

Supplementary Information

Core-shell structured $\text{Mn}_2\text{SnO}_4@\text{Void}@C$ as stable anode material for lithium-ion batteries with long cycle life

Yuanlin Tong^a, Xiangyang Xu^{a,b,*}, Yanru Liu^{a,c}, Yunfei Yao^a, Dongsheng Chen^a and Chenyu Huang^a

^a School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

^b Hunan Key Laboratory of Mineral Materials and Applications, Changsha 410083, China

^c Tsinghua-Berkeley Shenzhen Institute & Institute of Materials Research, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China

Figure Captions:

Fig. S1 XRD pattern of $\text{MnSn}(\text{OH})_6$

Fig. S2 SEM image of $\text{MnSn}(\text{OH})_6$

Fig. S3 TEM images of $\text{MnSn}(\text{OH})_6@\text{SiO}_2$

Fig. S4 TEM images of $\text{Mn}_2\text{SnO}_4@\text{SiO}_2@C$

Fig. S5 TEM images of $\text{Mn}_2\text{SnO}_4@C$

Fig. S6 High-resolution XPS spectra of C 1s peak for $\text{Mn}_2\text{SnO}_4@C$ and $\text{Mn}_2\text{SnO}_4@\text{Void}@C$

Fig. S7 Galvanostatic discharge/charge curves of $\text{Mn}_2\text{SnO}_4@C$ (a) and Mn_2SnO_4 (b) for selected cycles at 100 mA g⁻¹

Fig. S8 Cyclic voltammetry (CV) curves of $\text{Mn}_2\text{SnO}_4@C$ (a) and Mn_2SnO_4 (b) at a scan rate of 0.1 mV s⁻¹

Fig. S9 Corresponding relationships between $\omega^{-1/2}$ and Z' at a low frequency of Mn_2SnO_4 , $\text{Mn}_2\text{SnO}_4@C$ and $\text{Mn}_2\text{SnO}_4@\text{Void}@C$

Fig. S10 SEM images of cross-sectional morphology for $\text{Mn}_2\text{SnO}_4@\text{Void}@C$ electrode after 0 (a) and 1000 (b) discharge-charge cycles

Fig. S11 SEM images of surface morphology for Mn_2SnO_4 , $\text{Mn}_2\text{SnO}_4@C$ and $\text{Mn}_2\text{SnO}_4@\text{Void}@C$ electrode after 0 (a, b and c, respectively) and 1000 (e, d and f, respectively) charge-discharge cycles at 1.0 A g⁻¹

Table Captions :

Table S1. Vibration types of absorption peaks on FTIR spectra

Table S2. Fitted EIS results of raw materials

Table S3. Electrochemical performance comparison of $\text{Mn}_2\text{SnO}_4@\text{Void}@C$ and other Sn-based materials for lithium-ion half cell

* Corresponding author: School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

