Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2022

# Supporting information

# Bismuth Nanoparticle Embedded in Carbon Skeleton as Anode for High Power Density Potassium-Ion Batteries

Zhiqiang Hao[a,+], Xiaoyan Shi[a,+], Wenqing Zhu[a], Xiaoyue Zhang[a], Zhuo Yang[a], Lin Li[a,*], Zhe Hu[b,*], Qing Zhao[c,*], Shulei Chou[a,*]

[a] *Institute for Carbon Neutralization, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325035, China. E-mail: linli@wzu.edu.cn, chou@wzu.edu.cn*

[b] *College of Materials Science and Engineering, Shenzhen University, Shenzhen 518055, China. E-mail: huzhe@szu.edu.cn*

[c] *Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: zhaoq@nankai.edu.cn*

[+] These authors contributed equally to this work.

# Table of Contents

# Experimental Section

## Materials

Potassium citrate tribasic monohydrate ($K_3C_6H_5O_7·H_2O$, analytically pure) was obtained from Sinopharm Chemical Reagent Co., Ltd. Potassium ferrocyanide trihydrate ($K_4Fe(CN)_6·3H_2O$, ≥ 99.5%) was purchased from Aladdin. Nickel chloride hexahydrate ($NiCl_2·6H_2O$, ≥ 98.0%) was obtained from Tianjin Guanfu Fine Chemical Research Institute. Bismuth citrate (≥ 98.0%) was purchased from damas-beta.

## Synthesis of Bi@C composite sample

The Bi@C composite was prepared by annealing 2 g bismuth citrate at 900 $^{o}C$ for 2 h in an argon atmosphere with a heating rate of 3 $^{o}C$ min$^{-1}$. After cooling to room temperature (under argon atmosphere), the obtained black powder of Bi@C composite was collected.

## Synthesis of KNiHCF composite sample

The KNiHCF was synthesized according to our previous literature.[1] First, $K_3C_6H_5O_7·H_2O$ (4 mmol) and $NiCl_2·6H_2O$ (0.2 g) were added to deionized water (50 mL) with stirring for a few minutes to obtain the solution A. $K_4Fe(CN)_6·3H_2O$ (1 mmol) was added in another deionized water (50 mL) with stirring for few minutes to obtain the solution B. The solution B was added dropwise into solution A under stirring for 5 min. Subsequently, the mixture was aged for 48 h to get precipitate. The precipitate was obtained by centrifugation and washed with deionized water three times. In the end, the wet KNiHCF powder was dried in a vacuum oven at 80 $^{o}C$ for 12 h.

## Material characterization

XRD patterns were acquired on Rigaku SmartLab with Cu $K_{\alpha}$ radiation. Raman spectra were recorded on a Thermo Fisher Scientific DXR Raman microscope using 532 nm excitation. XPS spectra were collected on Perkin Elmer PHI 1600 ESCA. SEM and TEM were performed on JEOL JSM-7500F and

Taols F200X G2 microscopes, respectively. The $N_2$ adsorption-desorption isotherm was investigated using a Brunauer-Emmett-Teller analyzer (BELSORP-mini II). TGA was evaluated by Netzsch STA 449 F3 Jupiter analyzer. The Bi content of the Bi@C composite was calculated by the following equation:[2]

$$Bi(wt\%) = 100 \times \frac{2 \times molecular\ weight\ of\ Bi}{molecular\ weight\ of\ Bi_2O_3} \times \frac{final\ weight\ of\ Bi_2O_3}{initial\ weight\ of\ Bi@C}$$

