Supporting Information

Flexible All Inorganic Nanowire Bilayer Mesh as a High-Performance Lithium-Ion Battery Anode

Wei-Chung Chang, Tzu-Lun Kao, Yow Lin, and Hsing-Yu Tuan*

Department of Chemical Engineering, National Tsing Hua University, 101, Section 2,

Kuang-Fu Road, Hsinchu, Taiwan 30013, ROC

*Corresponding authors

Phone: (886)3-571-5131 ext:42509

Email: hytuan@che.nthu.edu.tw



Fig. S1 Analysis of germanium nanowires. (a) SEM image of germanium nanowires (b) TEM image of germanium nanowires (c) Fast Fourier transform (FFT) pattern of (d). (d) HRTEM image of germanium crystalline nanowire. Most of the germanium nanowires grow along the <111> direction. (e) EDS analysis of the tip of the germanium nanowire. (f) EDS analysis of the stem of the germanium nanowire (g) Current–voltage characteristic of the single germanium nanowire. The resistivity of the single germanium nanowire is $1.5*10^{-3} \Omega*m$ which is 300 times smaller than the bulk germanium ($4.6*10^{-1} \Omega*m$)¹.



Fig. S2 Photographs of fabricating process of layered Ge/Cu nanowire mesh electrode. (a) The solution of copper nanowires was dropped into a PTFE mold. (b) Dried Cu nanowire mesh, the toluene fully evaporated. (c) The solution of germanium nanowires was then dropped onto the copper nanowires in PTFE mold. (d) Dried Ge/Cu nanowire mesh electrode, the toluene fully evaporated. (e), (f) The flexible

Ge/Cu nanowire mesh electrode was peeled form the PTFE mold and tailored to adequate size for following electrochemical test or other analysis.



Fig. S3 Photographs of the mass of (a) Cu foil and (b) Cu nanowire mesh.



Fig. S4 Coulombic efficiency of layered Ge/Cu nanowire mesh electrode at the rate of

0.1 C and 1 C with FEC/DEC electrolyte.



Fig. S5 Cycling performance of the Ge nanowire mesh/Cu foil electrode at a rate of

0.1 C.



Fig. S6 Cycling performance of the Ge/Cu nanowire mesh electrode with EC/DMC electrolyte. (a) 0.1 C. (b) 1 C.



Fig. S7 Analysis of layered Ge/Cu nanowire mesh electrode after 200 cycles at a rate of 1 C with EC/DMC electrolyte. (a) Photograph of disassembling CR2032 coin cell. (b) Photograph of the fragments of Ge/Cu nanowire mesh electrode. Ge/Cu nanowire mash electrode was hard to peel from coin cell. (c) SEM image of Cu layer of layered Ge/Cu nanowire mesh electrode. (d) SEM image of Ge layer of Ge/Cu nanowire mesh

electrode. Most of the germanium nanowires were cracked and covered with thick SEI layer (e) High magnification SEM image of germanium nanowires. (f) TEM image of germanium nanowires. The inset image shows the germanium nanowire with incompact SEI layer. (g) Nyquist plots of layered Ge/Cu nanowire mesh electrode half-cell after various cycle 1st, 15th, 30th, 50th, 100th at a rate of 1 C (1st cycle at a rate of 0.1 C). (h) Differential capacity profile of layered Ge/Cu nanowire mesh electrode with the initial cycle at a rate of 0.1 C and the remaining 99 cycles at a rate of 1 C. The green arrow points out the first cycle. The red and blue arrow point out the gradually inward curve, which means the continuous fading of the cell.



Fig. S8 Half-cell test of commercial $Li(Ni_{0.5}Co_{0.3}Mn_{0.2})O_2$ cathode (a) Cycling performance. (b) Voltage profile corresponding (a) 1 C = 160 mA g⁻¹.

 Table S1 Comparison of bilayer Ge/Cu nanowire mesh electrode and conventional

 slurry-coating Ge nanomaterial electrodes.

