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2D amorphous iron phosphate nanosheets with high rate capability and ultra-long cycle life for sodium ion batteries†

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In our previous work, we reported the formation and mechanism of mono/bi-layer phosphate-based materials and their high performance as cathode materials for Li-ion batteries. In this work, we report that 2D amorphous nanosheets can be used as cathode materials to achieve outstanding performance for sodium ion batteries (SIBs) *e.g.* a high initial discharge capacity of 168.9 mA h g^{-1} at 0.1C, ultra-long life (92.3% capacity retention over 1000 cycles), and high rate capability (77 mA h g^{-1} at 10C) for Na-ion storage, whose electrochemical performance is also much superior to the reported amorphous $FePO_4$ or olivine $NaFePO_4$ with advantages of short paths and larger implantation surface areas for fast Na-ion diffusion and large specific surfaces with more interfacial capacitance. Interestingly, $NaFePO_4$ nanocrystals with about 10 nm sizes are self-nucleated from amorphous 2D nanosheets in the charge/discharge process, which was verified by transmission electron microscopy (TEM) and *in situ* electrochemical impedance spectroscopy (EIS).

Introduction

L (L)- a (LIB) a ... .[2] H, ... LIB ... .[3] U ... (SIB) ... Na ... L ... .[4] I ... Na a L ... LIB ... SIB.[5] N ... SIB ... LIB. F ... S ... SIB (*e.g.* fi ...) ... SIB.[6–8] A ...

... SIB,[9] a NaF PO$_4$ ( ),[10–13] $NaVPO_4F$,[14–16] $Na_3V_2(PO_4)_2F_3$,[17–19] $Na_{1.5}VOPO_4F_{0.5}$,[20,21] Na_2F PO$_4$F,[22] $Na_3V_2(PO_4)_3$,[23–26] $Na_3A\!\!\!\!\ (PO_4)_2F_2$,[27,28] Na_2N PO$_4$F,[29] Na_2(F$_{1-x}C_x$)PO$_4$F,[30] Na_2(F$_{1-x}M_x$)PO$_4$F,[31] *etc.* H ... SIB ... Na. T ... LIB ... ,[32,33] ... SIB. I ...,[1] ... / - ... LIB ... L- ff ... . W ... LIB ... . I ... 2D ... . H ... / - ... 2D ... SIB ... 168.9 A $^{-1}$ a 0.1C, ... (92.3% ... 1000), ... (77 A $^{-1}$ a 10C) Na- ... . I ..., NaF PO$_4$ ... 2D ... / ... .

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† E ... (ESI) ... : E ... fi ... . S DOI: 10.1039/ 6 a00454

Experimental

Materials

A a∫∫ a 2D- a ∫∫a∫ a a ∫ a∫∫ a a - , ∫a .[1] T a a a a a a a a a - a a a a ∫. F a a , F $SO_4 \cdot 7H_2O$, H_3PO_4, a L OH·H_2O a a a a∫. F ∫, 1.05 F $SO_4 \cdot 7H_2O$ a ∫ 33.30 ∫ ∫ ∫ . S ∫, 0.55 H_3PO_4 a 8.80 ∫ ∫ ∫a ∫ a ∫ ∫ F SO_4 ∫ . T ∫, 0.43 L OH a a 41.6 ∫ ∫ ∫, ∫ ∫ a a a ∫ a a ∫ , ∫ a a . F - , a a a a a ∫. F a∫∫, a a a 80 C.

Material characterization

X- a ff a a ∫∫ a B D8 A a ff a C Kα ($\lambda = 0.15418$) a 2θ a 10–80 a 0.02 a a 1 . T ∫ a SEM (ZEISS S a 55) a a TEM (FEI T a G2 F20 S-T). T - (EDS) a a O -Ma 20 a a SEM. T a a a a AFM (B M ∫ M 8).

