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### TABLE OF CONTENT (TOC). The biocarbon coated $Li_3V_2(PO_4)_3$

(LVP-C) cathode with high electrochemical performance was synthesized by a sol-gel method using abandoned tea as both structural template and carbon source.



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## Paper

# Synthesis of biocarbon coated Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C cathode material for lithium ion batteries using abandoned tea

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The biocarbon coated Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C (LVP-C) cathode material is synthesized by a facile sol-gel method using abandoned tea as both structural template and biocarbon source. X-ray diffraction (XRD) patterns show that the LVP has a monoclinic structure with space group P2<sub>1</sub>/n. High-resolution transmission electron microscope (HRTEM) images show that the LVP nanoparticles are surrounded by amorphous <sup>10</sup> biocarbon, and the thickness of the biocarbon shell is about 10–20 nm. Electrochemical measurements demonstrate that the LVP-C nanocomposite shows significantly better rate capability and cycling performance than the pure LVP. In the potential range of 3.0–4.3 V, the LVP-C nanocomposite delivers high initial discharge capacity of 132 mAh • g<sup>-1</sup> at 0.5 C, and maintains an initial discharge capacity of 110 mAh • g<sup>-1</sup> at 10 C. After 80 cycles at 10 C, it can still retain a discharge capacity of 110 mAh • g<sup>-1</sup>. <sup>15</sup> Electrochemical impedance spectroscopy (EIS) measurement discloses that the LVP-C sample exhibits enhanced electrode reaction kinetics and improved electrochemical performance. The good electrochemical performance of the LVP-C nanocomposite is mainly related to the existence of conductive biocarbon, thus leading to improvement in electron and lithium ion diffusivity. These results indicate that the biocarbon coated LVP-C material has potential to be a promising candidate as large <sup>20</sup> capacity and high power cathode material in the next generation lithium-ion batteries for electric vehicles.

#### Introduction

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With the rapid social development, vehicles are becoming more and more important in our daily life. However, for the past few years, with the decrease of nonrenewable energy resources such

- 25 as oil and natural gas, looking for a new energy for vehicles has become the most important question that the humanity has to face. Electricity as a kind of non-pollution clean energy has become the first energy choice for vehicles. Electricity can be converted from three major renewable sources: wind, solar and hydro, and
- <sup>30</sup> they are all clean energy. It is meaningful for improving the increasingly worse environment to apply electric energy to vehicles. At the same time, it is quite necessary to select a suitable electric energy storage device. At present, rechargeable lithium-ion batteries (LIBs) are considered as one of the most
- <sup>35</sup> important energy storage systems for the evergrowing demand from portable products and electric vehicles owing to their lightweight nature, high energy density, and durable cycling life.<sup>1,2</sup>

electrode (cathode), a separator and electrolyte (shown in Fig. 1). <sup>50</sup> Nowadays, most LIBs use LiCoO<sub>2</sub> as the main cathode material

A LIB mainly consists of a negative electrode (anode), a positive

- because of its simple synthesis, low irreversible capacity loss, and good cycling performance.<sup>3,4</sup> However, its high cost, safety problems and toxicity limit its further use in large-scale applications, such as electric vehicles and hybrid electric vehicles. <sup>55</sup> So, it is imperative to develop novel cathode materials for LIBs.
- Recently, lithiated transition-metal phosphates, such as LiMPO4 (M=Mn, Fe, Co, Ni) and Li<sub>3</sub>M<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (M=Ti, V, Fe), have attracted great interest as potential cathode materials for LIBs, because they have good electrochemical and thermal stabilities, 60 competitive energy density, and high operating potentials.<sup>5-8</sup> Among these phosphates, monoclinic Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (LVP) is one of the most promising cathode materials due to its high theoretical capacity (197 mAh • g<sup>-1</sup>), high operating voltage (up to 4.0 V), and safety performance.<sup>9,10</sup> In the potential range 65 between 3.0 and 4.8 V, the reversible cycling of all three lithiums from LVP would correspond to a theoretical capacity of 197 mAh  $\cdot$  g<sup>-1</sup>, which is the highest for all phosphates reported on cathode materials.<sup>11,12</sup> In the potential range between 3.0 and 4.3 V, a reversible capacity of 131 mAh • g<sup>-1</sup> can still be obtained.<sup>13</sup> 70 Furthermore, monoclinic LVP with slightly distorted VO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra in NASICON structure, provides efficient three-dimensional pathways for Li<sup>+</sup> extraction and reinsertion than the one-dimensional pathways in LiFePO<sub>4</sub>.<sup>14</sup> Luckily, LVP is a fairly well studied material for lithium battery cathodes.

