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Qidong Li,^a Yanming Zhao,^{b, c} Quan Kuang,^{*b} Qinghua Fan,^b Youzhong Dong^b and Xudong Liu^a

ZrV₂O₇ has attracted much attention as a negative thermal expansion (NTE) material due to its isotropic negative structure. However, rare investigation of the lithium storage behaviors has been carried out except our first report on it. Meanwhile, the electrochemical behaviors and energy storage characteristics have not been in-depth studied and will be explored in this project. Herein, we report on the synthesis, characterization and lithium intercalation mechanism of superstructure ZrV₂O₇ nanofibres that were prepared through a facile solution-based method with subsequent annealing process. Thermal *in-situ* XRD technique combined with *Rietveld* refinement method are adopted to analyze the change of temperature-dependent crystal structure. Benefiting from the nanostructured morphology and relatively high electronic conductivity, it presents acceptable cyclic stability and rate capability. According to the operando evolution of the XRD patterns obtained from electrochemical *in-situ* measurement, the Li intercalation mechanism of solid solution process with subsequent conversion reaction can be concluded. Finally, the amorphous state of the electrodes after initial fully discharged state can effectively enhance the electrochemical performances.

Introduction

Rechargeable lithium-ion batteries (abbreviated as LIBs, and similarly hereinafter) with high capacity, long lifespan, no memory effect, and environmental benignity have been extensively applied in portable electronic devices.¹⁻⁷ However, both the commercial used LiCoO₂ cathode and graphite anode encounter certain problem such as low-capacity which cannot meet the growing demand for high-energy/power densities applications like electric vehicles, plug-in hybrid electric vehicles, and further large-scale grid storage. So, it is an essential task to seek new materials with higher capacities to meet the rapidly growing requirements of LIBs with higher energy/power densities.⁸⁻⁹ Transition metal oxides (TMOs) including binary and ternary (also called the mixed transition metal oxides (MTMOs)) ones with their unique morphologies have attracted considerable interests in recent years because of their promising applications in many fields such as electrocatalysts for the oxygen reduction reaction,¹⁰⁻¹¹ electrode materials for electrochemical capacitors (ECs), and

*Corresponding author. E-mail: sckq@scut.edu.cn

Li-ion batteries (LIBs).¹²⁻¹⁴ Among them the binary TMOs always suffered from poor conductivity and huge volume change during electrochemical discharge/charge process for LIBs,¹⁵⁻¹⁷ while the ternary MTMOs showed their potential in synergistically enhancing the electronic/ionic conductivity, reversible capacity and mechanical stability.¹⁸⁻²⁰

As one of the MTMOs family, transition metal vanadates (TMVs) with abundant sources and relatively high ionic conductivity seem to be a superior group and have attracted many researchers' interests in recent years.^{18, 21-35} Apart from the excellent performed anode materials such as $Co_2V_2O_7$ ²¹ $Co_{3}V_{2}O_{8}$,^{18, 22} FeVO₄,²³ Zn₃V₂O₈,²⁴ etc., TMVs also show their versatile potentials in cathode materials. Layered structured α -CuV₂O₆ nanofibres were applied as a cathode material for LIB by Chen *et al.*, with high discharge capacities (447-514 mAh g^{-1} at 20 mA g^{-1} and 37 °C) and excellent high-rate capability displayed. 26 Alkali metal vanadates $Li_{1+x}V_3O_8$ has been researched for almost 40 years as a cathode material for its higher capacity and better safety features.²⁷⁻³⁰ Many lithiated Li_xV₂O₅ phases occurring during the electrochemical reaction $V_2O_5 + xLi^+ + xe^- = Li_xV_2O_5$ indicate the multi-electron transportation process, leading to the widespread study of different $Li_xV_2O_5$ phases as cathode materials.³¹⁻³³ Zhang *et al.* reported ε -Cu_{0.95}V₂O₅ nanoribbons as a high-capacity cathode. He found that the obtained materials could host 2.64 Li in a reversible way, leading to a reversible capacity up to 292 mAh $g^{-1.34}$ Recently, the sol-gel synthesized ZrV₂O₇ micro-particles had been evaluated as a Li-absent cathode material for rechargeable Li batteries.³⁵ The relatively high capacity and acceptable cyclic ability reveal its potential use in the future. While according to the reported TMVs electrodes, the

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^{a.} School of Materials Science and Engineering, South China University of Technology, Guangzhou, 510641, P. R. China.

^{b.} School of Physics, South China University of Technology, Guangzhou, 510641, P. R. China.

^c State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510641, P. R. China.