**Electrochemical characterization**

Electrochemical tests of the Bi@C composite electrodes and KNiHCF//Bi@C full cell were performed with CR2032 coin-type cells, which were assembled in an Ar-filled glove box. The Bi@C composite electrodes for the electrochemical test were prepared by mixing 70 wt% Bi@C composite powder, 20 wt% Ketjen Black, 10 wt% polyvinylidene fluoride, and the mass loading of the Bi@C composite is about 0.6-0.7 mg $cm^{-2}$. The mixture was coated on Cu current collector and dried at 80 $^{o}C$ for 12 h in a vacuum oven. The Bi@C composite electrodes for in situ XRD test was fabricated by rolling a mixture of 70 wt% Bi@C composite powder, 20 wt% Ketjen Black, and 10 wt% polytetrafluoroethylene into a thin film. The film was pressed onto a stainless-steel mesh and dried in a vacuum oven overnight at 80 $^{o}C$ for 12h. The fabricated method of KNiHCF electrodes was similar to the Bi@C composite electrodes for *in situ* XRD test. The mass ratios of the KNiHCF, super P, and polytetrafluoroethylene are 6:3:1. Glass fiber was applied as separators. 1 M $KPF_6$ in DEGDME or 0.8 M $KPF_6$ in EC/DEC (1:1, v/v) were used as electrolytes. For the half cell, potassium metal was used as the anode. For the full cell, the mass ratio between KNiHCF and Bi@C composite is ~3.6-3.8. CVs were conducted on the CHI660E electrochemical workstation. Galvanostatic charge/discharge data were tested by LAND-CT2001A battery-testing instrument. EIS test was performed on a CHI660E electrochemical workstation with an AC voltage of 5 mV amplitude in the frequency ranging from 100 kHz to 100 mHz. The GITT data were collected at a current density of 200 mA $g^{-1}$ for 5min and then followed by a rest of 25 min.

**First-principles calculations**

The first principle calculations were performed using the Vienna ab-initio Simulation Package (VASP) based on the density functional theory (DFT).[3] The projector-augmented wave (PAW) was used for the electron-ion interactions.[4] The generalized gradient approximation (GGA) functional of Perdew, Burke, and Enzerhof (PBE) was applied to evaluate the exchange-correlation energy.[5] For all calculations, cut-off energy of 500 eV was set. A Gamma centered 1 x 1 x 1 k-point grid was applied for molecular dynamics. The energy convergence tolerance was set to below $1 \times 10^{-5}$ eV/atom. The canonical (NVT) ensemble is used for Ab initio molecular dynamics (AIMD) simulations at 700K.

