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A facile spray drying route for mesoporous Li_3VO_4/C hollow spheres as an anode for long life lithium ion batteries[†]

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Mesoporous Li₃VO₄/C hollow spheres have been prepared by a facile drying method and subsequent heat treatment process. The unique structure of the composite offers a synergistic effect to facilitate the transport of Li⁺ ions and electrons and afford an anode with superior rate capability and cyclic stability.

Lithium ion batteries (LIBs) have been considered as one of the most promising electrochemical energy storage systems to power electric vehicles because of their high energy density, long cycling life and high working potential.^{1,2} The commercialized anode material in LIBs is commonly graphite. However, graphite anodes encounter severe safety issues of the dendritic growth of Li metals especially in the fast and long-term cycles, due to their low potential (<0.1 V *versus* Li⁺/Li).³ Therefore, many efforts have been focused on the development of anode materials having improved electrochemical and safety performances.⁴

Spinel Li₄Ti₅O₁₂ possesses a flat potential of 1.55 V (*versus* Li⁺/Li) with zero structural change during cycling; thus it has been used as a high safety and long life anode material.^{5,6} However, the estimated energy density of Li₄Ti₅O₁₂ would be restricted by the relatively high voltage plateau and low theoretical capacity (\sim 175 mA h g⁻¹).^{1,7} Recent studies showed that Li₃VO₄ was intercalated by Li⁺ ions mainly between 0.5 and 1.0 V *versus* Li⁺/Li, lower than Li₄Ti₅O₁₂ and, at the same time can deliver a much higher theoretical capacity (\sim 394 mA h g⁻¹) than Li₄Ti₅O₁₂.^{8,9} The energy density of full cells using Li₃VO₄ as the anode is slightly lower than that of full cells using graphite, but due to its intrinsic high safety, Li₃VO₄ could be a promising anode material for some LIB applications that require higher

safety such as electric vehicles and stationary power plants. Nevertheless, its poor rate capability and long-term performance owing to the low electrode kinetics and electronic conductivity impede its wide use.^{10,11} To overcome these two critical obstacles, research efforts have been divided into two aspects accordingly. To enhance the Li⁺ ion transport kinetics, reducing the particle size or constructing hollow structured Li₃VO₄ has been proposed,^{12,13} and to improve the electronic conductivity, the hybridization of Li₃VO₄ with electronic-conducting carbonaceous materials has been demonstrated to be effective.^{14,15}

In this study, we developed a method to solve these two problems simultaneously. The unique mesoporous $\text{Li}_3\text{VO}_4/\text{C}$ (LVO/C) hollow spheres were synthesized *via* a facile spray drying process and subsequent heat treatment. The surface-coated carbon layer can enhance the electronic conductivity. Meanwhile, the mesoporous and hollow geometry of the spheres is effective for increasing the wetting area for the electrolyte and decreasing the Li⁺ ion diffusion length, both of which are beneficial for the fast charge transport.¹⁶ The resultant LVO/C composite thus exhibits good rate capability and superior cycling life as an anode for LIBs.

The schematic of the formation mechanism of the mesoporous LVO/C hollow spheres is shown in Fig. 1. The micronsized droplets containing water, Li_2CO_3 , V_2O_5 , and glucose were produced using a two-fluid nozzle. The aerosol droplets underwent evaporation and solute condensation within the droplets at 210 °C. This step resulted in the solvent removal,



Fig. 1 The formation mechanism of the mesoporous LVO/C hollow spheres.

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while the solute was enriched to the surface layer. After the droplet-to-particle step was finished, the hollow spherical precursor containing lithium vanadate and glucose was collected, and annealed in an Ar atmosphere at 550 °C to obtain the LVO/C hollow spheres. More details of the device and experimental procedure are given in the ESI.[†]

X-ray diffraction (XRD) patterns of the prepared LVO and LVO/C composite are shown in Fig. 2a. The diffraction peaks of both samples are perfectly coherent with the orthorhombic Pnm21 phase of Li₃VO₄ (JCPDS no. 38-1247). Rietveld refinement of XRD data (Fig. S3[†]) indicates the cell parameters with a = 6.324043 Å, b = 5.444722 Å, c = 4.952347 Å and V =170.52 Å³, which are consistent with previous reports.^{8,14} The samples of the LVO and LVO/C composite were further analyzed by Raman microscopy (Fig. 2b). The peaks of LVO located at 200–500 cm⁻¹, and 800–900 cm⁻¹ are related to Li₃VO₄.¹³ The intensity of these peaks for LVO/C decreases sharply (only an obvious peak at 819 cm⁻¹ is observed as shown in the inset of Fig. 2b), which indicates that LVO is well encapsulated by the carbon and thus is hardly detectable by Raman spectroscopy.10 The peaks of LVO/C at 1350 cm^{-1} and 1600 cm^{-1} are the characteristic D-band and G-band of amorphous carbon or disordered graphite, respectively.17 The carbon ratio of the LVO/ C composite was estimated to be 24.0% by thermogravimetric analysis (Fig. S4[†]).