Electronic Supplementary Information (ESI) available: [The adjusting information of fabrication, EDS result of the fibrous section in Fig. 1(a), schematic of V-O-V linkages of normal and superstructure ZrV_2O_7 , coefficient of thermal expansion plot, dQ/dV curves and the detailed values from EIS fitting]. See DOI: 10.1039/x0xx00000x

ARTICLE

electrochemical performances have been found to be influenced by the morphologies of the synthesized materials].^{18, 21-24} As is known to us, different kinds of nanostructures have been fabricated and investigated chronically to relieve the strain and deformation of those materials for flexible usages, mechanical engineering, or battery electrodes with deformation before/after Li insertion/extraction. Also, the importance of nanoscale architecture had been proved in especially MTMOs on enhancing their electronic and ionic transportation properties. Downsizing materials to nanoscale level is an effective approach to enhance the electrochemical performance due to the increased surface areas and the shortened Li-ion diffusion paths of the active material particles.³⁶⁻³⁸

In this article, the traditional negative thermal expansion (NTE) material ZrV_2O_7 nanofibres (NFs) have been synthesized successfully by using a solution-based method under ambient conditions for the first time. XRD data together with the *Rietveld* refinement results indicates that the obtained ZrV_2O_7 nanofibres are in its superstructure form. The rate capability and cyclic performance are also enhanced by using the obtained superstructure ZrV_2O_7 nanofibres as cathode materials for Li-ion batteries. Furthermore, The Li intercalation mechanism was explored and discussed.

Experimental

Raw materials

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All chemicals, zirconium nitrate pentahydrate ($Zr(NO_3)_4 \bullet 5H_2O$), vanadium pentoxide (V_2O_5), oxalic acid ($H_2C_2O_4$) and urea ($CO(NH_2)_2$) were used as received without further purification to prepare the precursor. All aqueous solutions were freshly prepared using double distilled water as solvent.

Synthesis of nanofibres-composed $\rm ZrV_2O_7$ superstructure

A sol-gel method was used to synthesize the target product. In a typical process, 0.4042 g V_2O_5 and 0.8362 g $H_2C_2O_4$ in a stoichiometric ratio of 1:3 were firstly dissolved in 10 mL actively stirred deionized water at 60 °C until a clear blue solution was formed. The initial purpose to use oxalic acid was to dissolve V_2O_5 , namely the reducing agent. The reaction process can be described as the following formula:³⁰

Next, 0.8079 g Zr(NO₃)₄•5H₂O in stoichiometric amount was dissolved in 5 mL deionized water and then added dropwise to the aforementioned solution. The V/Zr ratio was set as 2.35 in which the V content was excess due to the easily vaporization of V in high temperature during annealing process. The detailed V/Zr ratio adjusting information can be found in the supplementary information (Fig. S1). 0.5 g of urea was used as surfactant agent, and the mixture was vigorously stirred at 60 °C until a sol formed. After drying at 90 °C in an air oven overnight, the gel was calcined at 800 °C for 2 h in a continuously flux of oxygen. The calcination process can be expressed as follows:

 $4VOC_2O_4 + 2Zr(NO_3)_4 + O_2 \uparrow = 2ZrV_2O_7 + 8CO_2 \uparrow + 8NO_2 \uparrow$ The whole process were conducted at atmospheric pressure.

Materials characterization

X-ray diffraction (XRD) data of ZrV_2O_7 NFs for comparison and *Rietveld* refinement analysis were collected on a Bruker D8 Advance diffractometer with Cu K α radiation (λ = 1.5406 Å). The XRD data acquired at temperature varied from room temperature (RT) to 400 °C were obtained from a PANalytical X'Pert Pro MPD diffractometer (Cu K α radiation: λ = 1.5406 Å) equipped with an auto-thermophilic sample stage. Morphology and composition were analyzed by field-emission scanning electron microscopy (FESEM, Nova NanoSEM430), and energy dispersive spectrometer (EDS, Oxford instruments) attached to the SEM.

Electronic conductivity measurements

Superstructure ZrV₂O₇ NFs were pressed into pellets (10 mm in diameter and ~1 mm in thickness) and annealed at 800 °C for 2 h under oxygen atmosphere to measure the direct current (dc) electronic conductivity. The two sides of the pellets were deposited with conductive silver epoxy to strengthen the contact between the ZrV₂O₇ pellets and electrical silver wires. An AUTOLAB PGSTAT302N (Metrohm, Netherlands) was used to acquire the I-V curves based on a cyclic voltammetry (CV) process with the scan rate of 0.1 V s⁻¹ in the voltage range of -1.0 V~1.0 V.

