Supporting Information

Kirkendall effect induced formation of FeP@C composites comprising interconnected carbon coated hollow FeP sub-nanoparticles for efficient alkaline metal storages

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1. Experimental Section

1.1 Materials Synthesis

Typically, 16 mmol fumaric acid and 1.5 mmol Fe(NO₃)₃ was dissolved in 20 mL N,N-Dimethylformamide (DMF) under magnetic stirring. The obtained homogeneous solution was subjected to a hydrothermal reaction at 100 °C for 12 h. The resulting Fe based metal organic frameworks, i.e. Fe-MOF, with a spindle-like morphology was collected through washing with DMF and ethanol and dried under vacuum at 80 °C for 12 h. The spindle-like Fe₂O₃/C was obtained by the calcination of the Fe-MOF at 450 °C for 2 h at a nitrogen atmosphere. For the synthesis of the spindle-like FeP@C, the obtained Fe₂O₃/C was first calcined at 500 °C and 700 °C for 2 h and 2 h under an H₂/N₂ (8%:92%) flow, respectively. This resulted in the formation of the spindle-like Fe@C. The S-HFeP@C was finally obtained by the calcination of the Fe@C in the presence of 500 mg NaH₂PO₂ at 350 °C for 3 h at an argon atmosphere. During the calcination, the Fe@C and NaH₂PO₂ were separately placed at the downstream and upstream sides of a porcelain boat, respectively. This well avoided the presence of the side products of Na4P₂O₇ and NaPO₃ generated from the calcination of NaH₂PO₂ in the S-HFeP@C.

1.2 Materials characterizations

XRD patterns were collected on a Bruker D8 ADVANCE using Cu K α (λ =1.54 Å). SEM and TEM images were obtained by scanning electron microscopy (Merlin) and transmission electron microscopy (JEM-2100HR), respectively. Raman spectra were collected on a Lab RAM HR800 with a 514 nm laser source. Thermogravimetric analysis (TGA) was carried out on TGA/DSC 3+ from 30 °C to 800 °C with the ramp rate of 5°C min⁻¹ in air. X-ray photoelectron spectroscopy (XPS) spectra were obtained on ESCALAB 250 (USA). The specific surface areas and pore-size distributions were measured using the Brunauer-Emmett-Teller analyzer of ASAP 2020M (USA), and the sample was degassed under vacuum at 200 °C for 6 h.

1.3 Electrochemical measurements

For the electrochemical performance evaluations, the working electrode was prepared by coating the slurry containing the active material, carbon black and poly(vinylidenedifluoride) at a weight ratio of 7:2:1 on the Cu foil and drying at 80 °C under vacuum for 12 h. The mass loading of the active materials on the Cu foil was well controlled to 1.0 mg cm⁻². The CR2025 coin cells were all assembled in an Ar-filled glovebox for the SIBs, the PIBs and the LIBs. For the SIBs, the sodium foil was used as counter electrode. The electrolyte was NaClO₄ (1.0 M) in propylene carbonate (PC) with addition of fluoroethylene carbonate (FEC) (3 wt.%) and the glass fibers were utilized as a separator. For the PIBs, the potassium foil was used as counter electrode. 0.8 M KPF₆ in EC:DEC (1:1, v:v) was employed as the electrolyte, and the glass fibers were utilized as a separator. For the LIBs, the lithium foil was used as counter electrode. The electrolyte was 1.0 M LiPF₆ dissolved in dimethyl carbonate (DMC)/ethylene carbonate (EC) (1:1, v/v) with additives of fluoroethylene carbonate (3 wt.%) and Celgard membrane was used as the separator. The volumes of the electrolytes for the PIBs and SIBs were ~88.0 µL and for the LIBs was ~66.0 µL, respectively. The cyclic voltammograms (CVs) were collected on an Arbin system. Galvanostatic charge/discharge curves were recorded in a voltage range of 0.01-3.0 V on a Land battery testing system at room temperature. Electrochemical impedance spectroscopy (EIS) was tested on electrochemical workstation between 100,000-0.01 Hz with

an amplitude of 10 mV. For the potassium ion battery, the assembly process is the same as sodium ion battery.

2. SEM and TEM images of the Fe₂O₃@C



Figure S1. (a) SEM, (b) TEM and (c) HRTEM images of the Fe₂O₃@C derived from the Fe-MOF.

