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Supporting Information 1 2 3 LiFePO₄/NaFe₃V₉O₁₉/ porous glass nanocomposite cathodes for 4 Li⁺/Na⁺ mixed-ion batteries[†] 5 6 Xudong Zhang,*a Xiaolong Xu, a Wen He,*a Guihua Yang,^b Jianxing Shen, a Jinhua Liu^a and 7 8 Qinze Liu^a 9 10 11 X.Z. and W.H. designed the experiments. X.X. performed experiments and calculations. G.Y., 12 J.S, J.L and Q.L.assisted in the experiments. X.Z. and W.H. wrote the paper. All authors discussed the results and commented on the manuscript. 13 14 15 ^a Shandong Key Laboratory of Glass and Functional Ceramics, Oilu University of 16 Technology, Jinan 250353, China. Fax: +86 531 89631080; Tel: +86 531 89631518; *Corresponding author. *E-mail: zxd1080@126.com; hewen1960@126.com;. 17 ^b Key Laboratory of Pulp and Paper Science and Technology of Ministry of Education, Qilu 18 University of Technology, Jinan 250353, China. 19 20 21 22 23 Sections: 24 S1. Network structure of NFVPB glass (Fig. S1) S2. Electrochemical performances of the different LFP/NFV/NFVPB cathodes (Fig. 25 26 S2, Fig. S3, Table S1) S3. Morphology and pore structure characterizations of the different LFP/NFV/NFVPB 27 samples (Fig. S4, Fig. S5) 28 29 S4. Structure characterizations of the different LFP/NFV/NFVPB samples (Fig. S6, 30 Table S2, Fig. S7 and Fig. S8) S5. Li⁺/Na⁺ mixed-ion diffusion coefficient studies. (Fig. S9, Fig. S10 and Table S3) 31 32 References 33

1 S1. Network structure of NFVPB glass



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- 3 Fig. S1 Schematic drawing of Network structure of NFVPB glass.
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5 S2. Electrochemical performances of the different LFP/NFV/NFVPB cathodes

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8 Fig. S2 The calculation method of the energy density based on the voltage plateau during discharging. First
 9 discharge curve of the LFP/NFV/NFVPB-2 cathode at 0.1C.

- 12 The energy density was obtained through calculation of integral area (such as the red area
- 13 in Fig. S2) of the discharge curve by using the origin 8.0 software.¹

¹⁰ 11



Fig. S3 Electrochemical properties of the different LFP/NFV/NFVPB cathodes for the coin cells tested between 2.5 and 4.2. All LFP/NFV/NFVPB samples have 6.244 wt% C. (a) First charge-discharge curves of the cathodes synthesized with different molar ratio at 700 °C at 0.1C, the optimal molar ratio of Fe/V is 1:1. (b) First charge-discharge curves of the different cathodes synthesized with the optimal molar ratio at different temperature at 0.1C, the optimal heat treatment temperature is 700°C.

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10 **Table S1.** Comparison of electrochemical performances of the different cathodes

Samples	Initial discharge capacities [mAh g ⁻¹]	Theoretical value of capacity [mAh g ⁻¹]	Redox couples	Charge potentials	References
LFP/NFV/NFVPB -2	202.8 (0.1C), 100.4 (10C)	170	Fe ²⁺ /Fe ³⁺ , V ³⁺ /V ⁴⁺	3.3–3.83 V	
Na ₃ V ₂ (PO ₄) ₃ @C core-shell nanocomposites	104.3 (0.5C), 94.9 (5C)	117	V ³⁺ /V ⁴⁺ , V ²⁺ /V ³⁺	1.6–3.4 V	ref. 2
ultra-thin LiFePO ₄ nanosheets	197 (0.1C), 60 (10C)	170	Fe ²⁺ /Fe ³⁺		ref. 3
$Na_3V_2(PO_4)_2F_3$	132 (0.1C), 87.5 (2C)	128	V ³⁺ /V ⁴⁺	2.5–4.6 V	ref. 4
Na ₃ V ₂ (PO ₄) ₃ /C	101 (0.1C), 39 (10C)	117	V ³⁺ /V ⁴⁺ , V ²⁺ /V ³⁺	1.6–3.4 V	ref. 5
LiMn ₂ O ₄ /Na _{0.22} MnO ₂ mixed-ion battery	30 (0.25C)	60	Mn^{3+}/Mn^{4+}	0.6–1.0 V	ref. 6
Na ₃ FePO ₄ CO ₃	121 (0.1C), 58 (2C)		Fe ²⁺ /Fe ³⁺ , Fe ³⁺ /Fe ⁴⁺	2.0–4.55 V	ref. 7
Na ₂ FePO ₄ F	182 (0.1C)		Fe ²⁺ /Fe ³⁺ , Fe ³⁺ /Fe ⁴⁺	1.5–4.6 V	ref. 8