Nitrogen adsorption isotherms of the LVO/C show a type-IV curve (Fig. 2c). The specific surface area is calculated to be 128.6 m² g⁻¹, which is several times higher than that of LVO (14.9 m² g⁻¹, Fig. S5†). The pore size distribution (Fig. 2d) indicates that the LVO/C composite mainly possesses mesopores at a narrow pore size distribution of about 3.9 nm. Compared to the pristine LVO, the larger specific surface area and porous structure of the LVO/C could provide a larger electrode–electrolyte contact area and reduced paths for Li⁺ ion diffusion, which should give rise to a higher apparent Li⁺ ion diffusion coefficient.^{18,19}

The morphology and structure of the LVO/C composite were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image shows that the particles of LVO/C are microspheres with a wide size distribution between 0.5 and 5 µm in diameter (Fig. 3a and S6[†]). The TEM images, as shown in Fig. 3b and c, clearly reveal the hollow structure of LVO/C microspheres. The selected area electron diffraction (SAED) image (the inset of Fig. 3c) of the LVO/C particles confirms the polycrystalline structure of LVO in the composite with the diffraction spots being clearly observed. As shown in the high resolution transmission electron microscopy (HRTEM) image (Fig. 3d), it is evident that the LVO particles are coated with a layer of carbon with a thickness of about 5 nm. The interplanar distance of the LVO particles inside is measured to be about 0.41 nm, which matches well with the *d*-spacing of (110) planes of the orthorhombic Pnm21 Li₃VO₄. There also exists an apparent carbon coating on the surface of the larger hollow LVO/ C sphere (Fig. S8[†]), which indicates uniformity of the composite structure even with a wide particle size distribution. The HAADF image of the single LVO/C sphere (Fig. 4a) further confirms the hollow structure of the composite. The elemental mapping results of the LVO/C sphere (Fig. 4b-d) reveal the homogenous distributions of C, O, and V elements in the shell.

Fig. 5a shows the first three cycles of discharge/charge curves at a rate of 0.2C. The initial discharge/charge capacity is 665.7 and 429.4 mA h g^{-1} , respectively, with the first coulombic efficiency (CE) of 64.5%. The cycling performance of both LVO/C and LVO at 0.2C is presented in Fig. 5b. The LVO/C delivers a charge capacity of 400 mA h g^{-1} after 100 cycles, indicating the excellent cycling stability of this material, but for LVO, it shows only 204 mA h g^{-1} after 100 cycles. It is well known that the insertion/extraction of Li⁺ into the LVO would generate a certain



Fig. 2 (a) XRD patterns, and (b) Raman spectra of the LVO and LVO/C composite; (c) N_2 adsorption–desorption isotherms, and (d) corresponding pore size distribution of the LVO/C composite.



Fig. 3 (a) SEM image of the LVO/C; (b and c) TEM images of the LVO/C, the inset is the corresponding SAED pattern indexed using the powder diffraction technique; (d) HRTEM image of the LVO/C.



Fig. 4 (a) High-angle annular dark field (HAADF) image of a single LVO/C sphere; (b-d) EDS mapping of C, O, and V elements in the single LVO/C sphere.

structural stress on the material.²⁰ The pristine LVO consists of irregular shaped dense particles with the maximum size of \sim 30 µm (Fig. S7†), which is adverse to release the structural stress. Thus large LVO particles may crack into several small particles during cycling. Because of the low electrical conductivity of pristine LVO, some small particles may lose conductive contact with the entire conductive framework of electrodes, leading to capacity fading.

The rate performance of both samples was also investigated by cycling at various current densities ranging from 0.5C to 80C (Fig. 5c). It can be seen that the LVO/C exhibits much higher capacity, especially at high rates. The LVO/C can reach a high specific capacity of 395 mA h g^{-1} at 0.5C. As the current densities increase from 1C to 2C, 5C, 10C, 20C, and 50C, the reversible capacity of the LVO/C composite decreases gradually from 385 mA h g $^{-1}$ to 372 mA h g $^{-1}$, 352 mA h g $^{-1}$, 333 mA h g $^{-1}$, 309 mA h g^{-1} , and 196 mA h g^{-1} , respectively. Even at an extremely high current density of 80C, the LVO/C electrode can still deliver a stable capacity of 125 mA h g^{-1} , whereas the capacity of LVO is almost zero. The LVO/C also shows much better high-rate performance than pristine LVO with smaller particle sizes (Fig. S9[†]). Encouragingly, the LVO/C exhibits a reversible capacity of 275 mA h g^{-1} (97% retention of the initial reversible capacity) after 3000 cycles at 10C (Fig. 5e). The capacity of carbon in LVO/C is 102 mA h g^{-1} at 0.2C, and 27 mA h g^{-1} at 10C, respectively (Fig. S10⁺). It can be seen that the capacity contribution of carbon in LVO/C is very low.