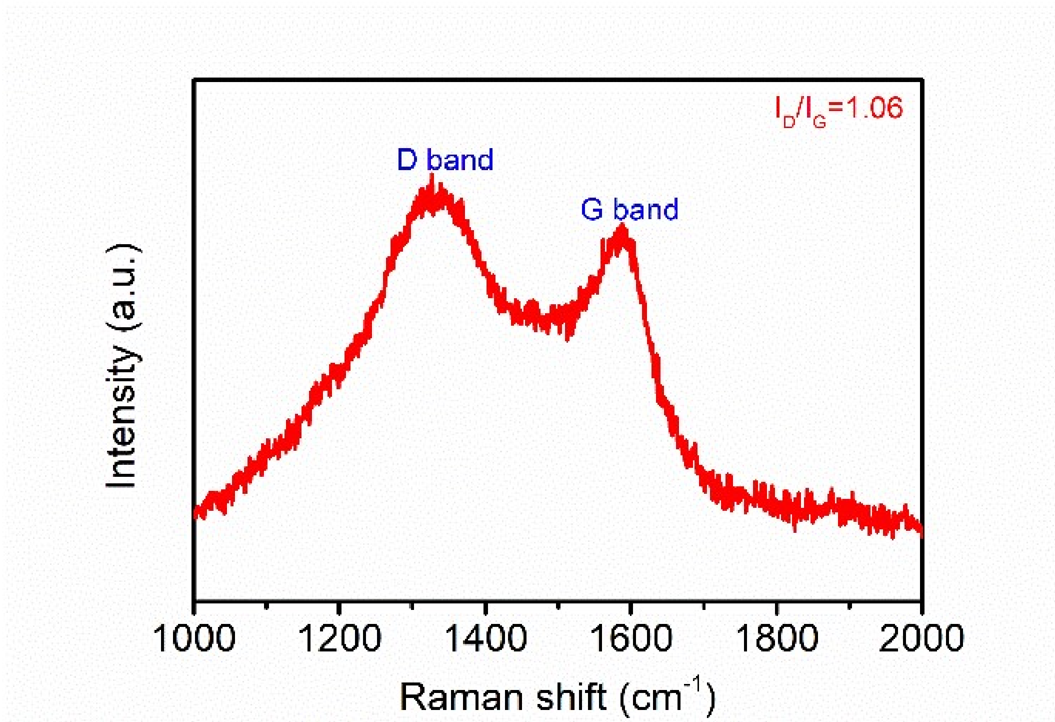


**Fig. S1.** Raman spectrum of Bi@C composite.

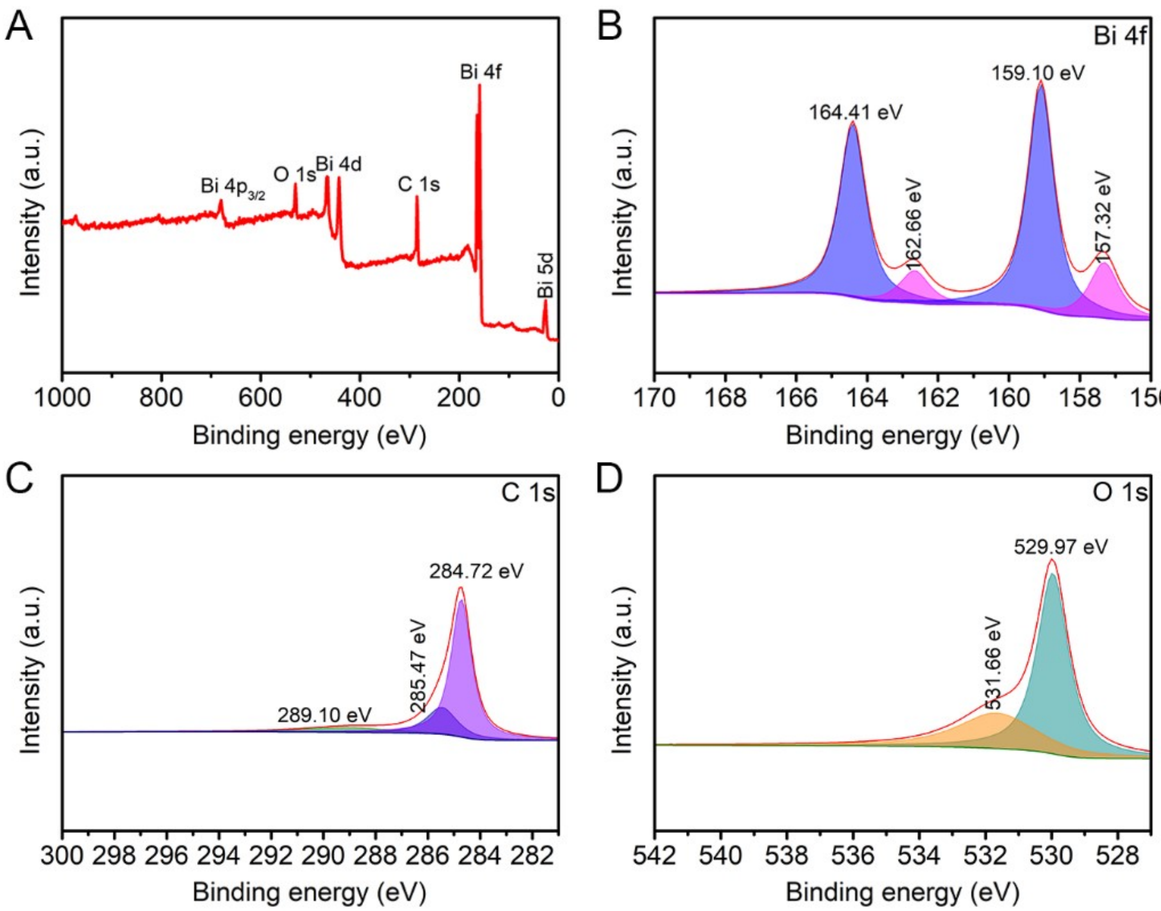


**Fig. S2.** (A) Full survey. (B) High-resolution Bi 4f. (C) High-resolution C 1s. (D) High-resolution O 1s.

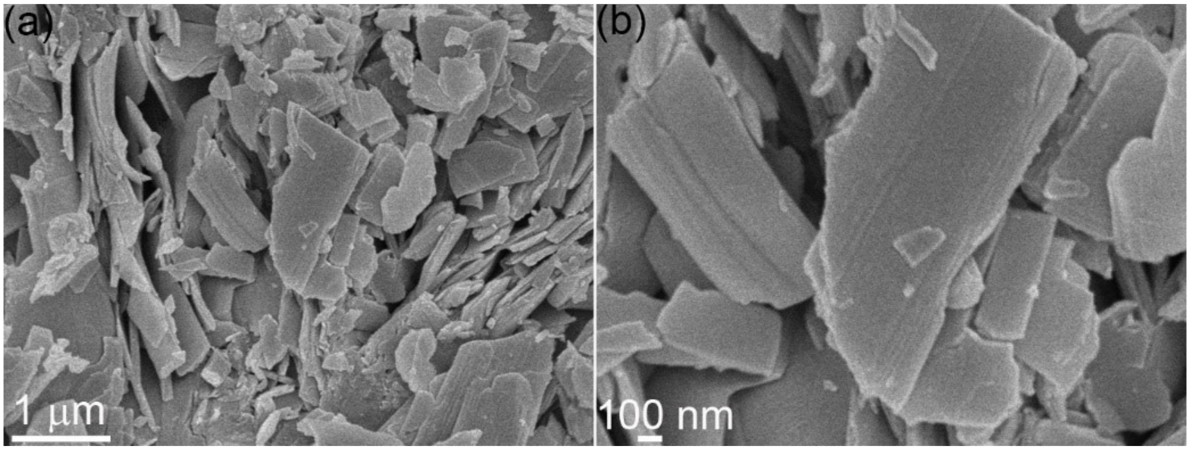


