Electronic Supplementary Information (ESI)

Maricite $NaFePO_4$/C/graphene: a novel hybrid cathode for sodium-ion batteries

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Table S1. Refined structural parameters of pristine $NaFePO_4$

Atom	Wychoff	X	y	z	SOF	ADP
NA1	4	0.25	0.8453(30)	0.503(4)	1	2.5
FE2	4	0	0	0	1	2.5(4)
P3	4	0.25	0.1732(31)	0.423(5)	1	7.0(10)
O4	4	0.25	0.1314(40)	0.729(7)	1	0.8(5)#
O5	4	0.25	0.3471(26)	0.466(5)	1	0.8(5)#
O6	8	0.0635(28)	0.1274(23)	0.339(4)	1	0.8(5)#

ADP = atomic displacement parameter, SOF = site occupation factors, # = constrained to be equal, space group = *Pmnb*, 31 refinement parameters, chi-squared = 1.04, a = 6.8490(16), b = 8.9888(20), c = 5.0492(14) Å

Table S2. Refined structural parameters of hybrid $NaFePO_4$/C/graphene

Atom	Wychoff	X	y	z	SOF	ADP*
NA1	4	0.25	0.828(4)	0.558(10)	1	2.5
FE2	4	0	0	0	1	2.5
P3	4	0.25	0.156(4)	0.489(11)	1	7
O4	4	0.25	0.1314*	0.729*	1	0.8
O5	4	0.25	0.3471*	0.466*	1	0.8
O6	8	0.0635*	0.1274*	0.339*	1	0.8

ADP = atomic displacement parameter, SOF = site occupation factors, *= constrained to be the same as original sample, space group = *Pmnb*, 24 refinement parameters, chi-squared = 1.13, a = 6.8521(24), b = 8.9767(29), c = 5.0453(22) Å

Experimental Section

Preparation of maricite $NaFePO_4$ nanoparticles: To prepare pristine $NaFePO_4$ nanoparticles, a suitable amount of Na_2CO_3 (Sigma Aldrich, 99%), $FeC_2O_4{\cdot}2H_2O$ (Sigma Aldrich, 99%) and $NH_4H_2PO_4$ (Fluka, 98%) with molar ratios of 0.5:1:1 were used as starting materials. All starting materials and four hardened steel balls with a diameter of 25.4 mm each were loaded in a stainless steel milling container. The milling container was then evacuated and purged with argon gas 3 times. A high energy ball in conjunction with an external magnet was used to mill starting materials at a rotation speed of 300 rpm for 30 h. The mixed precursors were then fired at 350^{o} C under Ar conditions for 5 h followed by re-ground and calcined at 600^{o} C under Ar conditions for 8 h.

In-situ preparation of hybrid $NaFePO_4$/C/graphene: Maricite $NaFePO_4$ nanoparticles and crystalline graphite (particle size < 20 mm, Sigma Aldrich) powders were mixed with a weight ratio of 4:1 and loaded inside a stainless steel milling container together with four hardened steel balls (diameter of 25.4 mm) along with a suitable amount of acetone as solvent. Mixtures were milled in a rolling ball-mill at a rotation speed of 75 rpm for 30 h at room temperature under an argon atmosphere of 100 kPa.

Material characterization: X-ray diffraction (XRD) data were collected from powder samples on a PANalytical X'Pert Powder instrument using CuKa radiation (1.54 Å) operated at 40 kV with 30 mA current. XRD data were recorded over a range of 10 to 60^{o} with a step time and size of 150 s and 0.02, respectively. The X'Pert data collector software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files were used to identify the phases present. Rietveld refinements were carried out using the GSAS software suite with the EXPGUI software interface.[S1, S2] Thermogravimetric analysis (TGA) was performed via a Q50 thermogravimetric analyser in air to determine the actual amount of carbon (including graphite and graphene) in the hybrid sample. Transmission electron microscopy (TEM) investigations were performed using a JEOL JEM 2100F instrument operated at 200 kV. Energy-filtered elemental maps were acquired using a Gatan Quantum ER 965 Imaging Filter installed on the JEOL JEM 2100F microscope, and a three-window method was used for acquiring elemental maps.