The cycling performance of our LVO/C is also compared with that of other LVO/carbon materials reported previously (Table S1†). Our LVO/C shows good cycling stability at high rates when the loading mass, cycle number, and capacity are comprehensively considered. And the electrochemical performance of



Fig. 5 (a) Galvanostatic discharge-charge profiles of LVO/C in the voltage range of 0.2–3 V vs. Li⁺/Li at a rate of 0.2C (1C \approx 400 mA h g⁻¹); (b) cycling performance of LVO/C and LVO at a current density of 0.2C; (c) discharge and charge capacities of LVO/C and LVO at various C-rates; (d) CV curves of the LVO/C composite at different scan rates ranging from 0.2 to 1.2 mV s⁻¹; (e) long-term cycling performance of LVO/C at 10C. All capacity calculations are based on the mass of LVO/C.

LVO/C is not very sensitive to the loading mass within the range of 0.56–0.94 mg cm⁻² (Fig. S11†). The packing density of an electrode is also very important in the LIB industry. As shown in Tables S2 and S3,† the packing density of the LVO/C electrode is 1.01 g cm³ which is almost the same as that of the graphite electrode (1.05 g cm³).

CV curves of both samples are also measured at different scan rates from 0.2 to 1.2 mV s⁻¹ (Fig. 5d and S13†). As the scan rate increases, the Li[†]-insertion/extraction peaks shift to low and high potential, respectively. However, the LVO/C electrode shows much smaller potential shifts than the LVO electrode, indicating improved electrode kinetics.²¹ There is a good linear relationship between the oxidation peak current (I_{pa}) and the square root of the scan rate ($v^{1/2}$) (Fig. S12†), suggesting a diffusion-controlled process in the charge and discharge process.^{22,23} Thus, the Li⁺ ion diffusion is a key factor to the electrode kinetics. Accordingly, the apparent Li⁺ ion diffusion coefficient can be calculated based on the Randles–Sevcik equation (eqn (1)):^{9,24}

$$I_{\rm pa} = 0.4463 n F C_{\rm Li} A \sqrt{\frac{n F v D}{R T}}$$
(1)

where *n* is the number of electrons involved in the reaction of the redox couple, *F* is Faraday's constant, C_{Li} is the concentration of Li⁺ ions, *A* is the working electrode area, *v* is the scan rate, *R* is the gas constant, and *T* is the absolute temperature.²⁵

From the slope of the fitting line (Fig. S12[†]), the apparent Li⁺ ion diffusion coefficient of LVO/C is calculated to be 2.57×10^{-12} cm² s⁻¹, which is four times that of LVO (5.95 \times 10 $^{-13}$ cm² s $^{-1}$, calculated in Fig. S13[†]). The EIS was used to provide further insight (Fig. S14[†]). Each plot shows two compressed semicircles in the high to medium frequency range of each spectrum, which reflects the solid electrolyte interface (SEI) resistance (R_f) and charge-discharge resistance (R_{ct}) , and an inclined line in the low-frequency range, which could be considered as Warburg impedance (Z_w) .²⁰ A good agreement is observed between the impedance and fitting data using the inset equivalent circuit model. The R_{ct} of the LVO/C electrode is 14.36 ohm, much smaller than that of LVO (50.93 ohm). These results show that the LVO/C has a smaller charge transfer resistance and higher Li⁺ ion diffusion coefficient,¹³ which are favorable for fast charge and discharge.

Conclusions

In conclusion, a facile route has been developed for simple yet scalable production of mesoporous $\text{Li}_3\text{VO}_4/\text{C}$ hollow spheres. The LVO/C has unique structural features for the good electrochemical performance because (1) the porous and hollow structure favors a shorter diffusion length for Li^+ ions; (2) the exterior electronic conductive carbon coating facilitates the electron transport. As a result, the LVO/C demonstrates much better high-rate capability and much improved cycle life. Therefore, the LVO/C composite is a promising anode candidate for the development of high-rate, long-life and high-safety LIBs.

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