Electrochemical measurements

LIR2032-type coin cells were assembled in a high purity argonfilled glove box. Lithium metal was used as counter and reference electrode. Superstructure ZrV₂O₇ NFs, conductive acetylene black and polyvinylidene fluoride (PVDF) with the weight ratio of 70:20:10 were blended in N-methyl-2pyrrolidone (NMP) solution to obtain a homogeneous slurry, and then coated onto clean aluminum foil which served as a current collector. After drying in an oven at 90 °C for 24 h, the electrode was cut into small discs to serve as working electrodes. 1 M LiPF₆ in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1, v/v) was used as the electrolyte and Celgard 2320 microporous membrane as the separator. Galvanostatic discharge/charge tests were performed with the current density of 10 mA g⁻¹ in the voltage range of 1.5- 4.0 V (vs. Li/Li⁺) using a LAND-CT2001A cell test system. The specific capacity was evaluated for the active material only. Cyclic voltammetry (CV) potentiostatic in the voltage range of 1.5-4 V (vs. Li/Li^{\dagger}) at a scanning rate of 0.1 mV s⁻¹ and electrochemical impedance spectroscopy (EIS) at the corresponding cell voltage in the frequency range from 100 kHz to 0.01 Hz was carried out by using an AUTOLAB PGSTAT302N (Metrohm, Netherlands) workstation. In-situ Xray diffraction experiments were performed using a specifically developed electrochemical cell formed with a beryllium window as current collector. The electrochemical measurements were controlled by a LAND-CT2001A test system. The cell was cycled at a current density of 10 mA g⁻¹ during discharging process and 20 mA g⁻¹ in following charging procedure. All the above measurements were conducted at room temperature.

Journal Name



Fig. 1 (a) (b) (c) SEM images of the as-synthesized superstructure ZrV_2O_7 nanofibres. (d) Point EDS result of the individual nanofibre in (c). The quantitative analysis is shown inset.

Results and discussion

Typical SEM images of the as-synthesized superstructure ZrV₂O₇ nanofibres were shown in Fig. 1. The overview image of Fig. 1(a) shows that the nanofibres have nearly uniform diameter along their entire length, which stretch along several micrometers. Moreover, these nanofibres are interconnected into a porous network architecture. Closer observations (Fig. 1(b)&(c)) indicate the uniform smooth surfaces of the nanofibres with width of 200- 400 nm. A representative X-ray energy dispersive spectrometer (EDS) image of the point marked with cross fork in Fig. 1(c) that taken from the FE-SEM attachment is demonstrated in Fig. 1(d), in which the signals of O, Si, V, Zr, Al and K can be observed. Zr/V/O signals reveal the existence of desired products. The excrescent element signals (K, Si and Al) were from the mica plate used as loading substrates in SEM testing. Quantitative analysis of the EDS result is presented as well (inset of Fig. 1(d)). The nearly same Zr/V/O atomic proportion (8.37/18.73/64.26) to the stoichiometric ratio further prove the formation of ZrV₂O₇ sample. In order to further confirm the element proportion of the synthesized sample, we did another experiment using Elemental Analysis technique to serve as an extra evidence. The results show that the weight percentage of Zr, V and O are 30.03 %, 32.01 % and 37.96 %, which correspond to the atomic percentage of 9.89 %, 18.85 % and 71.26 %. The atomic percentage also coincide with the stoichiometric ratio of ZrV₂O₇. Moreover, apart from the point EDS analysis of the obtained sample, a large selected area of the fibrous region was also applied for EDS quantitative analysis (See Fig. S2 in supplementary information). The much rational results compared to point EDS results indicate the homogenous and successful synthesis of ZrV₂O₇.

The phase composition and purity of the as-prepared samples were investigated by using XRD technique. Both standard XRD patterns of normal ZrV_2O_7 (space group: $Pa\overline{3}$, ICSD #59396) and its superstructure form (space group: $Pa\overline{3}$, ICSD #84883) were presented for comparison with the experimental result (shown in Fig. 2(a)). It can be clearly distinguished that all the diffraction peaks of the obtained sample correspond to that of the ZrV_2O_7 superstructure rather than the normal form according to the position and relative



Fig. 2 (a) XRD patterns of the as-synthesized superstructure ZrV_2O_7 nanofibres. (b) *Rietveld* refinement of the samples. (c) The crystal structure of ZrV_2O_7 superstructure. (d)(e) Crystal structure of normal structure of ZrV_2O_7 with different view directions.