3. XRD patterns



Figure S2. XRD patterns of (a) the $Fe_2O_3@C$, (b) the Fe@C, and (c) the $FeP/Fe_2O_3@C$. The standard XRD patterns of Fe_2O_3 , Fe, and FeP are also given.

4. TG analysis of the samples



Figure S3. TG curves of (a) the Fe₂O₃@C and (b) the Fe@C.

The TG curve in **Figure S3a** shows that the relatively weight percentage of Fe_2O_3 in the $Fe_2O_3@C$ is 67.4 wt.% if the physically adsorbed water is not removed. Theoretically, by this weight percentage, the Fe@C with 59.1 wt.% of Fe can be produced when the $Fe_2O_3@C$ is transformed into the Fe@C.

Figure S3b shows the TG curve of the Fe@C. Since the product of the TG analysis of the Fe@C is Fe₂O₃. Based on the relative weight of the production, it can be inferred that the weight percentage of Fe in the Fe@C is 73.0 wt.% if the physically adsorbed water is not removed. This value is much higher than the weight percentage of Fe in the Fe@C calculated based on **Figure S3a** (59.1 wt.%). This finding well demonstrates the depletion of some carbon in the Fe₂O₃@C during its transformation to the Fe@C.

Additionally, based on the TG curve of the Fe@C in **Figure S3b**, it can be inferred that the S-HFeP@C with 80.7 wt.% of FeP can be obtained when the Fe@C is transformed into the S-HFeP@C. This value is close to the experimentally obtained weight percentage of FeP in the S-HFeP@C (77.0 wt.%).

5. Raman spectrum



Figure S4. Raman spectrum of the S-HFeP@C.



Figure S5. (a) Wide-range XPS spectrum of the S-HFeP@C. High-resolution XPS spectra of (b) Fe 2p, (c) P 2p, (d) C 1s and (e) O 1s for the S-HFeP@C.

The wide-range XPS spectrum indicates the co-existence of Fe, P, C and O elements in the S-HFeP@C (**Figure S5a**). The high-resolution XPS spectrum of Fe 2p in **Figure S5b** reveals the presence of four peaks. The peaks at 720.0 and 707.2 eV can be attributed to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ of Fe bonded to P, while the peaks at 727.3 and 712.1 eV are assignable to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ of the oxidized Fe species.^{1, 2} **Figure S5c** gives the high-resolution XPS spectrum of P 2p. It shows the presence of the peaks at 129.6 and 130.5 eV, corresponding to P $2p_{3/2}$ and P $2p_{1/2}$ of P bonded to Fe, respectively.^{1, 2} The broad peak 133.7 eV is attributable to the oxidized P species. The existence of the peaks corresponding to the oxidized Fe and P species can be ascribed to the superficial oxidation of FeP caused by air contact.^{1, 2} **Figure S5d** displays the C 1s spectrum of the S-HFeP@C. It shows the peaks corresponding to C=O, C-O and C=C,

respectively. The predominance of the peaks corresponding to C=C indicates that carbon in the S-HFeP@C mainly exists in the form of the graphitic C. **Figure S5e** shows the O 1s spectrum of the S-HFeP@C. It indicates the presence of two peaks corresponding to C-O and physically adsorbed oxygen, respectively.

7. SEM and TEM images of the FeP/Fe₂O₃@C



Figure S6. (a) SEM, (b) TEM and (c) HRTEM images of the FeP/Fe₂O₃@C synthesized from direct calcination of the Fe₂O₃@C in the presence of NaH₂PO₂.

8. CVs and Discharge/charge voltage profiles



Figure S7. CVs of the S-HFeP@C for (a) SIBs and (b) LIBs. Discharge/charge voltage profiles of the S-HFeP@C for (c) SIBs and (d) LIBs at 0.1 A g^{-1} .

Similar to the case of the PIBs, the CVs of the S-HFeP@C for the SIBs and the LIBs also exhibit the cathodic peaks corresponding to the electrolyte decomposition and SEI film formation in the first cycles (0.77 V vs. Na⁺/Na for the SIBs, **Figure S7a**, and 1.17 V vs. Li⁺/Li for the LIBs, **Figure S7b**). The peaks corresponding to the formation of the intermediate phase M_x FeP (M=Na and Li) caused by the sodium/lithium intercalation reactions can be observed at 1.05 V vs. Na⁺/Na of the SIBs (**Figure S7a**) and 1.52 V vs. Li⁺/Li for the LIBs (**Figure S7b**).