75 Recently, Rui et. al<sup>15</sup> presented a review specifically on the recent

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Fig. 1. Schematic illustration of a lithium ion battery employing graphite as anode and monoclinic  $Li_3V_2(PO_4)_3$  as cathode.

development of monoclinic LVP cathode materials for LIB applications. Host structure, mechanism of lithium insertion/extraction, transport properties, synthesis methods and electrochemical properties in terms of rate capability and cyclic <sup>10</sup> stability were summarized and analyzed. An insight into the future research and development of LVP compound were also discussed.

However, similar to other lithium transition metal phosphates, poor intrinsic electronic transport of LVP limits its application.<sup>9,13</sup> <sup>15</sup> In order to improve the electronic transport of LVP, many conductive materials have been employed to build conductive layer for the phosphates.<sup>16-18</sup> Among these conductive materials, carbon is characterized by the fast electron transport and regarded as the excellent coating material.<sup>19-22</sup> The carbon coating is

- <sup>20</sup> usually realized by introducing an organic precursor in the starting materials. The organic precursor can be converted into electronically conductive carbon through pyrolysis process at high temperature under inert atmospheres. The carbon will coat on the particles to form a conducting LVP-C composite electrode
- <sup>25</sup> material.<sup>23</sup> Additionally, carbon can act as a reducing agent and thus simplify the atmosphere requirement in the synthesis.<sup>24</sup> Carbon-coated LVP can promote the contact between particles, decrease the polarization of electrode materials and eventually improve the performance of LIBs. The carbon sources are rich
- <sup>30</sup> and colorful, Rui et. al<sup>15</sup> summarized the effect of different kinds of carbon coating on the electrochemical performance of LVP cathodes. LVP using 3.98 wt% citric acid as carbon source could deliver a discharge capacity of 110.8 and 97.9 mAh • g<sup>-1</sup> at 5 C and 10 C in the potential region of 3.0–4.3 V.<sup>25</sup> LVP using 16.4 <sup>35</sup> wt% baker's yeast cell as carbon source could deliver a discharge
- capacity of 100.5 mAh  $\cdot$  g<sup>-1</sup> at 5 C in the potential region of 3.0– 4.3 V.<sup>26</sup>

The carbon coating plays a key role in improving rate capability and cycling retention of electrode materials. A variety 40 of biocarbon sources have been used for developing high

performance lithium-ion batteries (LIBs) such as Baker's yeast cell, tobacco mosaic virus, adenosine triphosphate, bacteria, lotus pollen grains, viruses, microalgae, rice husk and crab shell.<sup>27</sup> Tea



<sup>45</sup> **Fig. 2.** Schematic illustration of the fabrication process of LVP-C.

is one of the most popular drinks in the world, especially in China. Howeve, some tea is very expensive, such as Longjing Tea. Throwing it away after drinking one or two times is really wasteful. It will be a meaningful thing if we can recycle it. As far as we know, researchers usually choose the organic or polymer as carbon sources, here we choose a new carbon source (Abandoned tea), which has never been used as carbon source before. Different from ordinary carbon sources, the tea belongs to the biological carbon source, which is coming from the nature. There are different kinds of metal cations in tea, which can improve the electronic conductivity of LVP through cation doping to some extent.

Compared with solid-state reaction, solution method can mix <sup>60</sup> the starting materials in a molecular level, which is conducive to homogeneous reaction.<sup>28</sup> So in this work, we employ a facile solgel method to prepare biocarbon coated LVP-C cathode material using abandoned tea as both structural template and biocarbon source, introducing biocarbon to the surface of LVP particles by <sup>65</sup> thermal decomposition of abandoned tea under nitrogen atmosphere. Herein, biocarbon is not only providing a network to restrict the growth and agglomeration of the LVP crystallites, but also supplying a high electronically conductive layer which is expected to enhance the electrochemical performance of LVP.<sup>29</sup>