Electrochemical measurements

E∫ a∫ a a a a 2032 ∫∫ . F a , F PO_4

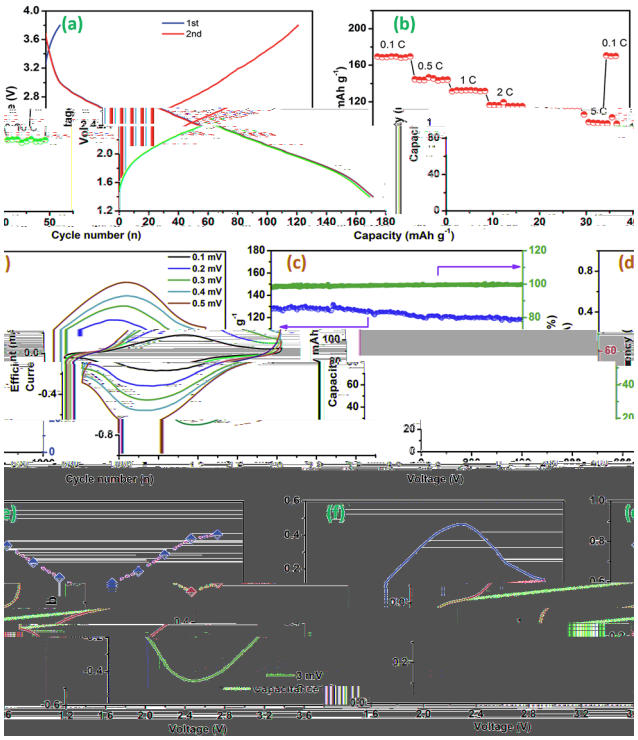

Fig. 2 (a) Galvanostatic discharging/charging profiles obtained at 0.1C. (b) Capacity *versus* cycle number at 0.1C, 0.5C, 1C, 2C, 5C, 10C and return to 0.1C. (c) Cycling performance of the sodium ion battery of 2D nanosheets. The capacity retention at 1C is about 92.3%, declining from 127.8 mA h g^{-1} at the first cycle to 117.9 mA h g^{-1} at the 1000th cycle. (d) CV curves conducted at scan rates of 0.1 mV s^{-1} to 0.5 mV s^{-1}. (e) The *b*-values of the different voltages. (f) CV curves and the capacitance contribution.

, a a a 2D a , a a X- a D ff a (XRD), a F . S5.† T fi a AFM a 0.76 a 1.55 , a F . 1 a S4.† I a 2D a a a a a , a a a 2D a a a , 2D a a a a a a a (F . 1). T , 2D a a a a a , a a a a

. Aft a , 2D a a a , a XRD (F . S5†). T SEM a a EDS a a 2D a - a a a a a “FP@C” (F . 1 a S6†).

T a a a a 2D a , a a a a a a SIB , a a a a 1 M NaC O$_4$ a EC a DMC a a .[34] F . 2a a / a 2D a a a - ff a 1.4–3.8 V *versus* Na$^+$/Na a a a 0.1C (1C = 170 A $^{-1}$). T fi a a a , a 168.9 A $^{-1}$. N a a a a , F (II) FP@C F (III) fi a a a a a 9.5 A $^{-1}$. Aft a / a , a a a a . T 2D a a a a 0.1–10C, a F . 2 . T a a a a a 168, 145, 132, 116, 96, a 77 A $^{-1}$ a a / a a 0.1, 0.5, 1, 2, 5 a 10C, . Aft - a a / a , a fi a a 170.1 A $^{-1}$ a 0.1C. A a 2D a a a a a a a a a . T , a a a- fi NaF PO$_4$ a a F PO$_4$. T a 2D a a a a a 1C, a F . 2 . Aft 1000 , a a 127.8 117.9 A $^{-1}$, a a 7.7%, NaF PO$_4$ a a . T - a (CV) a a a a 2.6 a 2.2 V (F . 2), a / a , . T a - a a a - a - a a , ff a NaF PO$_4$ a a a a a - a / a . Ta 1 a a SIB a a F PO$_4$ NaF PO$_4$ a . H [35] a a

Table 1 The comparison of our work with the reported studies on SIBs based on amorphous FePO$_4$ or olivine NaFePO$_4$

C	Ca a (A $^{-1}$)	Ra a a (A $^{-1}$)	C a
O a	169 (0.1C)	77 (10C)	92.3% (1000 1C)
A -F PO$_4$ (. 35)	120 (0.1C)	50 (1C)	98% (40 0.5C)
A -F PO$_4$ (. 36)	151 (0.1C)	44 (10C)	94% (160 0.1C)
A -F PO$_4$ (. 37)	142 (0.1C)	64 (1C)	92% (120 0.1C)
A -F PO$_4$ (. 38)	155 (0.1C)	75 (1C)	—
Ma -NaF PO$_4$ (. 12)	142 (0.05C)	66 (2C)	95% (200 0.1C)
O -NaF PO$_4$ (. 33)	111 (0.1C)	46 (2C)	90% (240 0.1C)
O -NaF PO$_4$ (. 39)	120 (0.05C)	25 (2C)	90% (100 0.1C)
O -NaF PO$_4$ (. 11)	125 (0.05C)	85 (0.5C)	90% (50 0.1C)

