

Order-disorder transition in amorphous vanadium-phosphorus-lithium cathode of lithium ion battery

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1 Order-disorder Transition in Amorphous Vanadium-Phosphorus-Lithium

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Cathode of Lithium Ion Battery

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15 Highlights

- 17 lithium (VPLi) battery cathode has been investigated for the first time.
- 18 > Li₃VF₆ and VF₄ nanocrystals were found to precipitate from VPFLi when V⁴⁺ content is ranged from
- 19 16.3% to 23.8%.
- 20 \triangleright VF₄ and Li₃VF₆ nanocrystals were converted into LiVP₂O₇ in VPFLi, which led to the increased specific 21 capacity of the resulting cathode.
- 22 > Density functional theory (DFT) simulation results show that fluorination has led to the movement of
- 23 Fermi level towards the edge of the conduction band, and the charge transfer from Li to O contributed to

the enhanced cycle stability.

25 **A B S T R A C T**

24

Vanadium-based amorphous materials are an emerging category of lithium ion battery cathodes with high specific capacity and high voltage performance. In this study, we investigated the effect of fluorination on the performance of an amorphous vanadium-phosphorus-lithium (VPLi) cathode for lithium ion battery applications. Results show that the fluorinated product consists Li_3VF_6 and VF_4 nanocrystals embedded in an amorphous phase when the V⁴⁺ content was in the range of 16.3% to 23.8%. VPFLi has an optimal

specific capacity of 344.3 mAh g⁻¹ in the first cycle and 269.7 mAh g⁻¹ after 200 cycles at a current of 50 31 mA g⁻¹ within the voltage range of 1.5-4.2V. VPLi has an amorphous structure, and the reversible V^{4+}/V^{5+} 32 lithiation process corresponds to the conversion between V₂O₅ and Li₂V₂O₅ during the charge-discharge 33 cycle. Compared to VPLi, VF4 and Li₃VF6 crystals were found to convert into LiVP2O7 in VPFLi, which led 34 to the increased specific capacity. Simulation based on density functional theory show that fluorine for 35 oxygen has led to the movement of Fermi level moves towards the edge of the conduction band. Charge 36 mostly transferred from Li to O which contributed to the improved cathode stability. This study provides a 37 38 new perspective towards selecting novel cathode for lithium-ion batteries.



GRAPHICAL ABSTRACT

41 Keywords

42 Lithium-ion battery; Vanadium; Cathode; Fluorination; Order-disorder transition;

43 **1. Introduction**

44 Due to the global energy challenge, low cost and high efficiency energy conversion / storage are 45 becoming increasingly important in today's society [1-4]. The global energy harvesting system market 46 accounted for \$449.75 million in 2019 and is expected to reach \$1,097.77 million by 2027 [5]. Lithium ion 47 batteries are widely used in energy harvesting because of their high specific capacity and cycle stability 48 [6-9].

However, conventional cathode materials such as LiFePO₄ [10] and NCM (Ni, Co, and Mn) -based materials [11] suffer from low specific capacity, lack of natural supplies and high cost. Transition metals (TM), such as vanadium-based compounds [12-14] (e.g. V₂O₅), are promising alternatives [15] due to their abundant natural supply source, multivalent states (V²⁺-V⁵⁺), and high specific capacity [16-19]. However, V₂O₅ being an amphoteric acid-base, has limitations such as high dissolution rate, irreversible phase change, severe volume expansion, and low electronic conductivity [20-22].

As a result, many strategies have been explored to improve the performance of vanadium-based electrode materials, such as deploying multi-dimensional structures [18.23.24], disordered rock salt [25-29], conductive coating [30-33], valence transition [34-38], and phase transformation [39-41], etc.