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17 S3. Morphology and pore structure characterizations of the different LFP/NFV/NFVPB

- 18 samples
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Fig. S4 (a-c) SEM images with different magnification factors show the lamellar structure of LFP/NFV/NFVPB-2 particles and the pore structure on the particle. (d-f) AFM images with different operating modes show the different surface morphologies of LFP/NFV/NFVPB-2 particles.



6 Relative Pressure (P/P_o)
7 Fig. S5 The hysteresis loop and Barret–Joyner–Halenda pore-size-distribution histogram of different
8 LFP/NFV/NFVPB samples synthesized with the optimal molar ratio (1:1) of Fe/V, (a) LFP/NFV/NFVPB9 Isample synthesized at 600°C; (b) LFP/NFV/NFVPB-2 sample synthesized at 700°C; (c)
10 LFP/NFV/NFVPB-3 sample synthesized at 800°C.

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12 S4. Structure characterizations of the different LFP/NFV/NFVPB samples

13 Table S2. Summary of the structural features of the synthesized samples calculated by using Jade 5 XRD 14 pattern-processing software

P P	00220002						
Sam	ples	Crystallite	(hkl)	Distance of crystal	Crystallite size	Crystallinity	Strain
				face [A]	[nm]	[%]	[%]
LFP/NFV/NFVPB -1	LiFePO ₄	(121)	2.9969	60.0	96.35	0.1573	
	NaFe ₃ V ₉ O ₁₉	(107)	2.7858	22.8	92.51	0.1659	
LFP/NFV/NFVPB -2	LiFePO ₄	(121)	2.9973	55.0	96.27	0.1943	
	NaFe ₃ V ₉ O ₁₉	(107)	2.7701	26.1	96.04	0.1514	
LFP/NFV/NFVPB -3	LiFePO ₄	(121)	2.9935	59.3	97.24	0.2379	
	NaFe ₃ V ₉ O ₁₉	(107)	2.7713	22.6	90.07	0.2097	



Fig. S6 XRD characterizations of the different LFP/NFV/NFVPB samples. (a) XRD patterns of the 4 LFP/NFV/NFVPB-2 nanocomposite sample (A) synthesized at 700 °C and pure LFP sample (B). (b) XRD 5 patterns of the different LFP/NFV/NFVPB samples synthesized at the different temperature. 6



7 8 9 LFP/NFV/NFVPB-2 nanocomposite sample and the pure LiFePO₄ (LFP) sample. (c) TGA profile of 10 the LFP/NFV/NFVPB-2 sample. 11

12 In Fig. S7a, the infrared spectral bands of LiFePO₄ (LFP) are mainly distributed over two wavenumber ranges from 400 to 650 cm⁻¹ and 940 to 1300 cm⁻¹. These bands respectively 13 correspond to the internal stretching, internal bending and external oscillation modes of PO_4^{3-} . 14 The dominant bands from 940 cm⁻¹ to 1300 cm⁻¹ are due to PO₄³⁻. The bands observed at 15 400–640 cm⁻¹, correspond to intramolecular symmetrical stretching vibrations of the Fe-O 16 bond in the FeO₆ unit. By comparing the infrared spectral bands of LFP/NFV/NFVPB-2 and 17 LFP, two main changes are seen in the FTIR spectra. First, for the LFP/NFV/NFVPB-2 18 sample all the PO₄³⁻ bands have shifted to lower wavenumbers from those of LFP sample. 19 20 This result demonstrates an increase of the P-O chemical bond length and the high-energy phosphate bonds have been introduced in crystal structure of LFP nanoparticles. Second, the 21 vibration transmittance of the PO4³⁻ bands strengthen. Thirdly, the V–O bands appeared at 22

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- 1 634/572/503 cm⁻¹, respectively. These changes indicate that there are in situ nanocomposit
- 2 linkages between the LFP nanoparticles and the NFV nanoparticles.
- 3



4 **Theta (degree)** Wavenumber (cm⁻¹) 5 **Fig. S8** Structure change characterizations of the LFP/NFV/NFVPB-2 sample after charging at different 6 rates. (a) XRD patterns. (b) FTIR spectra.