#### 70 Experimental

#### Sample preparation

The reagents used in this work were NH4VO3 (99%, Tianjin Bodi Chemical Co. Ltd.), C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> • 2H<sub>2</sub>O (99.5%, Tianjin Bodi Chemical Co. Ltd.), NH4H<sub>2</sub>PO4 (99%, Tianjin Bodi Chemical Co. <sup>75</sup> Ltd.), Li<sub>2</sub>CO<sub>3</sub> (97%, Tianjin Guangfu Fine Chemical Research Institute), and Abandoned tea (Jasmine tea, Fujian, China). Distilled water was used during synthesis of the LVP-C. The LVP-C samples were prepared using the biotemplate (Abandoned tea) by sol-gel method. The typical synthesis process is shown <sup>80</sup> in Fig. 2. Abandoned tea was put in an air oven at 100 °C for 10 h,

then the abandoned tea was ground into powder in a mortar. Tea powder used for experiment was obtained by centrifugation, washing with distilled water and drying. Oxalic acid (3.80 g) and NH<sub>4</sub>VO<sub>3</sub> (2.34 g) in a stoichiometric ratio were dissolved in 100

- <sup>85</sup> ml deionized water with magnetic stirring at 70 °C. Oxalic acid was used here not only as a chelating reagent but also as a reducing agent. After a clear blue solution of VOC<sub>2</sub>O<sub>4</sub> formed (eq1), quantitative tea powder (2.00 g) was added to the blue solution with magnetic stirring at 70 °C. After stirring vigorously
- <sup>90</sup> for 2 h, a mixture of stoichiometric NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (3.45 g) and Li<sub>2</sub>CO<sub>3</sub> (1.18 g) was added to the solution while stirring at 70  $^{\circ}$ C until the formation of sol , and then a gel formed in an air oven at 100  $^{\circ}$ C. The obtained product was dark green and sintered at

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700 °C for 8 h in flowing nitrogen (eq2), and the final products obtained were black powder. The LVP samples without tea powder assistance were prepared by the same process for comparison. The two samples were marked on LVP (without tea 5 powder) and LVP-C (2.00 g tea powder), respectively.

$$2NH_{4}VO_{3} + 3H_{2}C_{2}O_{4} \cdot 2H_{2}O \xrightarrow{70^{\circ}C} 2VOC_{2}O_{4} + 2NH_{3} + 2CO_{2} + 10H_{2}O \quad (1)$$

$$4VOC_{2}O_{4} + 3Li_{2}CO_{3} + 6NH_{4}H_{2}PO_{4} \xrightarrow{700^{\circ}C} 2Li_{3}V_{2} \quad (PO_{4})_{3} + 9H_{2}O + 9CO_{2} + 2CO + 6NH_{3} \quad (2)$$

#### Sample characterization

10 X-ray diffraction (XRD) patterns of the samples were measured using PANalytical X'Pert PRO X-ray diffractometer (Netherlands) with Cu Ka radiation in order to identify phase composition. The diffraction patterns were collected over a diffraction angle 20 range of 10 °-60°, with an acquisition time of 12.0 s at 0.02° step 15 size. Fourier transform infrared spectroscopy (FT-IR) was performed using a Nicolet Nexus spectrometer (Nicolet, NEXUS 470, USA) by using a KBr wafer technique in order to study the composition of the abandoned tea. Infrared spectra were recorded in the region 4000–450  $\text{cm}^{-1}$ , with a resolution of 4.00 20 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) of the samples was conducted in air at a heating rate of 10 °C min<sup>-1</sup> from 45 °C to 850 °C using a thermal analyzer (TGA1 STAR System) in order to study carbon content. High-resolution transmission electron microscopy (HRTEM) was carried out on a Philips FEI TF20 25 microscope, working at 200 kV. The procedure of preparing HRTEM samples is shown below: Firstly, cathode material (0.03 g) was ground using ethyl alcohol for 5 h in a mortar, then the cathode material was put into a beaker (50 mL) containing 30 mL ethyl alcohol, and the supernate was used for HRTEM test 30 after being placed for 12 hours.

#### Preparation of electrodes and electrochemical testing

The charge-discharge performances of the samples were evaluated using LIR2032 coin cells. The cathode materials were 35 prepared by mixing the sample with acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 in Nmethyl pyrrolidone ( NMP ) to ensure homogeneity. Here, acetylene black is conductive agent , PVDF is binder , and NMP is solvent. After the NMP was evaporated, the mixture was 40 coated on the aluminum foil, then aluminum foil was dried under an air atmosphere at 80 °C for 5 h and a vacuum atmosphere at 120 °C for 10 h and cut into circular strips of 15 mm in diameter. The mass calculation of the active materials was carried out based on the 80% of difference between the mass of active LVP-C 45 materials coated Al foil and the mass of pristine Al foil. The coin cells were assembled in a glove box filled with high-purity argon, where lithium metal was used as an anode, a polypropylene film as the separator, and 1 M LiPF<sub>6</sub> in an electrolyte consisting of ethylene carbonate/dimethyl carbonate/ethylene methyl carbonate

