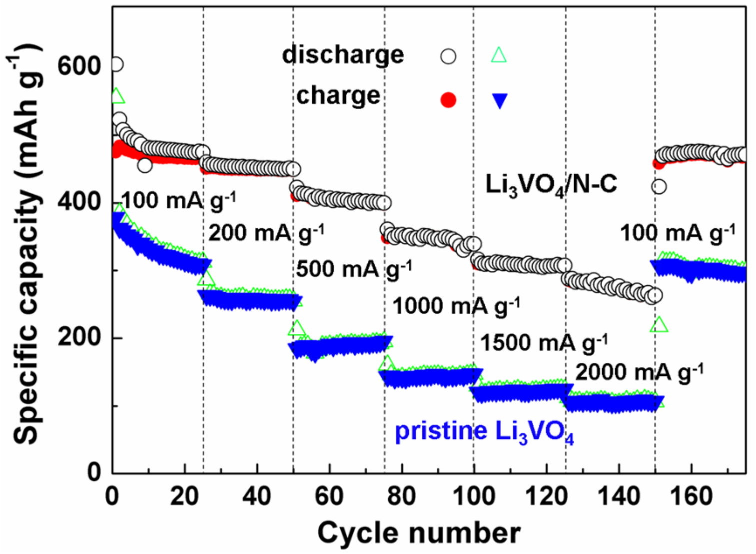

Fig. s5 Rate performance of pristine Li_3VO_4 and Li_3VO_4/N-C obtained with 0.5 mmol hexamethylenetetramine.

As shown in Fig. s5, the Li_3VO_4/N-C electrode shows distinct improved rate performance compared with that of pristine Li_3VO_4. After 150 cycles at various specific currents from 100 to 2000 mA g^{-1}, the 10th discharge and charge capacities of the Li_3VO_4/N-C can reach 476 and 474 mAh g^{-1} when reverting the specific current to 100 mA g^{-1}. For comparison, the 10th discharge and charge capacities of pristine Li_3VO_4 are 297 and 296 mAh g^{-1} when reverting the specific current to 100 mA g^{-1}.

References

[s1] Y.J. Zhu, C.S. Wang, J. Phys. Chem. C, 115 (2011) 823-832.