E-mail address: xuxiangyang@csu.edu.cn

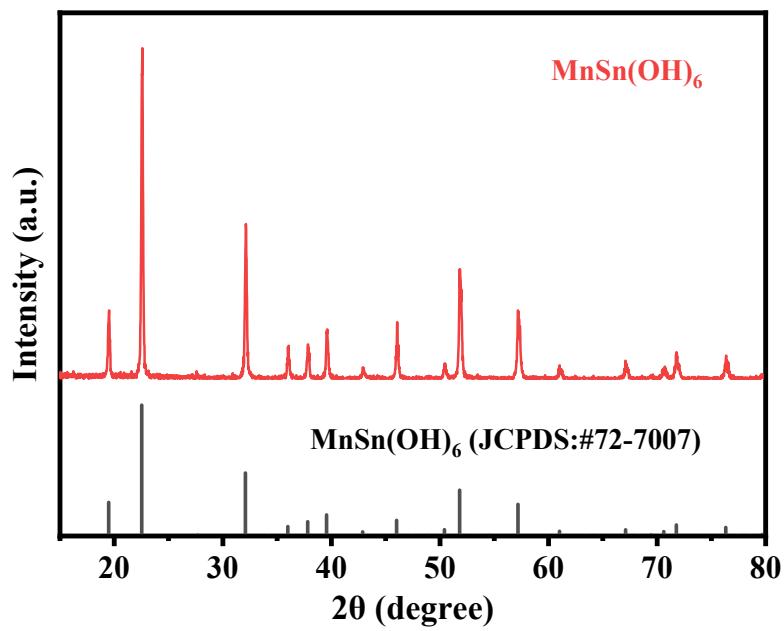


Fig. S1 XRD pattern of MnSn(OH)_6 precursor

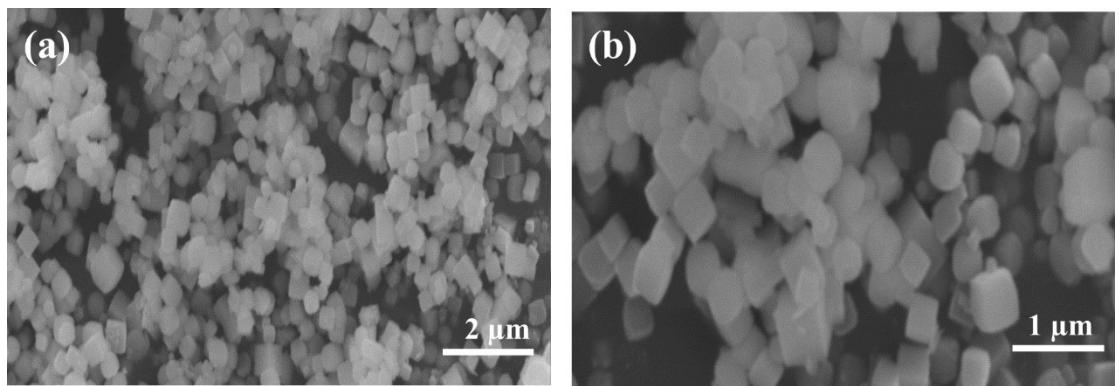


Fig.S2 SEM images of $\text{MnSn}(\text{OH})_6$

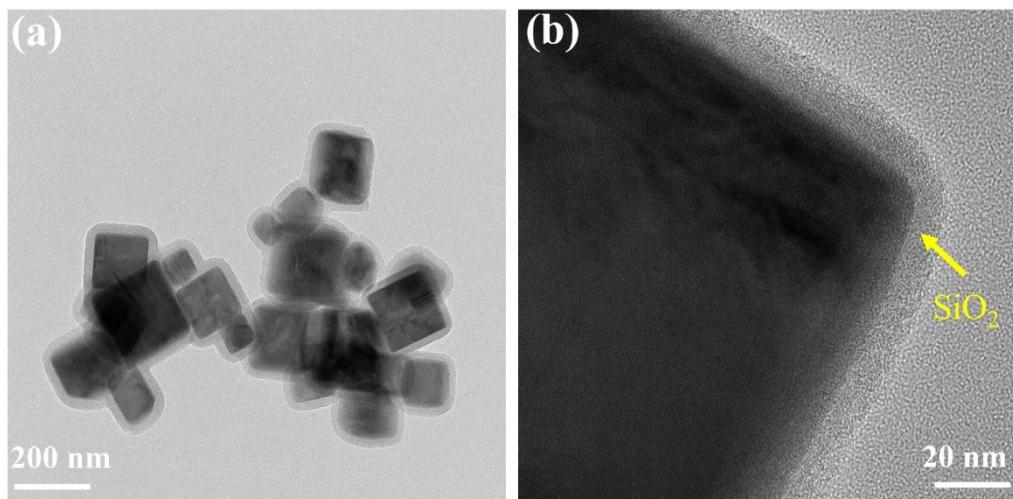


Fig.S3 TEM images of $\text{MnSn}(\text{OH})_6@\text{SiO}_2$