**Fig. S3.** SEM images of bismuth citrate.

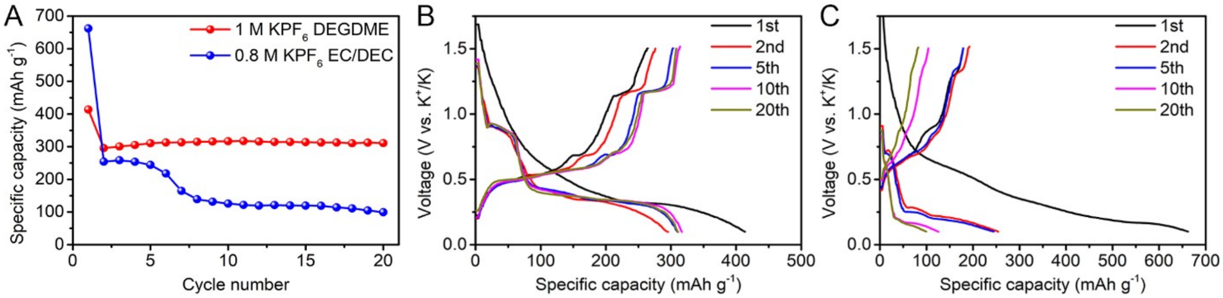


**Fig. S4.** (A) Cycling performance of Bi@C composites electrodes in the two electrolytes. Selected charge/discharge curves of Bi@C composites in (B) 1 M $KPF_6$ DEGDME and (C) 0.8 M $KPF_6$ EC/DEC.

