

Supplementary Information

Binder-Free Metal Fibril-Supported Fe₂O₃ Anode for High- Performance Lithium-Ion Batteries

Dong Jin Lee,^{a,‡} Jaecheol Choi,^{b,‡} Myung-Hyun Ryou^b, Chang-Hyeon Kim^c, Yong Min Lee^{b,*} and Jung-Ki Park^{a,*}

^a Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea.

^b Department of Chemical and Biological Engineering, Hanbat National University, Daejeon, 305-719, Republic of Korea.

^c Shine Co. Ltd., 192-12, Busan, 614-865, Republic of Korea.

Email: jungpark@kaist.ac.kr, yongmin.lee@hanbat.ac.kr

‡ These authors contributed equally to this work

Experimental Section

The fabrication of Fe₂O₃/SF was carried out by using RF magnetron sputtering method. The base vacuum pressure of the stainless-steel chamber was 2.0×10^{-5} Torr, and the working pressure was 7.0×10^{-3} Torr of Ar (99.999%). The target used was Fe₂O₃ (99.99%) and the distance between the target and the substrate was 7 cm. The Fe₂O₃ target was pre-sputtered for 10 min at 200 W to remove the contaminants on the surface before deposition on the SF substrates (Shine co. Ltd., Korea). The deposition was conducted for 20 min at 25 °C on both side of the SF substrate at 200 W. Copper foil was used for comparative study of different substrate structure and deposition conditions are same as the Fe₂O₃/SF cases. The surface morphology and cross-sectional image of the samples were examined using field emission scanning electron microscope (FE-SEM, S4800, Hitachi). In order to prepare a cross-sectional specimen of Fe₂O₃/SF electrode, it was cut by an argon-ion beam polisher (E3500, Hitachi) at a constant power of 2.1 W (6 kV and 0.35 mA) under vacuum ($< 2.0 \times 10^{-4}$ Pa). The surface chemical composition of Fe₂O₃/SF electrodes were investigated by X-ray photoelectron spectroscopy (XPS, Thermo VG scientific).

The 2032 coin type half cells were prepared by assembling the electrodes (Fe₂O₃/SF or Fe₂O₃/Cu foil), Li metal as counter electrodes, polyethylene separator (Asahi-Kasai) that was soaked with the liquid electrolyte (1 M LiPF₆ in EC/DEC (50/50 by vol%)) containing 5 wt.% of fluoroethylene carbonate (PANAX ETEC) in an Ar filled glove box. The H₂O content of the electrolyte was less than 10 ppm. The loading density of active material, Fe₂O₃, was 0.4 mg cm⁻². The assembled unit cells were cycled at various constant current rates from 40 mA g⁻¹ to 16000 mA g⁻¹ in the potential range of 0.05 - 3.0 V (vs. Li/Li⁺) using a WBCS 3000 battery tester (Wonatech) at 25 °C. Electrochemical impedance spectroscopy (EIS)

measurements were conducted using the VSP impedance analyzer (Bio-logic SAS) over a frequency range of 0.05 Hz to 1 MHz at an amplitude of 10 mV.

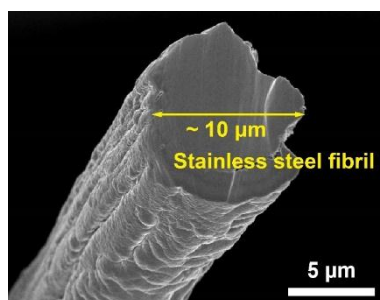


Figure S1. A cross-sectional SEM image of pristine stainless steel fibrils (SF) before Fe_2O_3 sputtering.