Ex-situ electrochemical characterization: To test the electrochemical performance, pristine $NaFePO_4$ and hybrid $NaFePO_4$/C/graphene powder samples were mixed with acetylene carbon black (AB) and a binder, polyvinylidene fluoride (PVdF, Sigma-Aldrich), in a weight ratio of 80:10:10 in solvent N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, anhydrous, 99.5%). The as prepared slurry was spread onto Al foil substrates, average loading of 1.0-1.2 mg, and these coated electrodes were dried in a vacuum oven at 90^o C for 24 h. The electrode was then pressed using a 25 mm diameter disc to enhance the contact between the Al foil and the active material. Subsequently, the electrodes were cut to 1×1 cm^2. The electrochemical half cells were assembled in an Ar-filled glove box (Innovative Technology, USA) using CR 2032 coin cells with Na metal as the counter electrode, 1M $NaClO_4$ dissolved in propylene carbonate (PC) with 2 % FEC (fluoroethylene carbonate) additive as the electrolyte, and Whatman Glass Microfibre Filter (Grade GF/F) as a separator. The cells were galvanostatically charged-discharged in the potential range of 4.3-1.5V with a Land battery testing system. Electrochemical impedance spectroscopy was performed on the cells over the frequency range of 100 kHz to 0.01 Hz using an Ivium-n-stat computer-controlled electrochemical analyser (Ivium Technologies, Netherlands).

In-situ electrochemical characterization: For in-situ electrochemical characterization, special coin cell casings with 3 mm diameter holes and stainless spacers with 5 mm diameter holes were used for the construction of the coin cells. The coin cells contained Na metal (~1 mm thickness) as reference electrode and Whatman Glass Microfibre Filter (Grade GF/F) separator with 1M $NaPF_6$ in EC and DMC (EC:DMC, 1:1 volume ratio) electrolyte solution.

Cells were made 3 days before the *in-situ* synchrotron XRD experiments. *In-situ* synchrotron XRD data were collected on the Powder Diffraction beamline at the Australian Synchrotron at a X-ray wavelength λ = 0.708735 Å, determined using the NIST 660b LaB_6 standard reference material. Each data set was collected for 3 minutes acquisitions (with detector position movement) on the coin cell in transmission geometry throughout the charge/discharge cycles, and the interval between datasets were 28 minutes. The current was systematically increased from 10 mA g^{-1} to 20 mA g^{-1} and 50 mA g^{-1} as the battery was charged to 4.3 V followed by a potentiostatic hold.

Fig. S1

To estimate the amount of carbon (including graphite and graphene) in the hybrid $NaFePO_4$/C/graphene sample, TGA was carried out in air (Figure S1). Both samples of pristine $NaFePO_4$ and hybrid $NaFePO_4$/C/graphene were heated from 100 to 900° C at a rate of 5°C min^{-1}. As can be seen from Figure S1, pristine $NaFePO_4$ and hybrid $NaFePO_4$/C/graphene powders started to oxidize slowly in air at temperatures above 300° C, with rapid oxidation above 500°C. The retained mass of the pristine $NaFePO_4$ powder was increased by 5 wt.%, which could be attributed to the oxidation of Fe (II) to Fe (III). Meanwhile, the hybrid $NaFePO_4$/C/graphene powders showed rapid mass loss between 550 and 800°C, which corresponds to the burning of carbon (including graphite and graphene). The difference in weight between pristine $NaFePO_4$ and hybrid $NaFePO_4$/C/graphene after the oxidation could be translates into the amount of carbon in the hybrid. With the use of this method, it was estimated that the amount of carbon (including graphite and graphene) in the hybrid was approximately 12 wt.%.