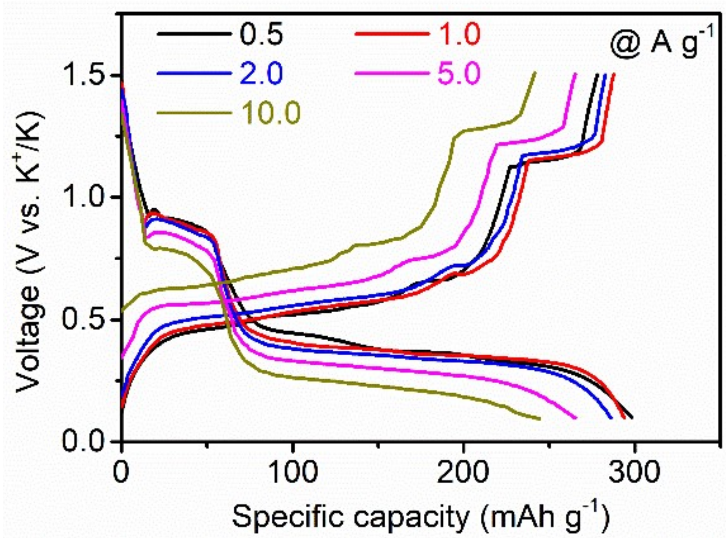


**Fig. S5.** The charge/discharge curves of the Bi@C composites electrode at different current densities.

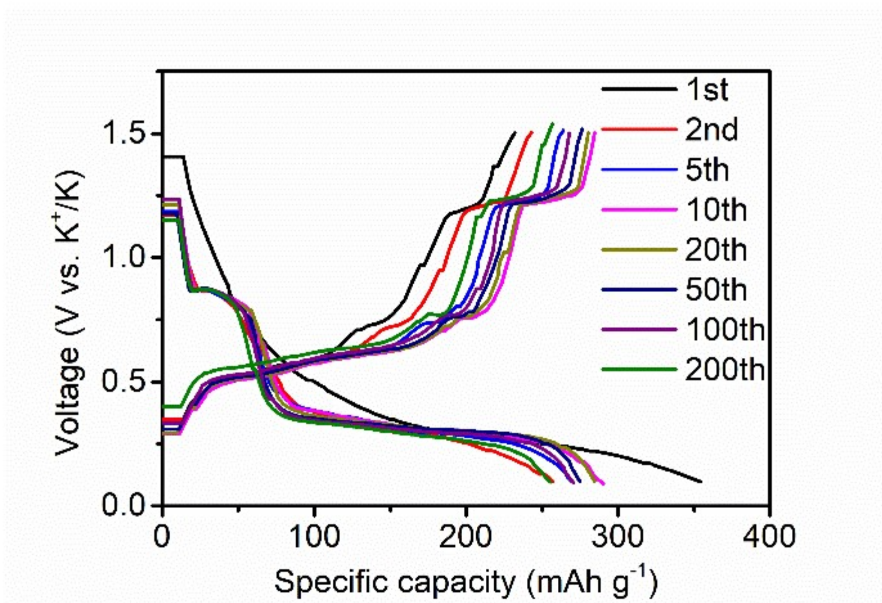


**Fig. S6.** Selected charge/discharge curves of the Bi@C composite electrode at a current density of 5.0 A $g^{-1}$.

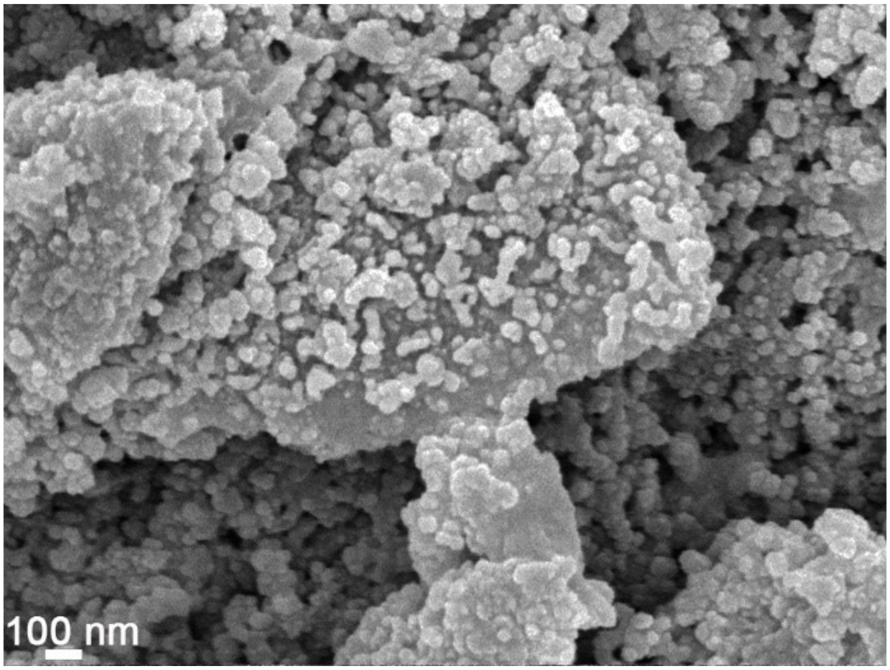


**Fig. S7.** SEM image of the Bi@C composite electrode after 20 cycles.

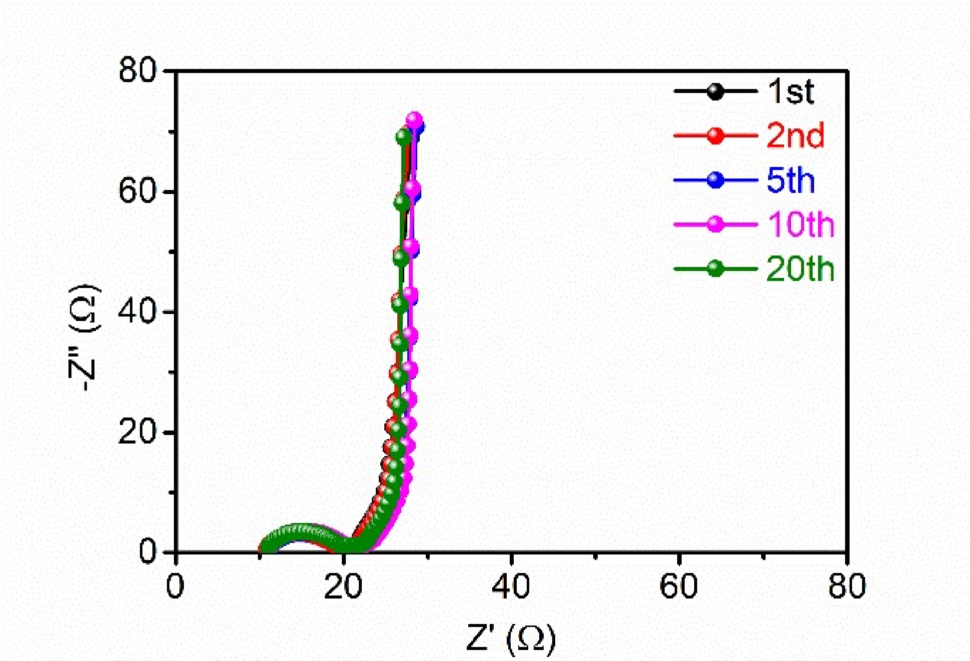