intensity of the peaks. Fig. 2(b) shows the Rietveld refinement for ZrV₂O₇ NFs carried out by using GSAS program via the EXPGUI interface, and a space group of Pa 3 in cubic superstructure was chosen as the refinement model. The computational XRD pattern fits the experimental data points very well as apparently indicated by the relatively small Rwp (9.06%) and Rp (6.64%), which reveals single phase superstructure ZrV₂O₇ NFs with no impurity phases detected were obtained under the fabrication conditions. The crystal structure of ZrV₂O₇ superstructure consists of corner-sharing VO₄ (light blue) tetrahedral and ZrO₆ (gray) octahedral has been shown in Fig. 2(c), from which VO₄ double layers along the b-direction can be clearly seen. The Zr cations lie in the interlayer space, coordinating with nearest six oxygen atoms to build ZrO₆ octahedral chains, which are separated from each other by VO₄ tetrahedral double chains. Each oxygen of a ZrO_6 octahedron is shared with a VO₄ tetrahedron. Each VO₄ tetrahedron shares three of its four O atoms with a ZrO₆ octahedron, whilst the fourth is shared with another VO₄ tetrahedron leading to a V_2O_7 pyrovanadate group. Obviously, the crystal structure of the ZrV₂O₇ superstructure form would be visually regarded as a 3×3×3 superposition of the cubic unit cell of normal ZrV₂O₇ as displayed in Fig. 2(c), (d)&(e). However, the superstructure form shows much weaker reflections according to the refinement results from singlecrystal synchrotron X-ray data of ZrV₂O₇.³⁹ Specifically, two of the six V₂O₇ groups in superstructure ZrV₂O₇ are constrained by symmetry to contain linear V-O-V linkages, while the remaining four are free to bend away from 180°. This is significantly different from the normal ZrV2O7 structure of which the six V_2O_7 groups are constrained to be 180° on account of the bridging O atom lies on a 3 site. The six linear V-O-V linkages endow it a much higher structure symmetry than

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ARTICLE

superstructure ZrV_2O_7 .³⁹ The lower symmetry of ZrV_2O_7 superstructure would affect the electron and Li-ion passageways along a, b, and c axes during discharge/charge process when applied as cathode materials for Li-ion batteries. Most obviously, the nonlinear V-O-V linkages of ZrV_2O_7 superstructure would result in zigzag Li-ion channels, thus reducing the ionic diffusion rate. This phenomenon can be clearly seen from the schematic V-O-V linkages of both normal and superstructure ZrV_2O_7 illustrated in Fig. S3 (Supplementary Information). Nevertheless, the stability of the superstructure would be better to buffer the volume change during Li ions insertion/extraction because of the static disorder of oxygen atoms in bent V-O-V linkages and the lower free energy.⁴⁰⁻⁴¹

Generally, ZrV₂O₇ was highly noted as a compound that showed a bulk contraction in volume on heating in the past few decades, so-called negative thermal expansion (NTE) material. Attributing mainly to its relatively high-symmetry structure originated from NaCl structure type (Space group $Fm\overline{3}m$) among which the cation is Zr^{4+} and $(V_2O_7)^{4-}$ radical acts as the anion,³⁹ the ZrV_2O_7 type structure is also unique in providing for isotropic negative structure over a very broad temperature range rather than the commonly anisotropic NTE materials.⁴¹⁻⁴² ZrV₂O₇ was studied to be above 102 °C to present the claimed feature.43-44 On the other hand, the thermal-related structure change is also seemed as helpful for safety issue in Li-ion batteries because the shrinking Li-ion passageways derived from lattice contraction of NTE materials is expected to obstruct the diffusion of Li ions just like the function of separator in the situation of thermal runaway. The thermal expansion investigation of superstructure ZrV₂O₇ NFs was therefore carried out from RT to 400 °C, attempting to find the morphology-structure-property relationship of this compound. One can see distinct peaks shift from Fig. 3(a), with their corresponding temperature labeled aside. The strongest peak is magnified to demonstrate the change clearly. As the temperature increases, the peaks move to lower angles, indicating the augment of *d*-spacings according to *Bragg* equation:45

$n\lambda = 2d \sin\theta$

Hence, the positive thermal expansion of the unit cell can be referred at the beginning due to the cubic structure of ZrV_2O_7 . The peaks move backward to higher angles with the continuously increasing temperature, revealing the negative



Fig. 3 (a) XRD patterns and (b) cell parameter of superstructure ZrV_2O_7 nanofibres in the temperature range of RT~400°C.

thermal expansion phenomenon. All the patterns were successfully indexed with a cubic lattice using the program Dicvol embedded in FullProf Suite, and the lattice parameters were further least-square refined by the program PIRUM. The obtained cell parameters versus temperature variation is plotted in Fig. 3(b), from which the positive thermal expansion (PTE) (RT~120 °C) and NTE (above 120 °C) stages are obviously presented. And the transformation temperature of about 120 °C is referred from the result, which differs to that of the reported normal ZrV₂O₇ (about 102 °C) to some extent. The morphology and structure may be responsible for the small difference. Except for the safety issue concerned in LIBs at higher temperature or self-heating during discharge/charge process, the nanofibres-composed ZrV₂O₇ are also believed to be significantly useful for thermal expansion areas used in cooperation with positive thermal expansion materials due to their tougher and stronger interfacial contact caused by larger contact area of nanoscale size. As can be seen from Fig. S4 in the supplementary information, the linear thermal expansion of superstructure ZrV₂O₇ nanofibres is presented. Above 120 °C in NTE area, a mean coefficient of linear expansion of - 5.57×10^{-6} °C⁻¹ can be obtained.