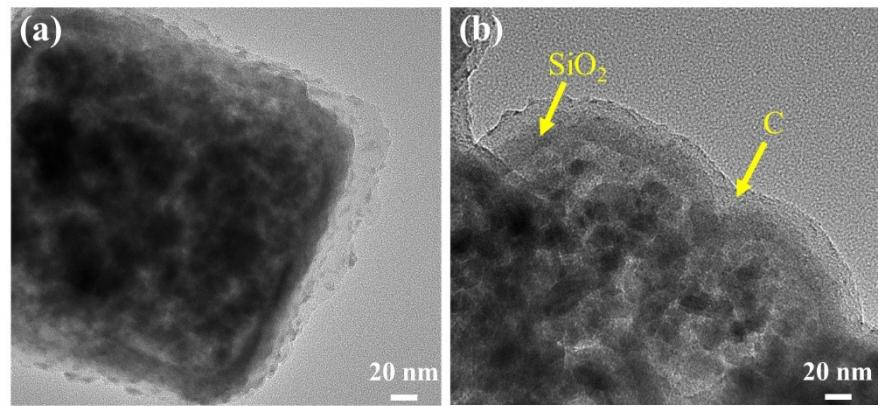


Fig. S4 TEM images of $\text{Mn}_2\text{SnO}_4@\text{SiO}_2@\text{C}$

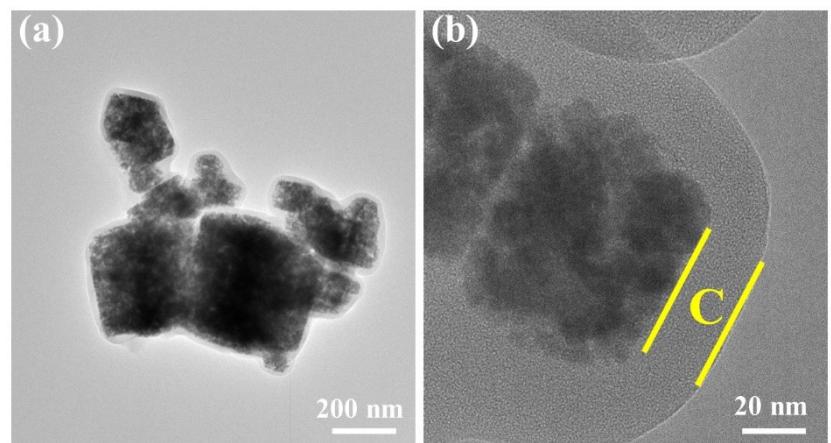


Fig. S5 TEM images of $\text{Mn}_2\text{SnO}_4@\text{C}$

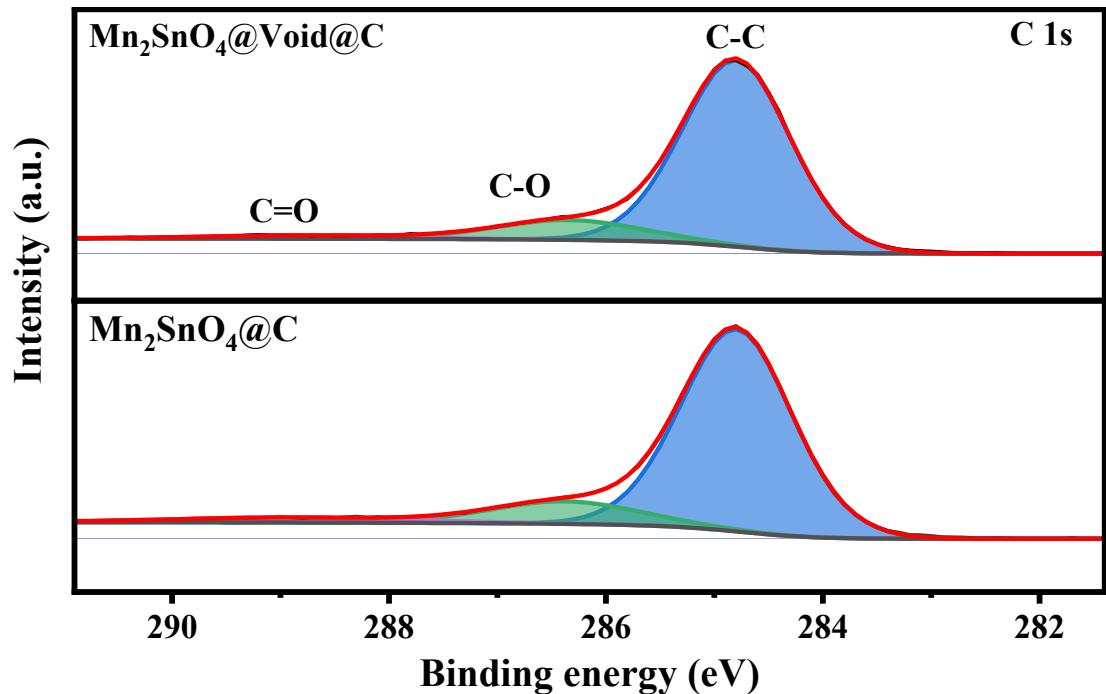