However, in contrast to the mature crystalline based lithium battery electrode material technologies, the performance and working mechanism of amorphous electrode materials are far less understood. In recent years, amorphous glass materials [42-44] have received increasing attention in lithium battery electrode development. Y. Zhang and Y. Yue et al [45] explored the structural factors that affect the electrochemical performance of glass anodes, especially the structural evolution during the discharge-charge process. In a separate study, they [46] found that the structural network of the electrode can be dissociated into isolated units through solid-state nuclear magnetic resonance, and form different types of highly ordered

nano-domains, which led to favorable rate capability and long-term cycle stability. H. Tao and Y. Yue et al 65 [47] succeeded in tuning the degree of disorder in NaFePO4 cathode material by a mechanochemical route, 66 thereby obtaining the excellent cycling stability. To date, applications of vanadium oxide-based amorphous 67 glass electrode materials have been reported by several research groups, examples include 68 vanadium-phosphorus [48-50], vanadium-boron [51], vanadium-tellurium [52-54], 69 and vanadium-silicon[55], etc. Due to the lack of accurate in situ characterization for amorphous electrode 70 structure, the current research mostly focus on the composition-performance improvement, and the results 71 72 cannot track the cycle process, reveal the lithiation mechanism, or support theoretical calculations.

Oxygen pairs, short-range O-O bonds and the formation of oxygen vacancies can lead to the voltage 73 drop and capacity degradation during long term cycling of the cathode [56]. Due to the greater 74 electronegativity of F (4.0) as compared to O (3.5), F has a stronger ability to attract electrons. In this work, 75 we reported the first study on fluorine-oxygen substitution in an amorphous lithium-ion battery cathode 76 system. An amorphous vanadium-phosphorus-lithium cathode material (VPLi) and its fluorinated product 77 78 (VPFLi) were prepared by melting quenching method. Specifically, the thermodynamic properties of both materials were characterized to reveal the difference in their lithiation mechanisms. This is followed by 79 detailed evaluation using DSC, in situ XRD, FT-IR, Raman, SEM, TEM, NMR, XPS, and EPR. The order 80 81 /disorder phase transformation in the fluorinated amorphous electrode material were revealed. The cathode materials electrochemical properties, including their specific capacity, rate performance, long-term cycling, 82 have been assessed and compared using a practical lithium-ion battery cell set up. Finally, DFT calculations 83 84 were performed to reveal the difference in the charge density distribution between the electrode materials with and without fluorination. 85

86 2. Methodology

87 2.1. Materials Preparation

88 Amorphous vanadium-phosphorus-lithium cathode materials with and without fluorine-oxygen 89 substitution were prepared by melting-quenching method [48]. VPLi was prepared by mixing raw materials

Li₃PO₄ (Macklin, CP, 99.0%) / V₂O₅ (Macklin, AR, 99.99%) with a molar ratio of 4:6, using a vertical mixer 90 for 30 min. The mixture was placed into an alumina crucible, heated in a tube furnace under Ar atmosphere 91 to 700 ℃ at a rate of 10 ℃/min. The temperature was maintained at 700 ℃ for 30 min and then raised to 92 900 \mathbb{C} for another 10 min of heating. The end of the tube furnace is connected to the quenching box 93 (30cm*30cm*30cm). The resulting molten liquid was passed between two copper plates and guenched in Ar 94 to room temperature to obtain a shaped glass specimen. The glass specimen was then annealed at 225 °C for 95 400 min to relieve the residual stresses and was cooled down to room temperature naturally. The glass 96 97 specimen was ground into glass powder (particle size $< 10 \mu m$) and the resultant amorphous material was named as VPLi. For fabrication of fluorinated VPFLi, a mixture of Li₃PO₄ (Macklin, CP, 99.0%), V₂O₅ 98 (Macklin, AR, 99.99%) and LiF (Macklin, AR, 99.0%) with a molar ratio of 3:6:3 were used and the 99 preparation process of VPFLi is the same as that of VPLi. The material preparation process is shown in 100 Fig.1. 101

102 2.2. Characterization

Differential scanning calorimetry (DSC, NETZSCH STA449) was conducted to study the materials 103 thermodynamic parameters under N₂, with a heating rate of 10 °C/min. X-ray diffractometry (XRD, Rigaku, 104 smartlab 9kw) and *in situ* high and low temperature XRD (Rigaku TTR3) were used to identify the materials 105 crystal structures. Fourier Transform infrared spectroscopy (FT-IR, Thermo fisher Nicolet iS5) and Raman 106 spectroscopy (HORIBA Scientific HORIBA LabRAM HR Evolution) using a laser Raman spectrometer 107 from Renishaw plc (532 nm) were performed. Microstructure analysis was carried out by transmission 108 electron microscopy (TEM, JEOL JEM-2100F) and scanning electron microscopy (SEM, Verios G4 UC) 109 with an energy dispersive spectrometer (EDS, Oxford Instruments). NMR measurements of ¹⁹F were 110 performed by a 600 MHz SS-NMR spectrometer JEOL ECZ600R/S3 equipped with a 14.09 T 111 superconducting magnet and a 3.2mm double-resonance MAS probe (JEOL RESONANCE Inc., Japan). 112 Particle size distribution was measured by a zetasizer nano ZS90 (Malvern Instrument). X-ray photoelectron 113 spectroscopy (XPS, AXIS Supra) with MgKa excitation source was used to detect the relative V content in 114