The electronic properties of the obtained superstructure ZrV_2O_7 NFs would be of great importance to the application in electrode materials for Li-ion batteries, in which the high internal electronic conductivity can reduce the voltage polarization and heat release. Furthermore, cathode materials with good conductivity can easily increase the electrochemical activity and benefit the charge transfer among the cathode materials.⁴⁶⁻⁴⁷ Hence, the electronic conductivity of superstructure ZrV_2O_7 NFs pellet at temperatures ranging from 100 to 220 °C were studied. Fig. 4(a) illustrates the schematic diagram of the electronic conductivity measurement set-up. The fast Ohmic response of the CV test can be shown as a



Fig. 4 (a) Schematic picture of the test of electronic conductivity. (b) (c) I-V curves of superstructure ZrV₂O₇ nanofibres pellet at temperature range of 100~220°C. (d) The In(σ T) vs. 1000/T plot.

4 | J. Name., 2012, 00, 1-3

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Journal Name

galvanostatic current-voltage process. I-V curves of the same ZrV₂O₇ pellet in different temperature ranges are shown in Fig. 4(b) and Fig. 4(c), respectively. All the curves seem to be linear, indicating favourable Ohmic contacts formed between the metal electrodes and the pellet. The linear fitting result shows that the conductivity of ZrV_2O_7 at RT is 2.8×10^{-5} S cm⁻¹, which is much higher than that of many traditional cathode materials, such as LiFePO₄ $(10^{-9} \text{ S cm}^{-1})^{48}$ and LiMn₂O₄ $(10^{-6} \text{ S cm}^{-1})^{.45}$ From the I-V curves, it is seen that the electronic conduction of the pellet progressively decayed with increasing temperature from 100 to 120 °C, and was back to a rising trend when the temperature was higher than 150 °C, which comply a similar tendency with the structural evolution versus temperature (indicated in Fig. 3). It's not difficult to connect the same trend with some causal relationship. In concrete terms, the ZrV₂O₇ superstructure started to inflate with the positive thermal expansion process beneath 120 °C, in which the length of bonds were enlarged, resulting in the increasing atom distance and transport distance. Electronic transport along lager distance generates a diminished electronic conductivity on this occasion.⁴⁷ When the temperature was increased to the NTE period, an opposite trend was shown in the same way. As a quasi-rigid unit modes (QRUMs) termed mechanism that display phonon-driven contraction material, the vibrations of V-O-V linkages are mainly responsible for its claimed NTE effect and the abrupt change of electronic

conductivity.⁵⁰⁻⁵¹ In detail, in PTE period, during which the scattering of phonon to transporting electrons become stronger with the increasing temperature, the electronic conductivity is apparently influenced to reduce. When the temperature increases continuously over 120 °C, mean oxygen angles in the structure may open up, causing the large amplitude transverse vibrations of the oxygens through coupled librations of the tetrahedra and octahedra until a higher symmetry state is reached.⁴⁰ The higher symmetry with better periodic lattice field would lower the scattering probability of phonon to electrons. Meanwhile, the intrinsic excitation of ZrV₂O₇ at higher temperature can enhance the electronic conductivity as well. An analogous abrupt tendency of conductivity and lattice constant has also been observed in other NTE materials such as $Mn_3Ga_{0.75}Si_{0.25}N$,⁵² $Mn_{3+x}Sn_{1-x}C$ (x \leq 0.1) and Mn₃Zn_vSn_{1-v}C (y= 0.4, 0.5) compounds,⁵³ in which the magnetic transition are primarily responsible for their unusual properties. Further exploration need to be conducted in the future whether the same reason can be used to explain the abnormal phenomenon. The conductivity, σ , of the superstructure ZrV_2O_7 NFs pellet is plotted in Fig. 4(d) as $ln(\sigma T)$ versus reciprocal temperature in the range of 100~220 °C. This plot is used to analyze the data in the frame of the general formula for electronic conductivity of transition metal oxides proposed by Mott,⁵⁴ where the conductivity is given by:



Fig. 5 (a) Galvanostatic discharge and charge curves of ZrV_2O_7 nanofibres at a current density of 10 mA g⁻¹. CV curves at a voltage window of $1.5^{\sim}4$ V vs. Li/Li⁺ are shown inset. (b) Rate capability of ZrV_2O_7 nanofibres tested at rates of 10, 20, 50, 100, and 200mA g⁻¹. (c) Cycle performance of superstructure ZrV_2O_7 nanofibres at open circuit state, after 1st and 2nd cycle. The inset is the corresponding equivalent circuit.