- <sup>50</sup> in a volume ratio of 1 : 1 : 1. The charge-discharge performances of the synthesized samples were tested using a Channels battery analyzer (CT3008W) at different current densities between 3.0 and 4.3 V cut-off voltages using the coin cells. The electrochemical impedance (EIS) and cyclic voltammetry (CV)
   <sup>55</sup> measurements were performed using a PARSTAT 2263
- electrochemical workstation. EIS was recorded with the frequency ranging from 100 kHz to 10 mHz and a AC signal of 5



Fig. 3. XRD patterns of LVP-C composite (a) and pure LVP (b).

Table 1 Lattice	parameters of	pure LVP	and LVP-C	samples

samples	a (Å)	b (Å)	c (Å)	β (°)	V (Å <sup>3</sup> )
LVP	8.51	12.06	8.58	89.42	881.57
LVP-C	8.53	12.04	8.59	89.90	884.21

mV in amplitude as the perturbation. The voltage range of the CV measurements was 3.0–4.3 V and the scanning rate was 0.1 <sup>65</sup> mV • s<sup>-1</sup>. All the tests were performed at room temperature.

#### **Results and Discussion**

#### Structural analysis and morphology characterization

LVP crystallizes in two different forms: a rhombohedral structure and a thermodynamically more stable monoclinic structure.<sup>30</sup> Fig. 70 3 shows the XRD patterns of the pure LVP and LVP-C composite It can be seen that both the patterns can be indexed to a monoclinic structure with space group P21/n, consistent with those previously published.<sup>13,30</sup> Furthermore, no diffraction peaks of carbon are detected, which may be attributed to the amorphous 75 state of biocarbon coating. The sharp diffraction peaks of both samples indicate a good crystallinity and the intensity of the diffraction peaks is obviously strengthened through biocarbon coating. The lattice parameters of pure LVP and LVP-C composite are calculated by Jade5, and the results are listed in <sup>80</sup> Table 1. It can be seen from Table 1 that the lattice parameters of LVP do not have much changes after biocarbon coating and this suggests the presence of biocarbon does not affect the structural properties of LVP. Moreover, there is no notable peak shifting change after the introduction of biocarbon.

<sup>85</sup> The FT-IR spectrum of the abandoned tea is shown in Fig. 4. The broad band at 3500 cm<sup>-1</sup> is ascribed to the O-H stretching vibration of water. The dominant bands near 1652 and 1534 cm<sup>-1</sup> are assigned to amide I and amide II of the proteins in the abandoned tea. The band at 2920 cm<sup>-1</sup> is derived from the CH<sub>2</sub> <sup>90</sup> asymmetry stretching vibration of protein and carbohydrate in the abandoned tea. The band at 1047 cm<sup>-1</sup> is caused by the C-O stretching of carbohydrates found in the RNA, the DNA, the cell membrane and cell wall of the tea cell.<sup>31</sup>



The carbon content of the samples is revealed by  $_5$  thermogravimetric analysis shown in Fig. 5. According to Rui etal.<sup>24</sup>, the composites initially undergo a weight loss in the temperature range of 300–500 °C, which is attributed to the removal of carbon by its oxidation into gaseous product (CO or CO<sub>2</sub>). And then above 500 °C, LVP gains weight due to the



Fig. 5. TGA curves of pure LVP and LVP-C composites.

oxidation of V(III) to higher valence states in air. According to 15 the weight loss step on the TGA curves, the carbon content of the pure LVP is very small and can be neglected, the carbon content of the LVP-C is about 5.0%.

To further investigate the microstructure of the samples and check biocarbon coating on the LVP particles, the



**Fig. 6.** HRTEM images of the samples. (a,b) Low magnification images, showing structures of pure LVP (a) and LVP-C (b), respectively. (c) An enlarged image of the partial area in (a). (d) An enlarged image in (b).