different valence states and the different coordination of O. The electron paramagnetic resonance (EPR,
Bruker A320) was used to detect the unpaired electrons in the atoms or molecules to explore the structural
characteristics of its surrounding environment.

118 **2.3. Electrochemical measurements**

Two different cathodes were prepared by mixing conductive carbon black (super P) and polyvinylidene 119 fluoride (PVDF) binder with VPLi and VPFLi, respectively, at a mass ratio of 7:2:1. N-methyl pyrrolidone 120 (NMP) (15 wt%) was added, and the mixture was ground into a slurry. The slurry was coated onto an 121 aluminum foil, dried thoroughly under vacuum condition, and cut into 10 mm diameter disks to be used as 122 the cathode. CR2016 type coin cells were assembled with lithium being the anode, Celgard 2025 being the 123 separator, and an electrolyte containing 1.0 M LiPF6 in ethylene carbonate (EC), dimethyl carbonate (DMC), 124 and ethyl methyl carbonate (EMC) with a volume ratio of 1:1:1. The entire assembly was completed in a 125 vacuum glove box filled with Ar (H_2O and O_2 content <1 ppm). The preparation process is shown in Fig.1. 126 Battery cycling (Land CT3001A) was conducted at a constant current of 0.1A g⁻¹ and 50 mA g⁻¹ to study the 127 cycling behaviour and rate capability within a voltage range of 1.5-4.2 V. Cyclic voltammetry (CV) was 128 performed on an electrochemical workstation (CHI660E) in a voltage range of 1.5-4.2 V, at a scan rate of 129 0.5 mV/s. CHI660E was used to perform electrochemical impedance spectroscopy (EIS) in a frequency 130 range of 10^{-2} – 10^{5} Hz, at an amplitude of 5 mV. 131



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134 **3. Results and discussion**

135 **3.1 Structure and thermodynamic properties of fluorination on VPLi**

DSC results in Fig.2(a) shows that the glass transition temperature (T_g) of VPLi was 224 °C, with three crystal precipitation temperatures (T_C), 259 °C (T_{C1}), 329 °C (T_{C2}) and 474 °C (T_{C3}) and a melting temperature (T_m) of 569 °C (T_{m1}). The T_g of VPFLi was found to be 220 °C, with T_{C1} and T_{C2} being 239 °C and 489 °C, respectively, and T_{m1} , T_{m2} and T_{m3} being 349 °C, 409 °C and 545 °C, respectively. The lower T_C of VPFLi as compared to VPLi suggests the lower activation energy of the crystallization process required for the fluorinated system. Compared with VPLi, VPFLi has fewer crystallization peaks and more melting peaks, indicating multiple crystal systems are present in the system.

VPLi was heated and studied in situ using high and low temperature XRD, as shown in Fig.2(b). The 143 sample (VPLi-25 $^{\circ}$ C) was first heated to 270 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min and held for 30 min (VPLi-270 $^{\circ}$ C), 144 followed by heating to 340 °C at a rate of 10 °C /min, and maintained for 30 min (VPLi-340 °C). Finally, the 145 material was cooled down to room temperature naturally (VPLi-C25 °C). Fig.2(b) shows that VPLi-25 °C has 146 an amorphous phase, at elevated temperatures, VPLi-270 °C showed the precipitation of crystalline Li₃P 147 (PDF#04-0525), and VPLi-340 ℃ showed precipitation of crystalline Li_{0.3}V₂O₅ (PDF#18-0755). The fact 148 that VPLi possesses two potential crystal precipitation pathways suggests the material is in a 149 thermodynamically metastable state and different heat treatment conditions can lead to precipitation of either 150 crystalline Li₃P or Li_{0.3}V₂O₅. Fig.2(c) compares the XRD pattern of VPLi and VPFLi at room temperature 151 (25 °C). Compared to the neat amorphous VPLi, VPFLi showed ordered crystalline precipitation of VF4 152 (PDF#19-1409) and Li₃VF₆ (PDF#28-0607). 153