Fig. S6 High-resolution XPS spectra of C 1s peak for $\text{Mn}_2\text{SnO}_4@C$ and $\text{Mn}_2\text{SnO}_4@\text{Void}@C$

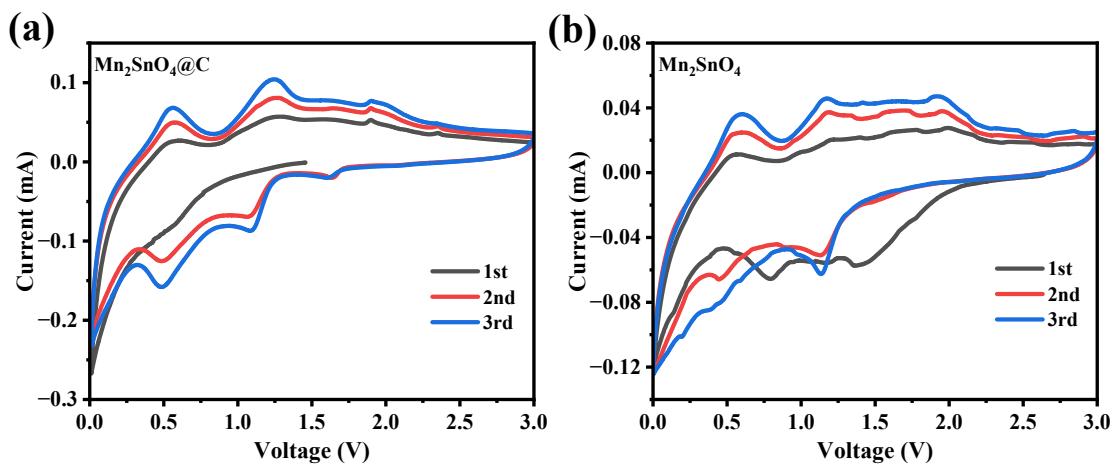


Fig. S7 Cyclic voltammetry (CV) curves of $\text{Mn}_2\text{SnO}_4@\text{C}$ (a) and Mn_2SnO_4 (b) at a scan rate of 0.1 mV s^{-1}