10 20 HRTEM images of pure LVP and LVP-C powder particles were also conducted. Fig. 6c, taken from the marginal part of Fig. 6a, shows that there is hardly any amorphous carbon around pure 5 LVP particles. These result is consistent with carbon content analysis (Fig. 5). The small amount of amorphous carbon may come from the pyrolysis processes of oxalic acid at high temperatures under inert atmosphere. Fig. 6d, taken from the

- marginal part of Fig. 6b, shows that LVP particles are surrounded <sup>10</sup> by amorphous biocarbon, and the highly crystalline particle is coated with an amorphous biocarbon shell, the thickness of the biocarbon shell is about 10-20 nm. It is quite necessary to stress that the thickness of the biocarbon shell can be controlled by quantity of tea powder. The existence of the biocarbon layer can <sup>15</sup> impede the grain growth of LVP particles and improve electronic
- conductivity of LVP cathode material. Fig. 6c and Fig. 6d both display clear lattice fringes with d-spacing of 0.365 nm, corresponding to (121) planes of monoclinic LVP, which is consistent with the XRD analysis.

#### Formation mechanism of LVP-C

Fig. 7a shows the structure of tea leaf.<sup>32</sup> Hydrophilic anion groups in biomacromolecules of tea leaf particles (Fig. 7b) can improve the electrostatic interaction of tea powder surface and cations and <sup>25</sup> regulate particles nucleation and precipitation.<sup>33</sup> When VOC<sub>2</sub>O<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> were added into the tea particle solution, the Li<sup>+</sup>, VO<sup>2+</sup> and V<sup>3+</sup> cations were combined with the negatively



**Fig. 7.** (a) Structure of tea leaf, (b-d) Formation mechanism of biocarbon 30 coated LVP-C.

charged OH<sup>-</sup> groups in the structure of tea leaf, and were self-assembled to the the tea leaf surface by electrostatic interaction (Fig. 7c). Then the biocarbon coated LVP-C cathode materials <sup>35</sup> are synthesized by heat treatment (700 °C) in a reducing atmosphere (N<sub>2</sub>) (Fig. 7d). Fig. 7d represents that LVP particles are surrounded by active biocarbon network after heat treatment of the precursor, which is consistent with the HRTEM



**Fig. 8.** (a) The initial charge-discharge curves of pure LVP at 0.1, 0.5, 1, 2 C, respectively. (b) The initial charge-discharge curves of LVP-C at 0.1, 0.5, 1, 2, 5, 10 C, respectively. (c) The rate capability and cycling performances of pure LVP and LVP-C. (d) The cycling performance of LVP-C at 10 C.

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images in Fig. 6d. Biocarbon not only enhances the conducting properties but also restrains the particle growth during the

<sup>5</sup> sintering process, and hence to significantly improve the electrochemical performance of LVP.<sup>13,34</sup> This structure can help to explain why the LVP-C sample can be used at very high rates in lithium ion batteries

#### 10 Electrochemical properties

Fig. 8a and b show the initial charge-discharge curves of pure LVP and LVP-C in the potential range of 3.0–4.3 V at different rates, respectively. It is necessary to point out that the cell was <sup>15</sup> firstly charged at a constant current density until the potential to 4.3 V, then charged at a constant voltage (4.3 V) until the current to minimum value (0.001 mA), then discharged at a constant current density. It can be seen that all the charge-discharge curves show a similar shape presenting three charge-discharge plateaus

- <sup>20</sup> that correspond to three kinds of reversible phase transformation between Li<sub>3-x</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (x=0, 0.5, 1.0, and 2.0). Fig. 8a shows that the initial discharge capacities of pure LVP are about 115, 92, 71, 52 mAh g<sup>-1</sup> at 0.1, 0.5, 1, 2 C, respectively. Fig. 8b shows that the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 131, 1400 the initial discharge capacities of LVP-C are about 124, 132, 1400 the initial discharge capacities of L
- <sup>25</sup> 128, 121, 110 mAh g<sup>-1</sup> at 0.1, 0.5, 1, 2, 5, 10 C, respectively. Compared with the above-mentioned LVP cathodes reported by Rui et. al.,1<sup>15</sup> it is easy to come to a conclusion that the LVP-C sample synthesized with tea powder biotemplate has a larger range of capacity and smaller potential differences of plateaus
  <sup>30</sup> than pure LVP, indicating that the LVP-C sample has lower electrochemical polarization and leads to better electrochemical performance in the charge-discharge processes. Fig. 8c shows the rate capability and cycling performances of pure LVP and LVP-C. Compared to the pure LVP, the LVP-C shows stable capacities at
- <sup>35</sup> each state (0.1, 0.5, 1, 2, and 5 C), while the capacities of pure LVP decay very quickly, especially at high rates. The capacity of LVP-C at 0.1 C is much lower than that of 0.5, 1 and 2 C and is comparable to 5 C. The increase of capacity at 0.5, 1 and 2 C can be attributed to the activation of the LVP-C cathode material after
  <sup>40</sup> several cycles, more fully contact between LVP-C particles and
- electrolyte, and formation of more lithium ion transport channels. Fig. 8d shows the cycling performance of LVP-C at 10 C. The discharge capacity of LVP-C is still maintained at 110 mAh • g<sup>-1</sup> after 80 cycles. Just as expected, the LVP-C sample exhibits
- <sup>45</sup> better rate capability and cycling performance than the pure LVP, mainly attributing to the existence of biocarbon framework, which can improve electronic conductivity of the composite and accelerate electron transport.