Fig.2(d) shows the FT-IR spectra of VPLi, VPFLi, and as purchased Li₃PO₄, and V₂O₅. The characteristic absorption peak at 1624 cm⁻¹ represents the stretching vibration of V=O. The absorption band at 1010 cm⁻¹, represents the tensile vibration of the V⁵⁺=O bond [57] of VPLi, VPFLi and V₂O₅. The characteristic absorption peak at 1030 cm⁻¹ represents the asymmetric stretching vibration of the tetrahedron [PO₄] [58]. The characteristic peaks at 946 cm⁻¹ and 922 cm⁻¹ can be correlated to the asymmetric vibration of P-O-P [58]. of the red shift of P-O-P can be attributed to the presence of F [59].

In the subsequent Raman analysis (Fig.2(e)), the peaks at 287 and 538 cm⁻¹ seen in VPLi and VPFLi can be attributed to the bending mode of the V-O-V bond [18]. Characteristic peaks such as 766 and 990 cm⁻¹ are related to the tensile vibrations of the double-coordinated oxygen (V₂-O) and vanadium oxide (V=O) [18]. δ^{19} F frequency-stepping spectra (Fig.2(f)) obtained from solid-state NMR of VPFLi exhibited strong signals and chemical shifts which can be referenced against fluorotrichloromethane (CCl₃F, $\delta_{(1^{9}F)} = 0$ ppm) [26]. However, no such signal has been found in VPLi in this region [46].



Fig.2. (a) DSC scan of VPLi and VPFLi, (b) *in situ* XRD pattern of VPLi at different temperatures, (c) XRD pattern of
VPLi and VPFLi, (d) IR spectra of VPLi, VPFLi, Li₃PO₄, and V₂O₅, (e) Raman spectra of VPLi and VPFLi, and (f) ¹⁹F
frequency-stepping spectra of VPFLi obtained by solid-state NMR.

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SEM images of VPLi and VPFLi are shown in Fig.3(a)-(b). Elements V, P, O and F within VPFLi were identified in the EDS elemental mapping and its associated spectra Fig.3(c)-(d). EDX point analysis confirms the substitution molar ratio of fluorine for oxygen is 1:10. The particle sizes of VPLi and VPFLi are in the range of 2-10 μ m according to the analysis using , Fig.3(e). Since F⁻¹ ion has a smaller radius (0.133nm) than O²⁻ (0.136nm), it is less prone to the concentration quenching effect [60], and can render a higher doping concentration. The TEM images and the associated SAED patterns suggest VPLi (Fig.3(f)) has a disordered amorphous structure. In contrast,VPFLi (Fig3(g)) features nano-polycrystals embedded in an amorphous phase, which corroborate well with the previous XRD pattern (Fig.2(c)). The insets shown in Fig.3(g1)-(g2) confirm the presence of nanocrystalline regions in VPFLi. The interplanar lattice spacing of 0.344 nm and 0.225 nm correspond to the (111) plane of VF₄ (PDF#19-1409) nanocrystal and (112) plane of Li₃VF₆ (PDF#28-0607) nanocrystal, respectively. Fig.3(h) shows the crystal structures of VF₄ and Li₃VF₆, respectively.



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Fig.3. Microstructure and elemental analysis of VPLi and VPFLi. (a) SEM of VPLi, (b) SEM of VPFLi, (c) elemental
mapping of VPFLi, (d) EDS of VPFLi (insets: comparison between VPLi and VPFLi), (e) Particle size distribution of VPLi
and VPFLi, (f) TEM of VPLi with SAED pattern, (g) TEM of VPFLi with SAED pattern (insets: lattice structure of (g1)
(111) plane of VF₄ and (g2) (112) plane of Li₃VF₆), (h) the crystal structure of VF₄ and Li₃VF₆.

Vanadium usually presents in V^{5+} , V^{4+} , and V^{3+} states in vanadate glass with their respective electronic structures $3p^63d^0$, $3p^63d^1$, and $3p^63d^2$. The electron paramagnetic resonance is an effective technique for detecting V^{4+} [61] as the unpaired electrons surrounding the V^{4+} nucleus can generate strong EPR signals. 190 VPLi and VPFLi have the same stoichiometry dring the test. Fig.4(a) shows that the EPR peak intensity of 191 VPFLi is ~ 1.46 times greater than that of VPLi, confirming the significantly increased V^{4+} content in 192 VPFLi.