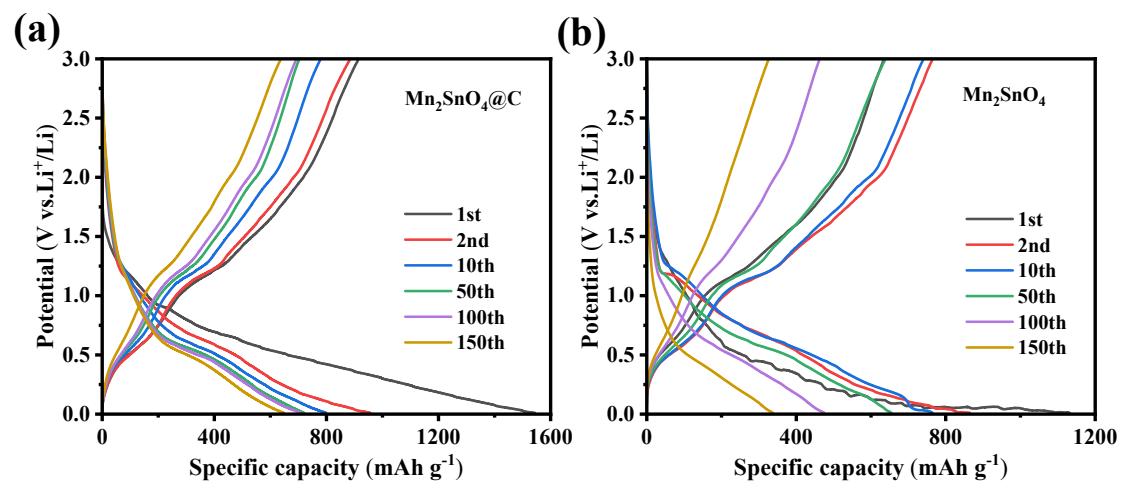


Fig. S8 Galvanostatic discharge/charge curves of $\text{Mn}_2\text{SnO}_4@\text{C}$ (a) and Mn_2SnO_4 (b) for selected cycles at 100 mA g^{-1}

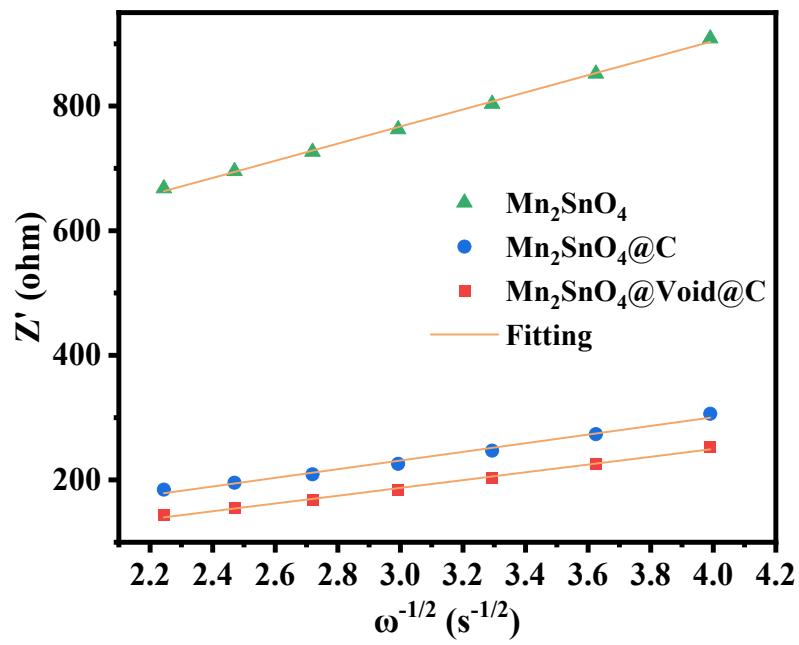


Fig. S9 Corresponding relationships between $\omega^{-1/2}$ and Z' at low frequency of Mn_2SnO_4 , $\text{Mn}_2\text{SnO}_4@\text{C}$ and $\text{Mn}_2\text{SnO}_4@\text{Void}@\text{C}$