#### **CV** measurement

- <sup>50</sup> For LVP, two lithium ions can be easily extracted/inserted reversibly between 3.0 and 4.3 V based on the V<sup>3+</sup>/V<sup>4+</sup> redox couple.<sup>35</sup> To verify this electrochemical behavior, Fig. 9 shows the CV curves of pure LVP and LVP-C at a scan rate of 0.1 mV  $\cdot$  s<sup>-1</sup> in the voltage range of 3.0–4.3 V. It can be seen from
- <sup>55</sup> Fig. 9 that the CV curves of pure LVP and LVP-C are so similar. They both have three oxidation peaks (around 3.68, 3.77, 4.21 V) and three corresponding reduction peaks (around 3.88, 3.51, 3.43 V) in 3.0–4.3 V, which are consistent well with lithium ion extraction/insertion during the phase transition processes:
- <sup>60</sup> Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>↔Li<sub>2.5</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>↔Li<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>↔LiV<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and also in good agreement with the charge-discharge curves in Fig. 8. However, there are some differences between the two samples.



Fig. 9. The CV curves of pure LVP and LVP-C at a scan rate of 0.1 mV  $\cdot$  s<sup>-1</sup> <sup>65</sup> in the voltage range of 3.0-4.3 V.

The curve of the LVP-C has better-defined peaks than the pure LVP, which demonstrates that the LVP-C has outstanding reversibility of the lithium extraction/insertion reactions.<sup>36</sup>

#### **EIS** measurement

To better understand the electrochemical kinetic properties of the samples, EIS is carried out after100 cycles at a charge of 4.3V. Fig. 10a shows the Nyquist plots of the materials. It can be seen <sup>75</sup> that both samples have similar EIS curves. The small intercept is related to the solution resistance ( $R_s$ ); the depressed semicircle in the middle frequency represents the charge-transfer resistance ( $R_{ct}$ ) and the double-layer capacitance ( $C_{dl}$ ); the sloping line in the low frequency is attributed to Warburg impedance associated <sup>80</sup> with the diffusion of lithium ions in the electrode ( $Z_w$ ).<sup>37</sup> An equivalent circuit model is shown in the insert of Fig. 10a for analyzing impedance spectra. From Fig. 10a, the  $R_{ct}$  value of the

LVP (199.5  $\Omega$ ), demonstrating that the electrons can transfer <sup>85</sup> more easily between LVP particles and the electrolyte for the LVP-C sample, as a result of its better biocarbon network<sup>38</sup>. Fig. 10b shows the linear fitting of Z<sub>real</sub> vs· $\omega^{-1/2}$  in the Warburg region. In comparison with the pure LVP, the LVP-C sample has a lower slope, indicating higher lithium ion diffusion coefficient of such

LVP-C sample is much smaller (74.8  $\Omega$ ) than that of the pure

<sup>90</sup> sample.<sup>39</sup> Thus, the LVP-C sample prepared using abandoned tea as both structural template and biocarbon source exhibits enhanced electrode reaction kinetics and improved electrochemical performance.

#### 95 Conclusions

In summary, LVP-C nanoparticles covered with amorphous biocarbon have been successfully synthesized by a facile sol-gel method using abandoned tea as both structural template and biocarbon source. Compared to the pure LVP, the LVP-C nanocomposite exhibits much improved electrochemical performance, particularly at higher current rates. The results should be attributed to the conductive biocarbon framework for LVP-C nanocomposite. The experimental results demonstrate

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**Fig. 10.** (a) Nyquist plots of pure LVP and LVP-C. (b) Relationship plots of impedance as a function of the inverse square root of angular frequency in the *s* Warburg region.

that biocarbon coating is an efficient route to prepare LVP-C with good electrochemical performance. Furthermore, the proposed approach also reminds us that the combination of biological and <sup>10</sup> chemical in the field of electrochemistry has very excellent prospects.

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