The full spectrum XPS survey (Fig.4(b)) shows that VPFLi contains V2p, P2p, O1s, Li1s, C1s and F1s, 193 and VPLi contains V2p, P2p, O1s, Li1s and C1s. The relative abundance of P-O-P, V-O-V, Li-O-Li and 194 non-bridging oxygen (NBO) can be found from the high-resolution O1s XPS spectra in Fig.4(c) (VPLi), 195 Fig.4(d) (VPFLi) and Table 1. After fluorination, O1s of the V-O-V bonds (531.3 eV) reduced significantly 196 from 56.7% to 46.9% and the Li-O-Li bonds (530.6 eV) reduced from 16.2% to 3.9%. This is because, the 197 Li-O-Li structure can induce non-hybridization of the oxygen atomic orbital. The orbital energy level is 198 raised to a level between the transition metal e_g^* and t_{2g} levels, which induces the redox reaction of oxygen 199 [56] and triggers the V-F bond formation. In contrast, O1s of the P-O-P bonds (532.4 eV) increased 200 significantly from 3.0% to 16% and the NBO bonds (530.9 eV) increased from 8.3% to 10%. 201

As shown in Fig.4 (e) and (f), the peak position of the V 2p3/2 XPS spectra at 516.5 eV can be assigned 202 to V^{3+} , 517.4 eV to V^{4+} , and 518.1 eV to V^{5+} [48.62] in VPLi and VPFLi. Literature [63] reports that V^{4+} 203 content is related to electrical conductivity. Table 2 shows that after fluorination, V^{3+} content increased from 204 3.0% to 16.2%, and the V⁴⁺ content increased from 16.3% to 23.8% with the V⁵⁺ content decreased from 205 206 80.7% to 60.0%, indicating effect of fluorination in reducing the valence state of V. As such, Li_3VF_6 can be considered as an emerging electrochemically active lithium intercalation material [64]. In Li₃VF₆, the 207 substitution of O by F leads to reduced overall number of negative charges. To maintain the material's 208 electrical neutrality, the average valence of V must decrease, which can be achieved by V_2O_5 to V_2O_4/V_2O_3 209 conversion during heating of VPLi [65]. From Table 2, it can be seen that the lower valence V is dominated 210 by V_2O_4 and with the greater number of V^{4+} participating in the electrode reaction (V^{4+}/V^{3+}) , the electrode's 211 discharge capacity is expanded accordingly. In addition, V_2O_4 has a unique structure consisting of $[VO_6]$ 212 octahedral double layers connected by shared corners, which provides efficient diffusion paths for Li⁺ ions 213

214 [19].



Fig.4. EPR and XPS spectra of VPLi and VPFLi: (a) EPR spectrum survey, (b) XPS full spectrum survey, (c) O1s
deconvolution for VPLi, (d) O1s deconvolution for VPFLi, (e) V 2p deconvolution for VPLi, (f) V 2p deconvolution
for VPFLi.

219 Table 1 Relative abundance of P-O-P, V-O-V,Li-O-Li and NBO obtained from high-resolution O 1s XPS spectra.

	P-O-P		V-O-V		Li-O-Li		NBO		FWHM	I orenz-Gaussian
	Main		Main		Main	Area	Main	Area	(eV)	ratio(%)
	peak(eV)	Area (%)	peak(eV)	Area (%)	peak(eV)	(%)	peak(eV)	(%)	, ,	
VPLi	522.4	18.8	521.2	56.7	520 6	16.2	520.0	8.3	1.25	80
VPFLi	552.4	39.2	551.5	46.9	550.0	3.9	550.9	10	1.25	80

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221 Table 2 Relative abundance of V obtained from high-resolution V 2p3/2 /(V 2p1/2 XPS) spectra.