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ARTICLE

$$\ln\sigma T = \ln A - \frac{W}{kT}$$

 $\sigma = \left[\frac{(v_0 e^2 C)(1 - C)}{kRT}\right] \exp(-2\alpha R) \exp(-\frac{W}{kT})$

where v_0 is a phonon frequency, *C* the concentration, *R* the average hopping distance, *W* the activation energy, and α the rate of wave function decay.⁵⁵ The two periods can be linearly fitted with different slope, indicating their conformation to the typical Mott law. As can be analogized to the reported Ca₂V₂O₇ single crystal,⁵⁶ the conduction mechanism should be attributed only to the electron conduction that stems from the vanadium ions at lower temperatures (< 102 °C). And the addition of predominantly ionic conduction by mobile Zr^{4+} or O^{2-} ions above 102 °C is the reason for the steeper slope shown in Fig. 4(d) in the corresponding temperature range.

Representative discharge/charge curves at 10 mA g⁻¹ for the 1st, 2nd and 10th cycles are depicted in Fig. 5(a) within a voltage window of 1.5~4 V vs. Li/Li⁺. The initial specific discharge and charge capacity of 279 mAh g⁻¹ and 208 mAh g⁻¹ can be achieved, which are much higher than that of most state-of-the-art Li-contained cathode materials. The resulting columbic efficiency of 74.6% indicates the irreversible conversion reaction and inert reaction products formed similar to most conversion electrode materials.⁵⁷ However, the values of charge and discharge capacity are slightly lower than the normal structured ZrV₂O₇ reported by our group recently (282.6 mAh g^{-1} and 227.7 mAh g^{-1} for discharge and charge respectively).³⁵ The reason would be related to the lower symmetry of ZrV₂O₇ superstructure, which has nonlinear V-O-V linkages induced zigzag Li-ion channels. CV curves in Fig. 5(a)inset reveal similar redox peaks to the dQ/dV results in Fig. S5. As detailed presented, the three main reduction peaks located at 2.37 V, 2.26 V and 1.94 V in first cathodic process entirely correspond to the differential capacity versus potential (dQ/dV) curves, in which the main plateau around 2.5 V vs. Li/Li^{+} , namely, the sharp peak centered at ~2.43 V in the dQ/dV results, is attributed to the reduction of V^{5+} to V^{4+} and partial reduction of V^{4+} to V^{3+} through typical conversion reactions according to the previously reported α -CuV₂O₆ nanofibres.²⁶ The other small peaks should be ascribed to the fully reduction of V^{4+} to V^{3+} together with the intercalation process of lithium. The splitting of the redox peaks was originated from the different lithium sites with small energy difference for holding the inserted Li-ions.⁵⁸⁻⁵⁹ The CV and dQ/dV results consistently affirm the plateau assignments of the initial discharge curve. The small difference of the peaks locations between dQ/dV and CV result comes from the voltage polarization at different of galvanostatic discharge/charge and CV testing potentiostatic conditions.³⁵There are no obvious oxidation peaks can be found in the anodic process of differential capacity curves, the relatively broad swell should be caused by the extraction of Liions from the Li_xZrV₂O₇ matrix. The subsequent discharge and charge process show the similar profiles in view of the discharge/charge curves and differential capacity of the 2nd to 10th cycles based on Fig. 5(a), revealing good reversibility of Li storage performances. The rate capability at different current densities of the superstructure ZrV₂O₇ NFs electrodes were carried out in ambient temperature to further investigate their application possibility. As shown in Fig. 5(b), the test was set at current densities of 10 mA g^{-1} , 20 mA g^{-1} , 50 mA g^{-1} , 100 mA g^{-1} and 200 mA g^{-1} every 5 cycles, and turned back to 10 mA g^{-1} in succession. The rate performance seemed to be much impressive than that of the normal structured ZrV₂O₇.³⁵ The better rate capability should be ascribed to the nanoscale architecture of ZrV₂O₇, which can shorten the Li diffusion distance in the bulk phase, increasing the electrode-electrolyte interface and availing the electrolyte penetration into the inter-connected electrode. The larger specific surface area makes more active material utilized at a high discharge/charge rate, thus a high specific capacity can be expected. Besides, the better electronic conductivity (Fig. 4) contributes to the rate performance as well. Cyclic performance was explored at the current density of 10 mA g⁻¹. As shown in Fig. 5(c), both charge and discharge capacities can retain at about 135 mAh g⁻¹ (64.5% of the reversible capacity of 1st charge) after 30 cycles. Although the cycle performance are not so impressive compared to some typical cathode materials on account of the serious voltage polarization, the properties are clearly improved by the nanostructured technique when compared with that of the micron-sized $\rm ZrV_2O_7.^{35}$ The columbic efficiency (CE), calculated by dividing the charge capacity by discharge capacity, increased rapidly from 74.6% for the first cycle to 99.1% for the second one. During the subsequent cycles, it maintains at a high level of 98%, demonstrating a good reversibility between the charge and discharge processes. It can be seen that some CE data points are above 100% which can be attributed to the slight variation of temperature during cycling.⁶⁰ The Nyquist plots at open circuit state, after 1st, 2nd, 10th and 20th cycles (Fig. 5(d)) present similar semicircles and quasi-straight lines. Fig. 5(d)-inset is the corresponding equivalent circuit model for the impedance response.26 Following the usual practice, R_s stands for the combination of electrolyte resistance and ohmic resistance of cell components. The semicircle could be attributed to the charge