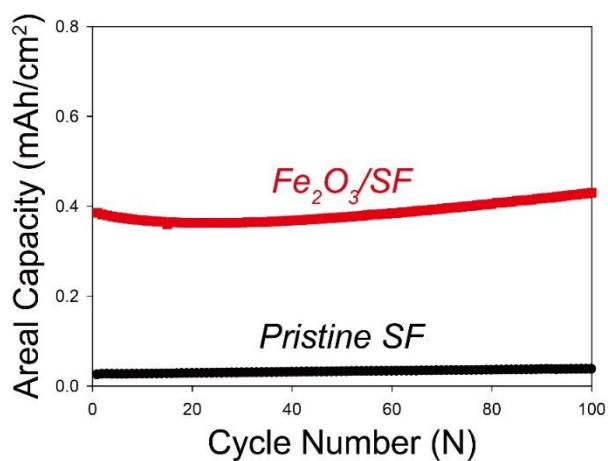


Figure S2. Cycling performance of $\text{Fe}_2\text{O}_3/\text{SF}$ and pristine SF at 0.16 mA/cm^2 .

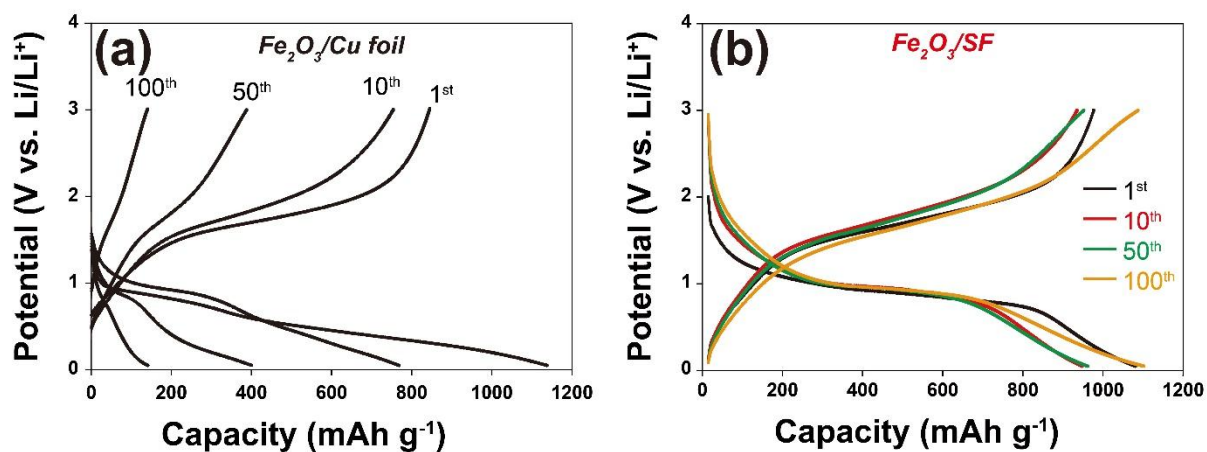


Figure S3. Potential profiles of (a) the $\text{Fe}_2\text{O}_3/\text{Cu}$ foil and (b) the $\text{Fe}_2\text{O}_3/\text{SF}$ electrode (the numbers indicate cycle number) at 400 mA g^{-1} .