**Fig. S8.** Electrochemical impedance spectroscopy profiles of the Bi@C composite electrode**.**

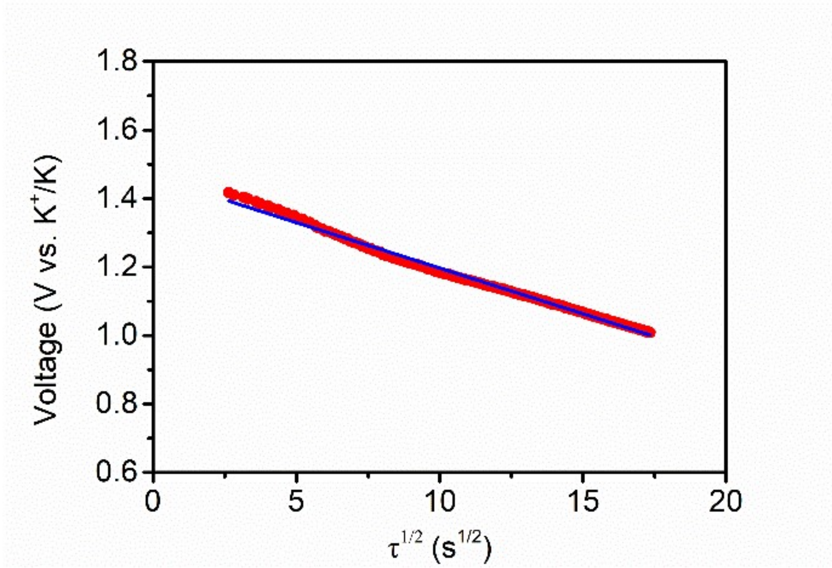


**Fig. S9.** Line relationship between the voltage ($E$) and $\sqrt{\tau}$ in GITT test.

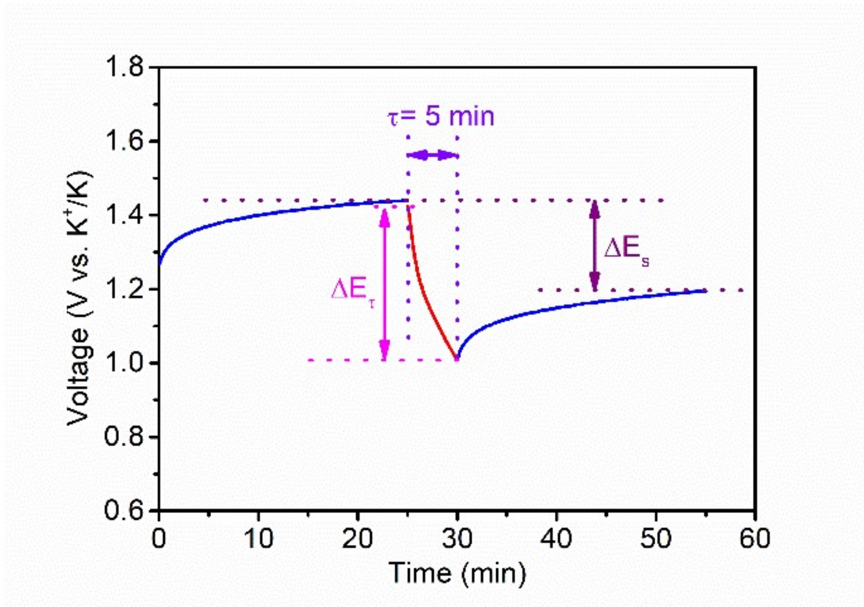


**Fig. S10.** The voltage versus time curve for a single titration of GITT.

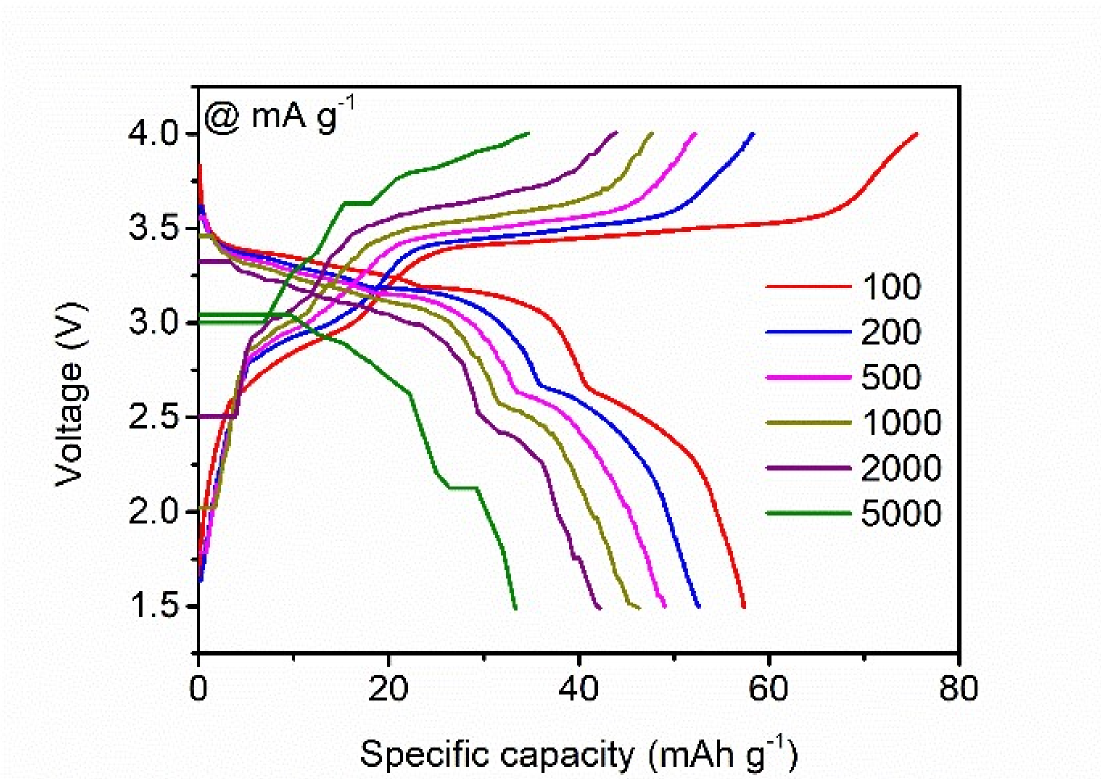


**Fig. S11.** The charge/discharge curves of KNiHCF//Bi@C full cell at various current densities.

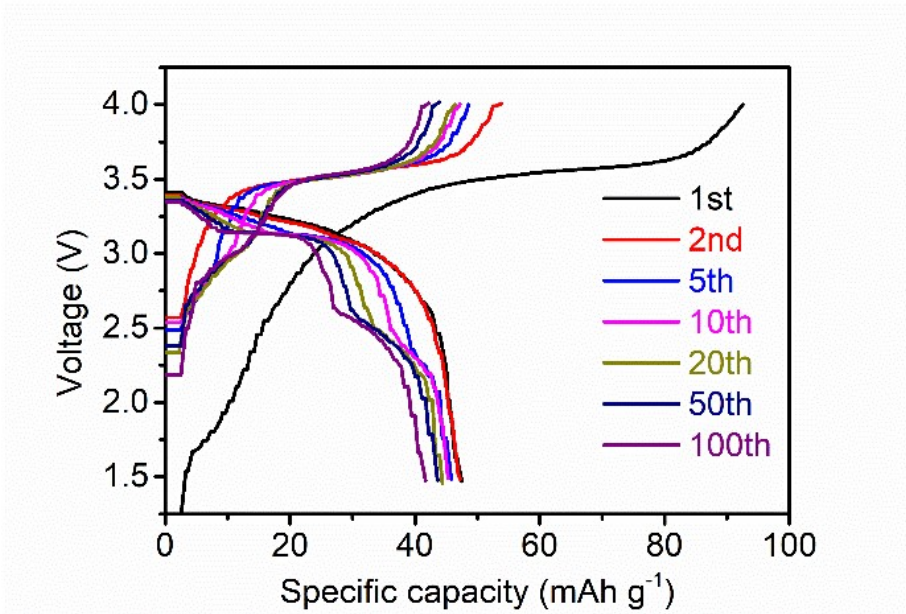