	V ³⁺		V ⁴⁺		V ⁵⁺		FWHM	Lorenz-Gaussian
	Main peak(eV)	Area (%)	Main peak(eV)	Area (%)	Main peak(eV)	Area (%)	(eV)	ratio(%)
VPLi	516.5/(523.8)	3.0	517.4/(524.7)	16.3	518.1/(525.4)	80.7	1.5/(2)	80
VPFLi		16.2		23.8		60.0	1.5/(2)	80

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3.2 Characterization of battery electrochemical performance

The electrochemical performance of CR2016 type coin cells was studied in detail. As shown in Fig.5(a), 224 VPLi provided specific capacities of 180.1, 166.4, 153.2, 137.7 and 125.3 mAh g⁻¹ for the 1st, 10th, 20th, 30th, 225 and 50th cycle, respectively, under a current density of 0.1A g⁻¹, within a voltage range of 1.5 - 4.2V. In 226 contrast, VPFLi (Fig.5(b)) presented enhanced specific capacities of 228.9, 210.8, 193.5, 186.7 and 174.7 227 mAh g^{-1} for the same cycles, under the same conditions. After 50 cycles, the specific capacity retention rates 228 were 76.3% for VPFLi and 69.6% for VPLi, respectively. Fig.5(c) gives the rate performance of the VPLi 229 and VPFLi under various current densities (100, 200, 400, 800 and 100 mA g⁻¹). The discharge capacities of 230 VPLi were 185–173, 157–142, 95–76, 30–19 and 145–135 mAh g⁻¹, respectively and for VPFLi, greater 231 discharge capacities have been observed (228-220, 208-198, 179-165, 120-99 and 210-205 mAh g⁻¹, 232 respectively) under the same testing conditions. 233

According to the long-term cycling results shown in Fig.5(d), VPLi presented optimal capacities of 266.8 234 mAh g^{-1} , and 197.6 mAh g^{-1} after 200 cycles at a current density of 50 mA g^{-1} with capacity retention rate 235 74.0%. VPFLi presented greater optimal capacities of 344.3 mAh g⁻¹, and 269.7 mAh g⁻¹ after 200 cycles 236 with the coulombic effciency approaching 100%, at a current density of 50 mA g⁻¹ with capacity retention 237 rate 78.3%. The result implies that VPFLi is a promising material for reversible Li⁺ storage. Due to the 238 greater electronegativity of F (4.0) as compared to O (3.5), it has a stronger ability to attract electrons, and 239 240 its resulting covalent bonding strength with V is higher. V-F covalent bond helps to maintain a stable crystal structure during repeated charge/discharge processes, and effectively improves the cycle stability of the 241 VPFLi. 242

The electrical conductivity of the assembled battery was evaluated by EIS [18]. Fig.5(e) shows that the charge transfer resistance of VPFLi ($R_{CT} = 704 \ \Omega$) was only half that of VPLi ($R_{CT} = 1499.7\Omega$). This suggests that substituting F for O of VPFLi and the associated increased V⁴⁺ content can improve the electrical conductivity of the electrode and hence enhance its rate performance. Fig.5 (f) compares the specific capacity values of VPLi and VPFLi with other cathode materials reported in the literature. In general, the capacity performance of VPFLi is better (particularly at low and high current densities) than the existing amorphous vanadium-based cathode materials, such as $H_2-V_2O_5-P_2O_5$ [48], V_2O_5 -LiBO₂ [51],Li₂O-V₂O₅-SiO₂-B₂O₃ [66], C-Li₂O-V₂O₅-P₂O₅ [67], ε -VOPO₄ [68], and vanadium-based crystal cathode materials V₂O₅ nanofibers [69], V₂O₅ nanoribbon [70].



Fig.5. Electrochemical performance of VPLi and VPFLi. (a)-(b) Galvanostatic charge and discharge profiles of VPLi and
 VPFLi at a current density of 0.1A g⁻¹, (c) Rate performance of VPLi and VPFLi, (d) Long-term cycling of VPFLi, (e) EIS
 measurements of VPLi and VPFLi, (f) Comparison of specific capacities with reported cathode materials in the literature.