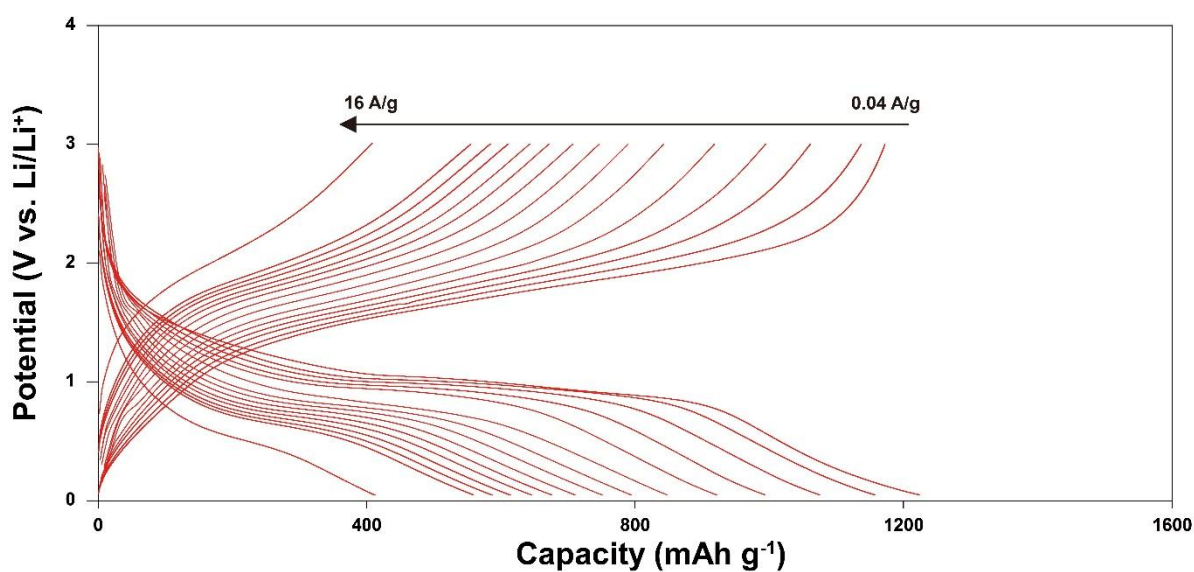


Figure S4. Potential profiles of the $\text{Fe}_2\text{O}_3/\text{SF}$ electrode measured at a series of current rates.

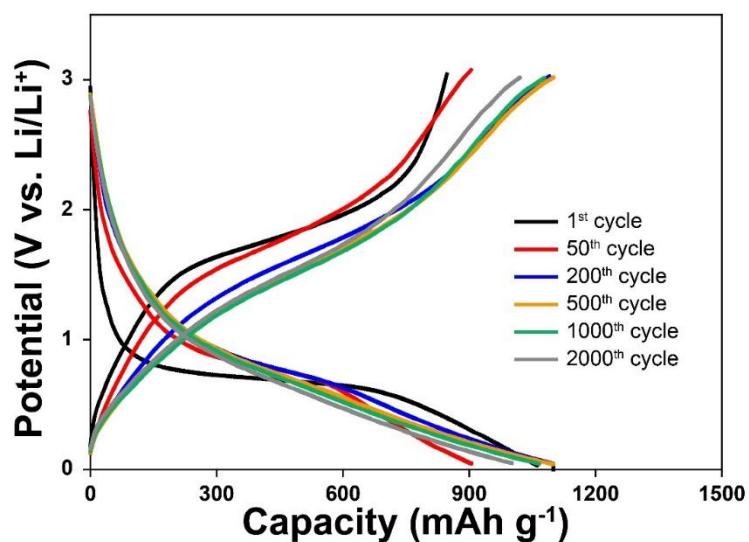


Figure S5. Potential profiles at 8000 mA g^{-1} of the $\text{Fe}_2\text{O}_3/\text{SF}$ electrode (the numbers indicate cycle number).

