Electronic supplementary information for

An advanced BiPO₄/super P anode material for high-performance

potassium-ion batteries

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Experimental Section

Synthesis of BiPO₄/SP and BiPO₄ sample

Sodium dihydngen phoshate anhydrous (NaH₂PO₄), glycerol, and Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) were of analytical grade and purchased from Aladdin Reagent Co. Ltd.. First, 20 mmol NaH₂PO₄ and 20 mL glycerol were mixed by magnetic stirring to form solution A, and then 20 mmol Bi(NO₃)₃·5H₂O was dissolved into solution A. 10 mg of super P (SP) was added into 10 mL of distilled water and ultrasound for 1h. The obtained aqueous solution was quickly poured into solution A and stirred for 30 min. Then, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 16 h. Next, the obtained solution was poured out for filtration and washed several times with ethanol and deionized water. Finally, the product was dried at 120 °C overnight and named BiPO₄/SP. The bare BiPO₄ was gained throughout the similar synthesis procedure without adding super P.

Materials characterizations

Scanning electron microscopy (SEM) images were acquired on a Nova Nano SEM 230. Transmission electron microscopy (TEM) images were taken on Tecnai G2F20S-TWIN TMP. X-ray diffraction (XRD) patterns were collected on a Rigaku 3014 with Cu Kα radiation. Raman spectra were obtained on a HR evolution with a 532 nm laser source. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 IR spectrometer. Nitrogen adsorption-desorption isotherm were obtained by using an ASAP 2460 (Micromeritics, USA). X-ray Photoelectron Spectroscopy (XPS) analysis was conducted on an ESCA LAB 250Xi spectrometer using an Al-Kα X-ray source. Thermogravimetric analysis (TA Q500) was performed in air with a heating rate of 10 °C/min in the temperature range of 30–700 °C.

Electrochemical measurements

The active material, acetylene black, and PVDF were mixed with the mass ratio of 70:20:10 to formulate a uniform slurry. Then scullery was paste evenly on the copper foil and vacuum dry at 80°C for 12 h. The loading mass of on the electrode was around 1.2 mg·cm⁻². Then, K metal foil, a glass fiber separator (Whatman GF/D), and anhydrous liquid electrolyte (0.8 M KPF6 in EC: DEC = 1:1 Vol%; 1.0 M KFSI in DME = 100 Vol%;1.0 M KFSI in EC: DEC = 1:1 Vol%; 3.0 M KFSI in DME = 100 Vol%, respectively) were used to assembled CR2032-type half-cells in an argon-filled glove box. The galvanostatic charge/discharge tests were measured with a LAND battery system within the voltage range 0.01 ~ 3.0 V. Moreover, the CV and EIS technologies were implemented utilizing a PARSTAT 2273 electrochemical workstation.



Fig. S1. (a) XPS survey spectrum, (b) O 1s, and (c) P 1s XPS spectra of BiPO₄/SP composite.



Fig. S2. SEM (a) and TEM (b) images of super P.



Fig. S3. N_2 adsorption/desorption isotherms of BiPO₄ and BiPO₄/SP composite.



Fig. S4. The ex-situ XRD patterns of BiPO₄/SP electrode.



Fig. S5. SEM images of BiPO₄/SP electrode after 100 cycles.



Fig. S6. Determination of the b-value using the relationship between peak current and scan rate.



Fig. S7. Capacitive contribution at versus scan rates of BiPO₄ electrode.



Fig. S8. Potential vs. time profile of the BiPO₄/SP composite for a single GITT during discharge process.

The pulse current of 20 mA g⁻¹ was used to discharge/charge for 20 minutes, followed by a relaxation step of 40 minutes. The diffusion coefficient $(D_{\rm K}^+)$ could be reckoned in accordance with Fick's second law as following^{1, 2}:

$$D_{K^{+}} = \frac{4}{\pi\tau} \left(\frac{m_{B}V_{M}}{M_{B}S} \right) \left(\frac{\Delta E_{S}}{\Delta E_{\iota}} \right)^{2}$$
(1)

where M_B, S, m_B, and V_M represent the molar mass, geometric area of the electrode, electrode active mass and molar volume, respectively, while τ , ΔE_s , and ΔE_{τ} can be obtained from Fig. S8.

Material	Voltage window (V)	Capacity (mAh g-	Final	
		1)/current density(mA g-	capacity(mAh g-	Reference
		1)	1)/cycle number	
graphite	0.01-1.5	80/279	100/50	3
RGO	0.01-2	141/200	125/175	4
PG	0.01-2	13.6/1000	75/300	5
HCS	0.01-1.5	136/1395	216/100	6
Sn-C	0.01-2	/	110/30	7
MoS ₂	0.1-2	/	63.8/200	8
K ₂ Ti ₈ O ₁₇	0.01-3	44.2/500	111/50	9
K ₂ Ti ₄ O ₉	0.01-2.5	20/2000	40/30	10
CoTP/SP	0.1-2	27/480	112/200	11
BiPO ₄ /SP	0.01-3	97.1/500	116.0/100	This work

Table S1 Summary of the anodes for PIBs.

REFERENCES

- 1 J. Hu, Y. Xie, M. Yin and Z. Zhang, J. Energy Chem., 2020, 49, 327-334.
- 2 J. Hu, Y. Xie, X. Zhou and Z. Zhang, ACS Appl. Mater. Interfaces, 2020, 12, 1232-1240.
- 3 Z. Jian, W. Luo and X. Ji, J. Am. Chem. Soc., 2015, 137, 11566-11569.
- 4 W. Luo, J. Wan, B. Ozdemir, W. Bao, Y. Chen, J. Dai, H. Lin, Y. Xu, F. Gu, V. Barone and L. Hu, Nano Lett., 2015, **15**, 7671-7677.
- 5 Z. Xing, Y. Qi, Z. Jian and X. Ji, ACS Appl. Mater. Interfaces, 2017, 9, 4343-4351.
- 6 Z. Jian, Z. Xing, C. Bommier, Z. Li and X. Ji, Adv. Energy Mater., 2016, 6, 1501874-1501878.
- 7 I. Sultana, T. Ramireddy, M. M. Rahman, Y. Chen and A. M. Glushenkov, Chem. Commun., 2016, 52, 9279-9282.
- 8 X. Ren, Q. Zhao, W. D. McCulloch and Y. Wu, Nano Res., 2017, 10, 1313-1321.
- 9 J. Han, M. Xu, Y. Niu, G. N. Li, M. Wang, Y. Zhang, M. Jia and C. M. Li, Chem. Commun., 2016, 52, 11274-11276.
- 10 B. Kishore, V. G and N. Munichandraiah, J. Electrochem. Soc., 2016, 163, A2551-A2554.
- 11 C. Fan, M. Zhao, C. Li, C. Wang, B. Cao, X. Chen, Y. Li and J. Li, Electrochim. Acta, 2017, 253, 333-338.