F PO_4 a a ∫ ∫ - a∫∫ a ◗ a ◗ ∫∫ a Na- a . T ∫ - a∫ a a a a a 120 A $^{-1}$ a 0.1C a (10 A $^{-1}$), a a a ∫∫ a a 50 A $^{-1}$ aft 300 ∫ a 1C a (100 A $^{-1}$). Ca [36] a a F PO_4 a - a ◗a a a∫ a a a 151 A $^{-1}$ a 20 A $^{-1}$, ∫ a◗ ∫ (94% a a a 160 ∫), a ∫∫a a a a◗ ∫ (44 A $^{-1}$ a 1000 A $^{-1}$). X [37] a a F PO_4 a a ∫ a a∫ fi - a a a 142 A $^{-1}$, ◗∫ a a 130.8 A $^{-1}$ aft 120 ∫ , a a a a◗ ∫ 63.5 A $^{-1}$ a 1C. L [38] a F PO_4@MCNT a ∫∫ ∫∫ a a a fi a a 155.2 A $^{-1}$ a∫ ∫ a 157.2 A $^{-1}$ aft 70 ∫ a 0.1C. F Ta◗ 1, a a 2D a ◗ ∫ a∫ a a a∫∫ . T a 2D a a a◗ ∫ a∫ a a a , a a a , a ∫ ∫ a ◗ a ◗ a ◗ ∫ . C a a F PO_4 a ∫ NaF PO_4, 2D a a a a ◗a ◗a a a a a L /Na- ff . T ◗a Na 2D-Na ∫ a a ◗ ∫ ∫ NaF PO_4. B a ◗a a , Na a ffi ∫ a ∫ ◗ ∫ ∫ NaF PO_4. F 2D a , ff ∫ /◗ -◗a a a∫ . A a a ◗a a 2D a ∫ ◗ ◗a a a∫ a a a a∫ a a . S ◗a 2D a ∫ ◗a , a ff a a a - ◗ a 2D a ∫ - a∫ a , a a CV a a a 0.1–0.5 V $^{-1}$. T a CV (F . 2) a - a , a a 2D a ◗ a ∫∫ a a a◗ ∫ . A a a a a a ∫∫ a -◗a ◗a ,[40] $I = av^b$, a a b a a a◗ ∫ a∫ . T b a∫ 0.5 a a ∫∫ ◗ - fi ∫ a ff , ∫ b a∫ 1 a a a - ∫∫ ∫ a a - a .[41] T b- a∫ ◗ a a 1.8–3.6 V a ◗ 0.503 a 0.838, a a ◗ - fi ∫ a ff a a - ∫∫ a a a (F . 2). W a a a a ◗ ◗a a a , a F . 2 . A CV , ∫ a ∫ ∫ a a a a a a∫ ◗a a a ∫ ◗ a∫ a . T ∫ a a a ◗ ◗a a∫ a a a a , a a a∫ a a a a 31.7–33.8% a∫ a a , a F . S7.† W a ∫ a∫ a 2D a SIB (2D-Na) a 2D a LIB (2D-L). A F . 3a, a a ∫a a

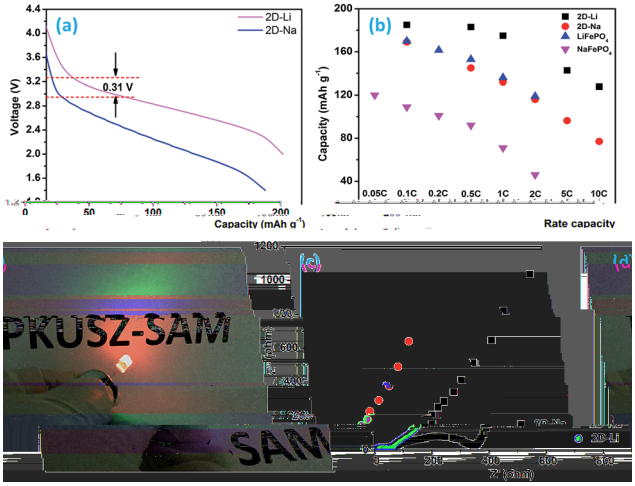

Fig. 3 (a) Discharge curve of 2D-Na and 2D-Li. (b) Rate capability of 2D-Li, 2D-Na, $LiFePO_4$ and $NaFePO_4$. (c) Electrochemical impedance spectroscopy (EIS) of 2D-Li and 2D-Na. (d) The image of an LED lit by a 2D nanosheet sodium ion battery.