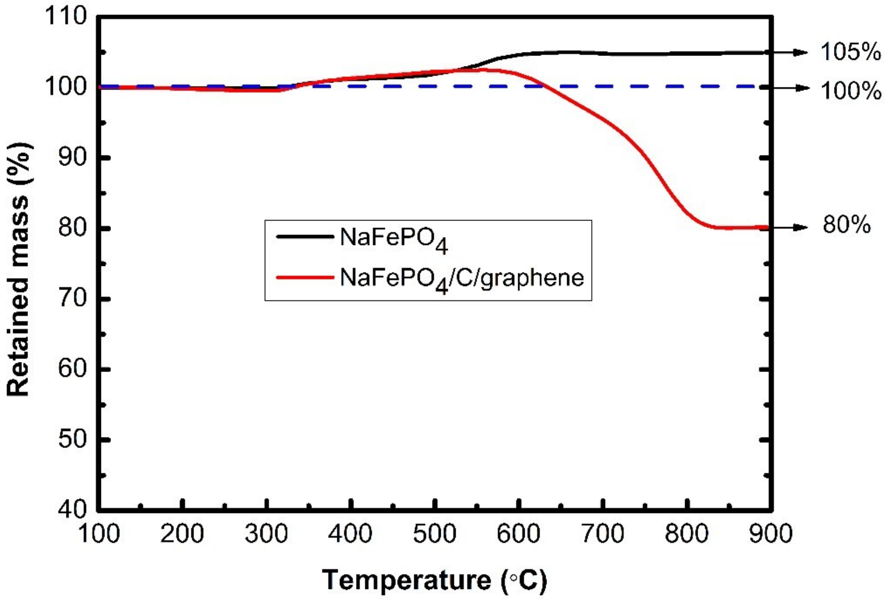

Fig. S1 TGA analysis of pristine $NaFePO_4$ and hybrid $NaFePO_4$/C/graphene samples.

Fig. S2

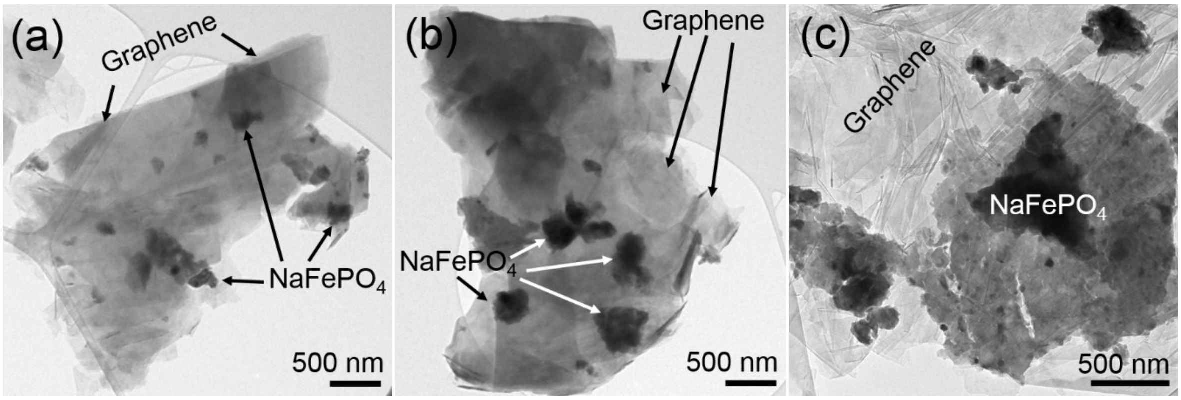

Fig. S2 TEM images of hybrid NaFePO$_4$/C/graphene samples: (a-b) bright-field images of local area taken from different locations.