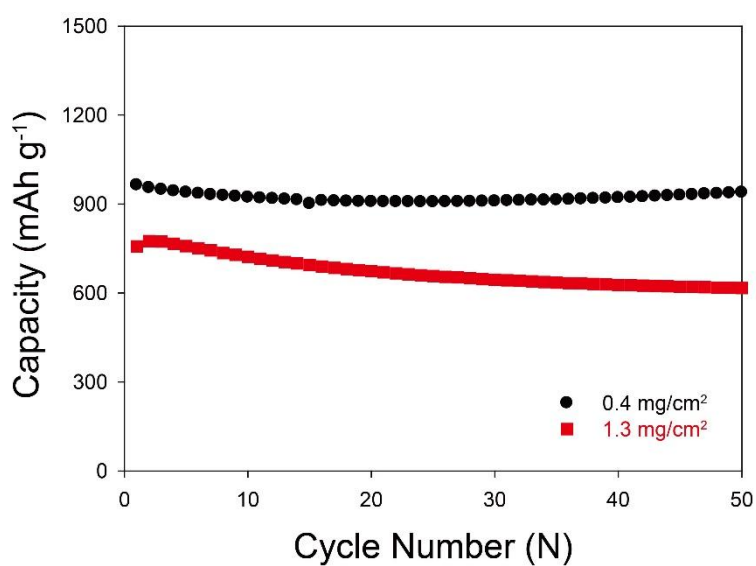


Figure. S6. Cycling performances of the unit cells using $\text{Fe}_2\text{O}_3/\text{SF}$ based on different mass loadings of Fe_2O_3 .

Reference	Anode Materials	Rate Capability (mAh/g)	Reversible Capacity (mAh/g)
In this work	Fe ₂ O ₃ /SF	~710 @ 4 A/g	~ 1000 @ 8 A/g after 2000 cycles
		~560 @ 8 A/g	
		~420 @ 16 A/g	
#1	α-Fe ₂ O ₃ /RGO composite	~332 @ 10 A/g	~ 516 @ 3 A/g after 150 cycles
#2	Mesoporous Fe ₂ O ₃	~424 @ 10 A/g	~ 911 @ 0.2 A/g after 50 cycles
#3	C/α-Fe ₂ O ₃ nanotube arrays	~250 @ 8 A/g	~ 659 @ 0.1 A/g after 150 cycles
#4	Hierarchical Hollow Spheres of Fe ₂ O ₃ @PANI	~724 @ 10 A/g	~ 893 @ 0.1 A/g after 100 cycles
#5	α-Fe ₂ O ₃ xerogel	~280 @ 10 A/g	~ 600 @ 5 A/g after 1000 cycles
#6	Fe ₂ O ₃ -GNS	~633 @ 5 A/g	~ 633 @ 5 A/g after 100 cycles
#7	Fe ₂ O ₃ /graphene	~420 at 5 A/g	~ 800 at 0.2 A/g after 100 cycles
#8	Fe ₂ O ₃ nanorods on CNFs	~245 at 10 A/g	~ 758 at 0.2 A/g after 50 cycles

Table S1. Summary of previous studies on electrochemical performances of various Fe₂O₃ anode materials.

1. J. Qu, Y.-X. Yin, Y.-Q. Wang, Y. Yan, Y.-G. Guo and W.-G. Song, *ACS Appl. Mater. Interfaces*, 2013, **5**, 3932-3936.
2. X. Xu, R. Cao, S. Jeong and J. Cho, *Nano Lett.*, 2012, **12**, 4988-4991.
3. J. Liu, Y. Li, H. Fan, Z. Zhu, J. Jiang, R. Ding, Y. Hu and X. Huang, *Chem. Mater.*, 2009, **22**, 212-217.
4. J.-M. Jeong, B. G. Choi, S. C. Lee, K. G. Lee, S.-J. Chang, Y.-K. Han, Y. B. Lee, H. U. Lee, S. Kwon, G. Lee, C.-S. Lee and Y. S. Huh, *Adv. Mater.*, 2013, **25**, 6250-6255.

5. X. Jia, J. J. Chen, J. H. Xu, Y. N. Shi, Y. Z. Fan, M. S. Zheng and Q. F. Dong, *Chem. Commun.*, 2012, **48**, 7410-7412.
6. Y. Zou, J. Kan and Y. Wang, *J. Phys. Chem. C*, 2011, **115**, 20747-20753.
7. M. Zhang, B. Qu, D. Lei, Y. Chen, X. Yu, L. Chen, Q. Li, Y. Wang and T. Wang, *J. Mater. Chem.*, 2012, **22**, 3868-3874.
8. Z. Liu and S. W. Tay, *Mater. Lett.*, 2012, **72**, 74-77.