The more distinctness of these peaks, in comparison with that in the PIBs (**Figure 3a**), can be attributed to the reason that the relatively smaller radius of Na⁺ and Li⁺ increases the sodium/lithium intercalation kinetics of the S-HFeP@C. Similarly, the S-HFeP@C exhibits obvious peaks corresponding to M_x FeP (M=Na and Li) to M⁰ and Li₃P (0.44 V vs. Na⁺/Na for the SIBs, **Figure S7a**, and 0.74 V vs. Li⁺/Li for the LIBs, **Figure S7b**). The anodic peaks at 1.85 V vs. Na⁺/Na and 1.12 V vs. Li⁺/Li are attributable to the recovery of MP from Fe⁰ and M₃P (M=Na and Li) through a sodium/lithium de-intercalation reaction. In the subsequent CV cycles, the S-HFeP@C shows the disappearance of the apparent peaks corresponding to the electrolyte decomposition and SEI formation. Meanwhile, the CVs of the S-HFeP@C for both the SIBs and the LIBs show good overlapping from the 5th cycle and on. It well evidences the high reversibility of the S-HFeP@C upon sodiation/desodiation and lithiation/delithiation.



Figure S8. (a) EIS spectra of the S-HFeP@C before and after 100/200/300/500 cycles for the Li storage. The inset shows the equivalent circuit used for the EIS fitting. (b) Linear fits of Z' vs. $\omega^{-1/2}$ at the low frequency region of the straight line in the EIS spectra.

The straight line at the low frequency region of the EIS spectra corresponds to the diffusion of the AM ions into the electrode materials. Analysis of Z' at the low frequency region using Eq. S1 gets the straight line (**Figure S8**), whose slope corresponds to the Warburg impedance coefficient (σ_w). Base on σ_w , the diffusion coefficient of the AM ions in the electrode materials can be obtained.

$$Z' = \mathbf{R}_{s} + \mathbf{R}_{cT} + \sigma_{w} \omega^{-1/2}$$
(S1)
$$D = R^{2} T^{2} / 2 A^{2} n^{4} F^{4} C^{2} \sigma_{w}^{2}$$
(S2)

Where R_s is Ohmic resistance, R_{CT} is charge transfer resistance, ω is the frequency, R is gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (K), A is the electrode area (cm²), n is the number of electrons involved in the redox reaction, C is the shuttle concentration, and F is the Faradiac constant. According to the result shown in **Figure S8**, it can be inferred that the Li diffusion coefficients in the S-HFeP@C are ~3.67×10⁻¹² and ~3.20/3.25/4.06/2.07×10⁻¹² cm² s⁻¹, respectively, before and after 100/200/300/500 cycles.

10. Capacitive contribution



Figure S9. CV curves of the S-HFeP@C with the black area representing the capacitive contributions at the scan rates of (a) 0.1, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8 and (f) 1.0 mV s⁻¹ for LIBs.



Figure S10. CV curves of the S-HFeP@C with the black area representing the capacitive contributions at the scan rates of (a) 0.1, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8 and (f) 1.0 mV s^{-1} for PIBs.



Figure S11. CV curves of the S-HFeP@C with the black area representing the capacitive contributions at the scan rates of (a) 0.1, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8 and (f) 1.0 mV s^{-1} for SIBs.

11. Determination of b values



Figure S12. CVs of the S-HFeP@C for (a) PIBs and (b) SIBs at the different scan rates. Determination of b values using the relationship between $log(i_p)$ and log(v) for (c) PIBs and (d) SIBs.

The relative contributions of the diffusion-controlled redox reactions and capacitive electrochemical processes on the higher specific capacities of the S-HFeP@C are determined by analyzing the CVs using the following equation:

$$i = k_1 v + k_2 v^{1/2}$$
(S3)

Where $k_2 v^{1/2}$ and $k_1 v$ represent the currents in the CVs from the diffusion-controlled redox reactions and capacitive electrochemical processes, respectively.

12. SEM images of the S-HFeP@C before and after cycling



Figure S13. SEM images of the S-HFeP@C before and after 150 cycles of (a, b) potassiation/depotassiation, (c, d) sodiation/desodiation and (e, f) lithiation/delithiation at 1.0 A g^{-1} in the presence of the additives and carbon black.