**Fig. S12.** The selected charge/discharge curves of KNiHCF//Bi@C full cell at a current density of 1000 mA $g^{-1}$.

**Table S1.** Summary of energy density and power density of KNiHCF//Bi@C full cell at different current densities.

| Current density (mA $g^{-1}$) | 100 | 200 | 500 | 1000 | 2000 | 5000 |
|---|---|---|---|---|---|---|
| The energy density (Wh $kg^{-1}$) | 135.73 | 121.25 | 111.60 | 103.38 | 92.94 | 68.64 |
| Power density (W $kg^{-1}$) | 235.93 | 461.91 | 1134.95 | 2228.49 | 4402.26 | 10296.64 |

**Reference**

1 L. Li, Z. Hu, Y. Lu, C. Wang, Q. Zhang, S. Zhao, J. Peng, K. Zhang, S. L. Chou, J. Chen, *Angew. Chem. Int. Ed.,* 2021, **60**, 13050.

2 P. Xiong, P. Bai, A. Li, B. Li, M. Cheng, Y. Chen, S. Huang, Q. Jiang, X. H. Bu, Y. Xu, *Adv. Mater.,* 2019, **31**, 1904771.

3 G. Kresse, Furthmüller J., *Comp. Mater. Sci.,* 1996, **6**, 15.

4 P. E. Blochl, *Phys. Rev. B,* 1994, **50**, 17953.

5 J. P. Perdew, Yue, W., *Phys. Rev. B,* 1986*,* **33**, 8800.