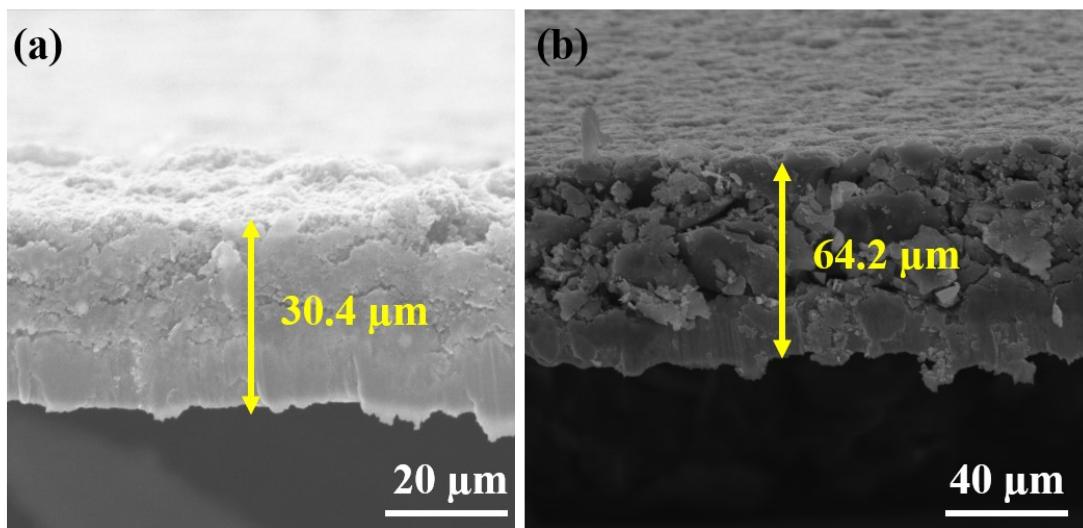


Fig. S10 SEM images of cross-sectional morphology for Mn_2SnO_4 @Void@C electrode after 0 (a) and 1000 (b) discharge-charge cycles

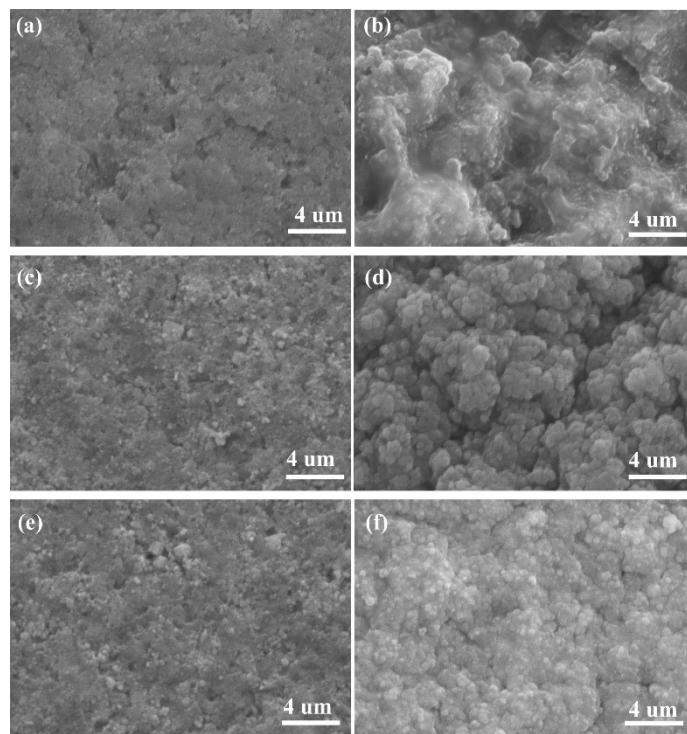


Fig. S11. SEM images of surface morphology for Mn₂SnO₄, Mn₂SnO₄@C and Mn₂SnO₄@Void@C electrode after 0 (a, b and c, respectively) and 1000 (e, d and f, respectively) charge-discharge cycles at 1000 mA g⁻¹