2D-Na ∫ a a 2D-L ◗ 0.31 V, a∫∫ a ∫a 0.53 V ∫ L F PO_4 NaF PO_4.[42] I a , a ◗ ∫ a∫∫ a - a∫ , a a a a a◗ ∫ ◗ 2D-L a 2D-Na a∫∫ (F . 3◗). F a ∫ , a a ◗ ∫ ∫ NaF PO_4 a 120 A $^{-1}$ @ 0.1C 40 A $^{-1}$ @ 2C, 2.5 ◗a a a a a ∫ L F PO_4 (168 A $^{-1}$ @ 0.1C *vs.* 120 A $^{-1}$ @ 2C). I a , a a 2D-Na a 169 A $^{-1}$ @ 0.1C 77 A $^{-1}$ @ 10C, 1.5 ◗a a a a a 2D-L (185 A $^{-1}$ @ 0.1C a 127 A $^{-1}$ @ 10C 2D-L). T ◗ a a a◗ ∫ - a 2D-Na a◗ a ∫ ff . W a a 2D-L a 2D-Na (F . 3), a a a a a∫ a ∫∫ a :[43]

$$D_{Li^+} = R^2T^2/2A^2n^4F^4C^2\kappa^2$$

R a a , T a◗ ∫ a , A a a a ∫ , n ◗ ∫ ∫ ∫ , F Fa a a a , C a L - , a κ Wa ◗ a ◗ ∫ ∫ a a . I a ◗ a 2D-L a 2D-Na a a ◗a κ, ff ffi- a ◗a , a 2D a - ff a a a .

E∫ a∫ a (EIS) ∫ a 2D-Na. W EIS ∫∫aft 1, 10, 20, 40, a 100 ∫ a 1C a F . 4a a F . S8,† ◗∫ ∫ a ∫ a fl ∫ - ∫ ∫ a (SEI) a (R_{SEI}) a a a a (R), ∫ . S ◗a . 1, ∫ a a ∫ a a / a ∫ , a a a a∫ ff ◗ a a a -

fi ⌡ a ff . W ⌡a a a a⌡ ff ◆ a a a a NaF PO_4 a - a⌡⌡ a ⌡ a “ - a ”(F . 4 a). T “ a ⌡ ” ⌡ ⌡a a⌡EIS a . D a a a⌡ a 2D a , Na^+ a ff / a a a NaF PO_4 a - a⌡⌡ a ⌡ a / a , ⌡a ff ◆ a a ⌡. T a⌡ a a a aft ⌡ , a ⌡ ⌡⌡aft 1000 ⌡ a 1C a ⌡a ⌡ a a⌡ EDS, XRD a TEM a a⌡ . T EDS a (F . S9†) Na 2D a . F . 4◆ XRD a ⌡ a a⌡ fl a a 28.2 a 41.4, a (020) a (212) ⌡a a⌡⌡ NaF PO_4, ⌡ . T TEM (F . S10† a F . 4) a a ⌡ 2D a a a a a a - a⌡ a ⌡ 10–15 a 2D a . F , a fi a TEM a (F . 4 a F . S11†) a⌡ ◆ ⌡a a a ⌡ a - a ⌡ - ⌡a a a a◆ 0.22 a 0.32 . T fi d_{212} a⌡ (0.22) a d_{020} a⌡ (0.32), a⌡ ⌡a XRD a ⌡ NaF PO_4 a⌡ . T , ◆ TEM a XRD ⌡ ⌡ a ⌡ NaF PO_4 a - a⌡ a ◆ ⌡ a a a a⌡⌡ a 2D a ⌡ - a⌡ a / a ⌡ . T ⌡ a NaF PO_4 a - a⌡ (⌡ a◆ 10–15) a a . I a a ◆ a NaF PO_4-⌡ - a 2D a a ◆ ⌡ a - , ◆ a a ⌡ ◆ ◆ a ◆ ⌡ - a a ⌡ a a . T a NaF PO_4 a - a⌡⌡ a a ffi ⌡ ◆ fi .

Conclusions

W /◆ -⌡a a - a a ⌡⌡ a ◆ ◆⌡a a ◆ a a a⌡ SIB , a ◆⌡ a a 168.9 A $^{-1}$ @ 0.1C, a a a◆ ⌡ 77 A $^{-1}$ @ 10C, a a ⌡⌡ ⌡ a◆ ⌡ 92.3% a a aft 1000 ⌡ . T ⌡ a⌡ a a⌡ a SIB ◆a a F PO_4 ⌡ NaF PO_4. T a a ◆ a ◆ a a ⌡a ⌡a a a a a a Na- ff a a a⌡ a a a /◆ -⌡a a - a a . I ⌡ , ⌡- ⌡ a NaF PO_4 a - a⌡ a◆ 10–15 a a a ◆ *in situ* ◆ ◆ EIS ⌡ a⌡ a / a ⌡ . T a⌡ a a a⌡⌡ 2D a a ◆ ⌡ ⌡ a a⌡ ◆ ◆ a ◆a a a a - a ◆a .

Acknowledgements

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