Fig. 6 Operando evolution of the XRD patterns using *in-situ* measurement technique. The left is the magnification of the highest peak of ZrV_2O_7 superstructure. The corresponding discharge and charge profile is shown on the right of the XRD patterns.

6 | J. Name., 2012, 00, 1-3

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Journal Name

transfer resistance of the electrode reaction R_{ct} and constant phase element (CPE) of the electrode/electrolyte interface, and the inclined line in the low frequency region to Li^{\dagger} diffusion processes within the active material (Z_w , Warburg impedance). The specific values (Table S1) can be obtained by data fitting according to the equivalent circuit model in Fig. 5(d)-inset. As can be seen from Table S1, for the fresh electrode, the charge transfer resistance value is 502.5 Ω . After 1^{st} and 2^{nd} cycle, the values of R_{ct} decrease to 235.3 Ω and 166.8 $\Omega.$ And to 140.53, 87.39 after 10^{th} cycle and 20^{th} cycle, respectively. Change of charge transfer resistance was reported as the important factor to capacity fading and rate performance.⁶¹⁻⁶² Specifically, lower R_{ct} can upgrade the rate performance and cycling stability. The decreasing R_{ct} upon cycling reflect a better electronic contact of the electrode superior to the initial electrode, indicating a decrease in inner resistance after cycling.⁶³ With lithiation and de-lithiation, the nanofibres constitution of the active material would turn into increasingly inter-connected and densely packed structure, which can enhance the inter-particle contact and electrical contact.⁶⁴ While the plot and values of R_s did not change much, revealing the electronic conductivity and ion diffusion pathways in the composite electrodes are well maintained after several cycles, leading to a good cycling stability during the chemical process. The values of R_s and R_{ct} are also similar to other TMVs electrodes such as α -CuV₂O₆ nanofibres and CoV₂O₆ nanosheet,^{26, 65} indicating the suitability of TMVs in application of electrode materials. The above results demonstrated that the superstructure ZrV₂O₇ nanofibres can serve as a promising cathode material for lithium-ion battery after optimization. And the further optimization strategy to enhance the electrochemical performance may lie in the better morphology construction and electronic conductivity promotion such as carbon coating.