Table S1 Vibration types of absorption peaks on FTIR spectra

| Wavenumber (cm ⁻¹) | Chemical bond | Vibration type |
|---------------------------------|---------------|----------------------|
| 499 | Mn-O-Mn | bending vibration |
| 541 | Sn-O-Sn | bending vibration |
| 887 | C-H | bending vibration |
| 1257 | C-O | stretching vibration |
| 1598 | C=C | stretching vibration |
| 3372 | -OH | stretching vibration |

Table S2 Fitted EIS results of as-prepared materials

| Sample | Rs (Ω) | Rct (Ω) | CPEct-T (μF) | CPEct-P (μF) |
|--|-----------------|------------------|---------------------------|---------------------------|
| Mn_2SnO_4 | 6.021 | 353.3 | 1.6325E-5 | 0.79427 |
| $\text{Mn}_2\text{SnO}_4@\text{C}$ | 3.265 | 90.69 | 1.0669E-5 | 0.86296 |
| $\text{Mn}_2\text{SnO}_4@\text{Void}@\text{C}$ | 4.04 | 51.35 | 1.4388E-5 | 0.82645 |

Table S3 Electrochemical performance comparison of Mn₂SnO₄@Void@C and other Sn-based materials for lithium-ion half cell

| Materials | Current density (A g ⁻¹) | Cycles | Reversible capacity (mAh g ⁻¹) | References |
|---|---|--------|---|--------------|
| Sn@Mn ₂ SnO ₄ -NC | 0.1 | 100 | 1039.5 | ¹ |
| Mn ₂ SnO ₄ @Carbon Nanotube | 0.1 | 100 | 611 | ² |
| Mn ₂ SnO ₄ /Sn/C Cubes | 0.5 | 100 | 908 | ³ |
| Mn ₂ SnO ₄ @RGO | 0.1 | 100 | 542 | ⁴ |
| Flake-like Mn ₂ SnO ₄ /C | 2.0 | 100 | 428 | ⁵ |
| SnO ₂ /Mn ₂ SnO ₄ @C | 0.2 | 100 | 1293 | ⁶ |
| Bouquet-Like Mn ₂ SnO ₄ @GS | 0.4 | 200 | 1070 | ⁷ |
| | 0.1 | 150 | 783.1 | |
| Mn ₂ SnO ₄ @Void@C | 1.0 | 1000 | 553.3 | This work |
| | 2.0 | 400 | 419.6 | |

Supplementary Information References:

1. S. Wan, Q. Liu, M. Cheng, Y. Chen and H. Chen, *ACS Appl. Mater. Interfaces*, 2021, **13**, 38278-38288.
2. G. N. Suresh babu and N. Kalaiselvi, *J. Alloys Compd.*, 2021, **889**, 161679.
3. K. Liang, T. Y. Cheang, T. Wen, X. Xie, X. Zhou, Z. W. Zhao, C. C. Shen, N. Jiang and A. W. Xu, *The J. Phys. Chem. C*, 2016, **120**, 3669-3676.
4. L. Cui, X. Li, C. Yin, J. Wang, S. Li, Q. Zhang and S. Kang, *Dalton Trans.*, 2019, **48**, 504-511.
5. X. Shi, X. Lin, S. Liu, A. Li, X. Chen, J. Zhou, Z. Ma and H. Song, *Chem. Eng. J.*, 2019, **372**, 269-276.
6. J. Tian, L. Yang, L. Zha, R. Wang, S. Huang, G. Xu, T. Wei, H. Li, J. Cao and X. Wei, *J. Power Sources*, 2021, **506**, 230243.
7. W. U. Rehman, Y. Xu, X. Sun, I. Ullah, Y. Zhang and L. Li, *ACS Appl. Mater. Interfaces*, 2018, **10**, 17963-17972.