256 3.3 Lithiation mechanism and DFT calculations

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Fig.6(a) shows the CV curves of VPLi and VPFLi at a scan rate of 0.5 mV/s. For VPLi, the peaks at 1.2 V 257 /0.6V and 3.5 V/3.8V can be associated with the redox reaction processes V⁴⁺/V⁵⁺ due to the extraction and 258 insertion of Li⁺ [71.72]. The broad peaks at 1.7 V and 2.6V seen for VPFLi can be associated with the redox 259 reaction processes V^{3+}/V^{4+} [68]. Fig.6(b) - (c) shows the *ex situ* XRD spectra of VPLi and VPFLi at different 260 stages of the first charge /discharge cycle at a current rate of 200 mA g⁻¹, *i.e.*, in the initial state (OCV, 3 V), 261 1.2 (2.6) V (discharge), 0.01 V (discharge), 0.6 (1.7) V (charge), 3.5 V (charge), and 3 V (discharge). As 262 shown in Fig.6(b), nanocrystal Li₂V₂O₅ (PDF#48-0076) precipitation within VPLi can be signified by the 263 characteristic peaks at 0.6 V (charge) and 3.5 V (charge). These peaks subsequently disappeared at 3.0 V 264 (discharge) in the first cycle of VPLi. In contrast, LiVP₂O₇ (PDF#46-0311) and Li₂V₂O₅ (PDF#48-0076) 265

nanocrystals precipitation was found for VPFLi at 1.7 V (charge) and 3.5 V (charge), which subsequently
disappeared at 3.0 V (discharge) in Fig.6(c).

The TEM image of VPLi at 3.5 V (charge) in the first cycle (Fig.6(d)) confirms the material is in a single

crystal Li₂V₂O₅ state. The inter-planar distance of 0.281 nm in Fig (d1) further confirms it is correlated to the

- 270 (112) plane of $Li_2V_2O_5$ (PDF#48-0076). The theoretical specific capacity of the V_2O_5 electrode with one Li^+
- inserted is 147 mAh g^{-1} and that with two Li⁺ inserted is 294 mAh g^{-1} [16]. The specific capacity of VPLi
- has an intermediate value (180 mAh g^{-1}), see Fig.5(a), which indicates the associated V⁴⁺/V⁵⁺ lithiation process involves conversion of V₂O₅ into Li₂V₂O₅ in the first cycle of VPLi [22.73].

On the other hand, the TEM image in Fig.6(e) shows that VPFLi at 3.5 V (charge) is in a polycrystalline 274 state in the first cycle. Fig.(e1) shows the inter-planar distance of 0.656 nm corresponds to the (001) plane of 275 LiVP₂O₇ (PDF#46-0311. Fig.(e2) shows the inter-planar lattice spacing of 0.323 nm corresponds the (103) 276 plane of Li₂V₂O₅ (PDF#48-0076). These results corroborate well with the XDR data in Fig.6(c). Addition of 277 LiVP₂O₇ is known to improve the electrode materials capacity and rate performance [74.75], as it can 278 generate a series of V-based multiple redox couples, which offers additional active locations for Li⁺ ion 279 storage and effectively shortens the Li⁺ ion diffusion pathway. Li⁺ is stored in the channel formed by the 280 corner-sharing [VO₆] octahedron and the P₂O₇ group, which is coordinated by four oxygen atoms in the 281 LiVP₂O₇ crystal structure [76]. The volume of VPLi and VPFLi remain constant during the Li⁺ insertion or 282 extraction process (no significant peak shift in XRD spectra). The reversible peak position and peak 283 intensity in the XRD pattern of VPLi and VPFLi during the charge-discharge cycle indicate both materials 284 are intercalation-type lithium storage materials[77]. The reaction mechanism is shown in Fig.7. 285



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Fig.6. (a) CV curves of VPLi and VPFLi during the first two cycles, (b)-(c) *Ex situ* XRD of VPLi and VPFLi under different
charge/ discharge states in the first cycle, (d)-(e) TEM images of VPLi and VPFLi at 3.5 V (charge) in the first cycle (insets:
SAED patterns and lattice spacing information).



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Fig.7. Schematic showing the reaction mechanism during the battery cycles

The presence of nanocrystals within the amorphous glass matrix could lead to a synergistic effect that effectively improve the battery electrical cycle performance [53]. Fluorinated product VPFLi features a polycrystalline structure in which the precipitated Li_3VF_6 and VF_4 nanocrystals were embedded in amorphous phase. Compared to VPLi, VF₄ and Li_3VF_6 crystals were converted into $LiVP_2O_7$ in VPFLi, which led to the increased specific capacity. This is evident by the symmetrical charge/discharge curve and the improved capacity retention rate. It involves reversible order-disorder transition between crystal and amorphous phases during the preparation process and charge-discharge cycles.