Fig. S3

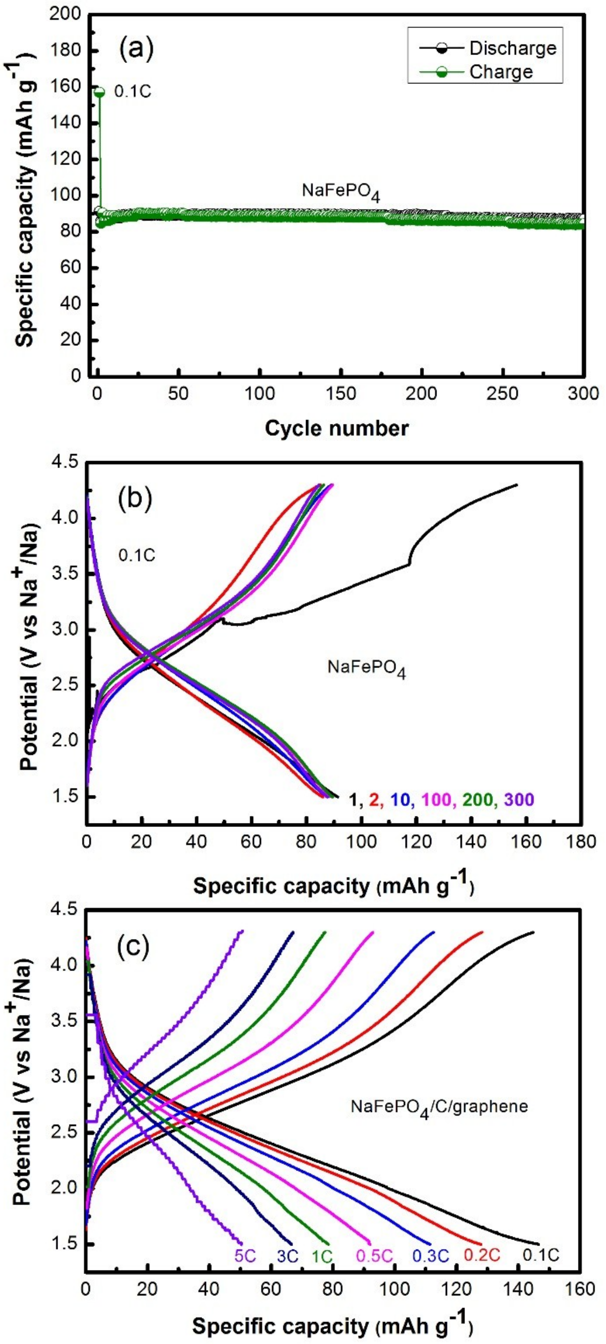

Fig. S3 Electrochemical performance of the pristine $NaFePO_4$ and hybrid $NaFePO_4$/C/graphene electrodes: (a) cycling stability of pristine $NaFePO_4$ electrode at 0.1C (1C = 155 mA g^{-1}); (b) corresponding charge-discharge potential profiles of pristine $NaFePO_4$ electrode at 0.1C and (c) charge-discharge potential profiles of the hybrid $NaFePO_4$/C/graphene electrode at different current rates.

Table S3. Results of applying linear fits to the peak fitting parameters as shown in Fig. 5 (c, d).

Reflection	**Position intercept**	**Position slope**	**Adjusted R^2**	**Area intercept**	**Area slope**	**Adjusted R^2**
220	15.825 （1）	1(2)x10^{-6}	-0.02714	8.5（5）	-2(12)x10^{-4}	-0.03258
121	15.049 (4)	5(7) x 10^{-6}	-0.01948	11 (1)	-6(27)x10^{-4}	-0.03137

Reflection	**Peak width intercept**	**Peak width slope**	**Adjusted R^2**
220	0.0596(44)	-6(9)x10^{-6}	-0.01624
121	0.043(2)	3(5)x10^{-6}	-0.02185

References

S1 A. C. Larson and R. B. Von Dreele, *Book*, **1994**, pp. 86-748.

S2 B. Toby, *J. Appl. Cryst.*, 2001, **34**, 210.