To better understand the reaction mechanism and the structural change of ZrV₂O₇ during electrochemical Li insertion/extraction between 1.5 and 4.0 V vs. Li/Li⁺, the initial discharge and charge processes were investigated by in-situ XRD detection (Fig. 6). At the beginning of the reaction, only the well-defined peaks of crystalline ZrV₂O₇ are visible in the diffraction pattern at the open-circuit voltage (OCV) of 3.12 V vs. Li/Li⁺. We mark the whole discharging process into two main stages, of which the stage-1 is from OCV to 1.65 V vs. Li/Li⁺ and 1.65~1.5 V vs. Li/Li⁺ belongs to stage-2. During the stage-1 of the initial discharge, the intensities of these peaks decrease progressively without observing any new peaks of second phase in the diffraction patterns. Note that the peaks positions shift to lower angles and gradually become broader and weaker (clearly shown in the magnification of the highest peak of ZrV₂O₇ superstructure), which indicates the start of a $Li_xZrV_2O_7$ solid-solution reaction with subsequent conversion reaction which gradually degraded the crystallinity and/or reduced the crystalline size of ZrV₂O₇. The shift of the peaks, which should be attributed to the insertion process of Li ions intercalation into the interstitial sites of ZrV₂O₇ matrix, implies the expansion of the ZrV₂O₇ structure. On account of the cubic nature of ZrV₂O₇ superstructure, the linear evolution of the lattice parameter is consistent with its volume change. When the solid-solution limit of Li^{*} in $\mathrm{ZrV}_{2}\mathrm{O}_{7}$ superstructure was reached with further insertion, no prominent peaks were detected in the as-defined stage-2 except the diffraction peaks of BeO under the resolution of the diffractometer, revealing that the Li_xZrV₂O₇ solid solution in stage-1 totally decomposed into an amorphous state via conversion reaction. Even after recharged to 4.0 V, the superstructure or normal form of ZrV_2O_7 were no longer recovered from the non-crystalline composite. Namely, despite modification of the coordination environment of the local vanadium or zirconium ligands during the following discharge/charge process, the electrodes of superstructure ZrV₂O₇ NFs still stay in an amorphous state throughout the whole discharge/charge process in subsequent cycles. The in-situ XRD detection results unfortunately negates the aforementioned thermal safety advantage in virtue of its NTE characteristic under higher temperature. The excellent electronic conductivity of ZrV₂O₇ is also beyond hope after the collapse of the initial structure. However, from the EIS results we can see the well-retained conductivity by the decomposed VO_x and ZrO_{xy} which is still helpful for the electrochemical performance. Much deeper research for detailed reason why the final amorphous state of the electrode materials exist had already been demonstrated by Tarascon et al. They investigated copper vanadium oxides (CVOs) with different stoichiometric constitution (Cu₅V₂O₁₀, Cu₂V₂O₇, ε-Cu_{0.95}V₂O₅, $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ and $\text{Cu}_{1.1}\text{V}_4\text{O}_{11})$ as cathode materials for LIBs. $^{34,\,66-67}$ Though with entirely same anions and cations, different Li intercalation mechanisms are presented by them on account of the diverse vanadium sites derived from crystal structures. In detail, $\epsilon\text{-}Cu_{0.95}V_2O_5,\ Cu_{2.33}V_4O_{11}$ and $Cu_{1.1}V_4O_{11}$ can react with Li through a reversible combination of displacement and intercalation process. While for $Cu_5V_2O_{10}$ and $Cu_2V_2O_7$, the initial phase would convert into amorphous state upon electrochemical discharge. Structural considerations involving cation local stability and long-range crystal stability are responsible for the significant difference. They found the vanadium and oxygen in Cu₅V₂O₁₀ and Cu₂V₂O₇ bond as VO₄ tetrahedrons. Because the V^{4+} and V^{3+} ions are not stable in a tetrahedral environment, the $V^{5+}/V^{4+}/V^{3+}$ reduction process would involve a change in vanadium coordination, leading to the noncrystallization of the initial structure. We know that the vanadium coordination in ZrV₂O₇ also lie in tetrahedral sites from Fig. 2 (c), which is in consistent with the final amorphous phase after electrochemical discharge. However, from the insitu XRD detection of ZrV_2O_7 during discharge, we found that before the conversion reaction to ultimate amorphous state, the electrode undergo a solid-solution process during which the Li ions are inserted into ZrV₂O₇ matrix without structural collapse. This phenomenon is different from that of the reported ones. In addition, the amorphous nature of cycled electrode that indicates the structural consistency has been proved to be in favor of effectively preventing the lattice stress as well as buffering the huge volumetric change during the Li ions insertion/extraction and providing continuous Li ions diffusion pathways and insertion sites, which greatly improve the reversible capacity and sustain the structural stability.⁶⁸⁻⁶⁹

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Conclusions

In summary, we have fabricated ZrV₂O₇ nanofibres via a facile solution-based route. The homogeneous 1D fibrous morphology after calcination can widen and upgrade their NTE and electrochemical performances. The XRD pattern combined with Rietveld refinement reveals that the obtained ZrV₂O₇ NFs are crystallized in a 3×3×3 superstructure form. As a conventional negative thermal expansion material, the nanoscale form would highly widen its use in corporation with other positive thermal expansion materials on account of the tougher interfacial contaction between them. After being evaluated as a cathode material for Li-ion batteries, the enhanced rate capability and cyclic performance are impressing on account of the nanoscale effect. In-situ XRD analysis preliminarily demonstrates the Li intercalation mechanism of this compound should be a solid solution process with subsequent conversion reaction to an ultimate amorphous state. Combining major merits of this superstructure form ZrV₂O₇ NFs such as the high capacity and electronic conductivity, this functional material possesses bright prospects in developing advanced materials for the next generation NTE application and LIBs through rational and delicate design.

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