Density functional theory (DFT) based electronic structure calculations for crystalline vanadium-based 299 electrode materials have been widely reported to date [78.79], and such calculation can reflect the structure 300 stability, the electrons transfer and the atomic bonding within the materials. However, research into 301 amorphous materials such as long/short range disordered structures is still in its infancy. The details of the 302 calculation method based on DFT theoretical model for this study can be found in **Supporting Information**. 303 As shown in Fig.8(a)-(b), the theoretical structural models of VPLi and VPFLi reactants are constructed, 304 which are V_2O_5 and $V_2O_{4.5}F_{0.5}$ (molar ratio O/F=9), respectively. Density of states (DOS) is essentially the 305 number of different states at a specific energy level that electrons are allowed to occupy (the number of 306 electronic states per unit volume per unit energy). Fig.8(c)-(d) display the total density of states of VPLi and 307 VPFLi before and after insertion of a single Li⁺. VPLi and VPFLi have semiconductor characteristics with a 308 large characteristic band gap. After a single Li atom was inserted into VPFLi, its Fermi level moves to the 309 edge of the conduction band. This indicates a transition into an n-type semiconductor state as the insertion of 310 Li⁺ helps reduce the electrical conductivity and electrode impedance of the structure. Fig.8(e)-(f) show the 311 312 charge density distribution map of VPLi and VPFLi with a single Li atom insertion, respectively. The simulation result shows the electronic structure (charge accumulation and depletion) and the chemical 313 environment of the lattice structure, which is otherwise difficult to measure experimentally. In VPLi, Li 314 accepts most of the charges transferred from O, while for VPFLi, charges mostly transferred from Li to O 315 due to the presence of F. Therefore, the substitution of fluorine for oxygen contributes to the improvement 316 of the electrical conductivity of the structure and the further reduction of the electrode impedance. Since the 317 battery cycle redox reaction is dependent on reduced oxygen, the reduced irreversible oxygen loss can lead 318 to the imporved cycle stability. 319



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Fig.8. DFT simulation of VPLi and VPFLi for Li ion storage processes. (a)-(b): the theoretical structure models of VPLi and
 VPFLi, (c)-(d): total density of states of VPLi and VPFLi before and after Li insertion, (e)-(f): charge density difference of
 VPLi and VPFLi after single Li atom insertion (light blue: charge depletion; yellow: charge accumulation).

324 **4. Conclusions**

This work presents the first investigation on a fluorinated vanadium-phosphorus amorphous lithium 325 battery cathode material and the associated structure-performance relationship. After fluorination, the V⁴⁺ 326 content in the cathode material increased from 16.3% to 23.8%. The fluorinated product VPFLi consists of 327 10% of precipitates (Li₃VF₆ and VF₄ nanocrystals) and shows an optimal specific capacity of 344.3 mAh g⁻¹ 328 in the first cycle and 269.7 mAh g⁻¹ after 200 cycles at a current density of 50 mA g⁻¹ within a voltage range 329 of 1.5-4.2V. The charge transfer resistance of VPFLi ($R_{CT} = 704 \Omega$) was only half that of VPLi ($R_{CT} =$ 330 1499.7 Ω). Modelling through density functional theory shows that that fluorination contributes to the 331 moving of Fermi level towards the edge of the conduction band, and that charges mostly transferred from Li 332 to O, which led to improved cycle stability. 333

334 The lithiation process (V^{4+}/V^{5+}) in amorphous VPLi can be related to the conversion of V₂O₅ to Li₂V₂O₅

in the cycling process. Compared to VPLi, VF₄ and Li₃VF₆ crystals were converted into LiVP₂O₇ in VPFLi, which increased the specific capacity. It is believed that having VF₄ and Li₃VF₆ nanocrystals embedded in the amorphous glass matrix and the associated order-disorder transition between crystal and amorphous phases can lead to a synergistic effect that enhances the electrical cycle performance of fluorinated vanadium-phosphorus amorphous cathode in practical lithium ion battery applications. This study provides a new perspective towards selecting novel cathode material for future lithium-ion batteries.

341 **Declarations of interest**

342 The authors declare that they have no known competing financial interests or personal relationships that

343 could have appeared to influence the work reported in this paper.

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