8 S5. Li⁺/Na⁺ mixed-ion diffusion coefficient studies











15 16 Fig. S10 Cyclic voltammetry (CV) curves of LFP/NFV/NFVPB-2 cathode at different scanning rates (a)



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1 To further understand the electrochemical behaviors of the the different samples, EIS measurements were carried out. In Fig.S9a each EIS curve has an intersection with the Z_{real} 2 axis, semicircles and an oblique line. The intercept in the high frequency region is related to 3 the ohmic series resistance (R_e) . It includes the interparticle contact resistance, electrolyte 4 resistance and other physical resistances between the electrolyte and electrode. The radius of 5 the semicircle at high frequency region on the Z'-axis is related to the charge transfer 6 resistance (R_{ct}) . The slope of inclined line in low frequency represents the Warburg 7 impedance (W), which is associated with Li⁺/Na⁺ mixed-ion diffusion in LFP/NFV/NFVPB-2 8 cathode. The diffusion coefficient (D) of Li⁺/Na⁺ mixed-ions can be calculated from the plots 9 in the low frequency region using the following equation:⁹ 10

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$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$
 (1)

12 Where *R* is the gas constant, *T* is the absolute temperature, *A* is the surface area of the cathode, 13 *n* is the number of electrons per molecule during oxidization, *F* is the Faraday constant (96, 14 486 Cmol⁻¹), *C* is the concentration of Li⁺/Na⁺ mixed-ion, and σ is the Warburg factor which 15 obeys the following relationship:

16
$$Z_{real} = R_e + R_{ct} + \sigma \omega^{-1/2}$$
 (2)

17 Where ω is angle frequency.

Fig.S9c shows the linear fitting of Z_{real} vs. $\omega^{-1/2}$, from which the slope σ can be obtained. 18 Using this σ value it is possible to calculate the lithium diffusion coefficients of the material. 19 The results showed that the lithium diffusion coefficient D values of the LFP and 20 LFP/NFV/NFVPB-2 cathodes are 5.4×10⁻¹⁵, 3.0×10⁻¹⁴ cm² s⁻¹, respectively. The 21 LFP/NFV/NFVPB-2 cathode has the bigger D value and the smaller R_{ct} value (66.3 Ω) than 22 that of LFP. The D_{Li} value of the LFP/NFV/NFVPB-2 cathode at 4.0 mV s⁻¹ scanning rate 23 reduced to 5.0×10^{-15} cm² s⁻¹ and R_{ct} value reduced to 57.9 Ω (Fig.S10b). Thus, the D and R_{ct} 24 values indicate that the electrochemical kinetics of LFP/NFV/NFVPB-2 cathode is easier than 25 that of LFP cathode (Fig.S9ac). Furthermore, LFP/NFV/NFVPB-2 cathode has a higher slope 26 of the inclined line in low frequency (Fig.S9c), indicating lower Warburg impedance. This 27 means that Li⁺/Na⁺ mixed-ion movements in the LFP/NFV/NFVPB-2 cathode are rapider 28 than Li⁺ movements in the LFP cathode. Results of EIS tests indicate that the 29 LFP/NFV/NFVPB-2 cathode has the lowest charge transfer resistance, and its electrochemical 30

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1 kinetics is easier regarding Li⁺/Na⁺ mixed-ion extraction than Li⁺ extraction of the LFP blank

2 cathode. The summary of the electrochemical performances for the different

- 3 LFP/NFV/NFVPB cathodes at different scanning rates is given in Table S3.
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Table S3. Summary of the structural features of the synthesized samples calculated by using Jade 5 XRD pattern-processing software

Samples	$R_{\rm ct}\left(\Omega\right)$	σ	$D \ (\mathrm{cm}^2 \mathrm{s}^{-1})$
LFP-700	2316.1	623.4	5.4×10 ⁻¹⁵
LFP/NFV/NFVPB-1	507.2	116.3	9.7×10 ⁻¹⁵
LFP/NFV/NFVPB-2-0.1	199.1	66.3	3.0×10 ⁻¹⁴
LFP/NFV/NFVPB-3	146.8	99.4	1.3×10 ⁻¹⁴
LFP/NFV/NFVPB-2-1.0	102.8	80.4	2.6×10 ⁻¹⁵
LFP/NFV/NFVPB-2-2.0	80.6	78.3	2.7×10 ⁻¹⁵
LFP/NFV/NFVPB-2-4.0	64.7	57.9	5.0×10 ⁻¹⁵

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