13. Performance comparison

Table S1. Stable reversible capacity comparison of the S-HFeP@C with other FeP based anodes for PIBs, SIBs and LIBs.

Туре	Electrode	Mass	Current	Cycles	Capacity	Ref.	
	material	loading	density		/ mAh g ⁻¹		
		/ mg cm ⁻²	/ mA g ⁻¹				
PIB	S-HFeP @ C	1	100	90	345	This	
_	(This work)		1000	2000	164	work	
	FeP@CNBs		100	300	205	3	
	3DG/FeP		100	100	327	4	
	h-FeP@3D-PC	0.6-0.7	50	40	283	5	
	FeP/C		50	50	182.6	6	
	FeP@C	0.7-1.2	200	100	163	7	
	N-CNF@FeP 1.0		100	1000	210	8	
LIB	S-HFeP @ C	1	100	100	1368	This	
_	(This work)		1000	800	1107	work	
	FeP@CNBs		500	400	476	3	
	FeP@C	0.7-1.2	100	180	700	7	
	H-FeP@C@GR	1.2	500	300	542	9	
-	M-FeP@C	1.5	250	100	806	10	
	FeP@CNs	1.0-1.2	200	300	837	11	

	FeP@N,C hybrid	0.7	500	300	569	12
	FeP@C nanocages	1.0	500	800	~680	13
	FeP@C/rGO		100	100	949.7	14
	FeP@C-600		100	100	902.4	15
	FeP@C/rGO		1000	500	596	16
SIB	S-HFeP @ C	1	100	120	492	This
	(This work)		1000	480	286	work
	FeP@C	0.7-1.2	100	100	387	7
	H-FeP@C@GR	1.2	100	250	400	9
	M-FeP@C	1.5	100	100	474	10
	FeP@NPC	0.5-0.8	100	1000	391	17
	film					
	FeP NRs/Ti	0.2-0.5	500	1000	207.7	18
	Ni _{2.3} FeP _{3.4} /CNTs	1	1000	120	143.1	19

Table S2. Rate capacity comparison of the S-HFeP@C with other FeP based anodes for PIBs,
SIBs and LIBs.

Туре	Electrode material	Mass loading mg cm ⁻²	0.1 A g ⁻¹	0.2 A g ⁻¹	0.5 A g ⁻¹	1.0 A g ⁻¹	2.0 A g ⁻¹	5.0 A g ⁻¹	10.0 A g ⁻¹	15.0 A g ⁻¹	Ref.
PIB	S-HFeP@C (This work)	1	371	367	301	240	183	124	75		This work
	FeP@CNBs		201	156	101	65	37				3
	3DG/FeP		332	277	195	164	126	101			4
	h-FeP@3D-PC	0.6-0.7	296.9	259.5	204	171.3	140.2				5
	FeP/C		185.82	156.29	112.52	78.69					6
	FeP@C	0.7-1.2	204	188	147	95	59	31			7
	N-CNF@FeP	1.0	195	167							8
	S-HFeP @ C (This work)	1	1208		786	656	625	522	454	412	This work
	FeP@CNBs		608	563	490	441	380				3
	FeP@C	0.7-1.2	760	685	623	579	521				7
	H- FeP@C@GR	1.2	1030	876	755	657	577				9
LIB	M-FeP@C	1.5			694	580	460				10
	FeP@CNs	1.0-1.2		870	733	665	614				11
	FeP@N,C hybrid	0.7	679.82	563.54	467.10	422.32	404.44	331.94			12
	FeP@C/rGO		942.1	862.4	743.2	686.2	601.4				14
	FeP@C-600		825.7	674.9	608.2	556.2	498.7	416.5			15
	FeP/NPCS	1.0	764	619	542	474	385				20
SIB	S-HFeP @ C (This work)	1	426	334	300	280	260	239	222	213	This work
	FeP@C	0.7-1.2	408	366	295	235	173				7
	M-FeP@C	1.5	532	428	331	271	200				10
	FeP NRs/Ti	0.2-0.5	414.7	372.4	300	252.6	196.2				18
	CoP/FeP@PC NF	1.0	424			356		261	213		21
	Ni2.3FeP3.4/CN Ts	1	335.1	218.3	164.1	129.5	101.5	70.8	58.3		19
	YS-Cu-FeP@C	1.0	406	387	342	302	260	188	145		22

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