Materials	Gravimetric	Loading mass	Current	Cruele	Gravimetric	Ref.
	Capacity (only	(mg cm ⁻²)	rate	Cycle	Capacity	

	active materials mA	(include binder,			(mA h g ⁻¹)	
	h g-1)	conductivity agent)			(whole	
					electrode)	
Ge/Cu mesh	832	0.5	1 C	1000	208	
Graphite***	330	12.012	1 C	1000	193	
Ge NWs	940	1	1 C	50	72	2
Ge NPS	1152	0.5	1 C	200	37	3
Ge NWs	600*	1	1 C	300	64	4
Ge NTs	765	1**	1 C	10	63	5
Gr/Ge NWs	1150*	1-1.9	1 C	200	115	6
Ge/RGO/C	993	0.6	1 C	600	48.	7
3D porous Ge	1415	1**	1 C	100	116	8
C-Ge/C	896	1	1 C	120	73	9
Sn-Ge	990	0.5	1 C	100	34	10
Ge NPs	1100	1**	0.8 C	40	90	11
Ge@C/RGO	800*	1**	0.9 C	40	70	12
Ge VNWs	550	1**	0.8 C	30	45	13
Ge/C	736	1	0.1 C	20	60	14
Ge NWs	660*	0.75 **	0.5 C	100	41	15
Ge NPs	789	1**	0.15 C	20	65	16
Ge/Cu ₃ Ge/C	530	1**	0.1 C	50	38	17

*The estimation of graphs of literatures.

**The literature does not provide the loading mass; we assume that the loading mass is 1 mg cm⁻².

*** Assume the areal capacity of graphite is 4 mA h cm⁻² and the reversible capacity is 330 mA h g⁻¹.

 Table S2 Comparison of bilayer Ge/Cu nanowire mesh electrode and conventional

 slurry-coating Si nanomaterial electrodes.

Materials	Gravimetric Capacity (mA h g ⁻¹) (only active materials)	Loading mass (mg cm ⁻²) (include binder, conductivity agent)	Curren t rate	Cycle	Gravimetric Capacity (mA h g ⁻¹) (whole electrode)	Ref.
Ge/Cu mesh	832	0.5	1 C	1000	208	
Graphite***	330	12.012	1	1000	193	
Si NWs	1800	1	0.1 C	100	129	18
Si NPs	2600	0.5	0.2 C	100	56	19
Si NWs	1500	0.2 (Si)	0.05 C	30	33	20
Si NPs	1500*	1**	1 C 500		100	21
Si fabric	804	1**	0.05 C	20	82	22
Si NPs	1250*	1**	0.5 C	100	90	23
Si NPs	1160	0.2 (Si)	0.5 C	1000	25	24
Si NWs	1300*	0.1 (Si)	0.5 C	800	14	25
Si MPs	1750	0.7 (Si)	0.1 C	130	125	26
Si NPs	1600*	0.3 (Si)	0.3 C	500	52	27
Si NPs	2200	0.2 (Si)	0.2 C	100	48	28

*The estimation of graphs of literatures.

**The literature does not provide the loading mass; we assume that the loading

weight is 1 mg cm⁻².

*** Assume the areal capacity of graphite is 4 mA h cm⁻² and reversible capacity is 330 mA h g^{-1} .

Table S3 Loading mass and volumetric capacities of graphite, Ge/Cu nanowire mesh

 and other Ge flexible electrodes.

Loading mass of active materials (mg cm ⁻²)	Thickness of Cu (µm)	Thickness of active materials (µm)	Thickness of whole electrodes (µm)	Volumetric capacity based on the total volume of whole	Ref.
(mg cm)		(μm)	(μm)	whole electrode	

					(m Ah cm ⁻³)	
Graphite	4	10	146.6	156.6	255.3	
Ge/Cu mesh	0.5~6	15	8~96.3	23~111.3	217~539	
Ge@CNFs	0.291	-	-	500	5.82	29
Ge@CNFs-2	0.504	-	-	200	25.2	30
Ge@Graphene	1.32	-	-	-	-	31
Ge@CNFs-3	0.404	-	-	-	-	32

Reference

- 1. R. A. Serway and J. W. Jewett, *Physics for Scientists and Engineers with Modern Physics*, Cengage Learning, 9th edn., 2013.
- 2. F.-W. Yuan, H.-J. Yang and H.-Y. Tuan, ACS Nano, 2012, 6, 9932-9942.
- K. C. Klavetter, S. M. Wood, Y.-M. Lin, J. L. Snider, N. C. Davy, A. M. Chockla, D. K. Romanovicz, B. A. Korgel, J.-W. Lee, A. Heller and C. B. Mullins, *Journal of Power Sources*, 2013, 238, 123-136.
- 4. A. M. Chockla, K. C. Klavetter, C. B. Mullins and B. A. Korgel, *ACS applied materials & interfaces*, 2012, **4**, 4658-4664.

- M. H. Park, Y. Cho, K. Kim, J. Kim, M. Liu and J. Cho, *Angewandte Chemie*, 2011, 50, 9647-9650.
- H. Kim, Y. Son, C. Park, J. Cho and H. C. Choi, *Angewandte Chemie*, 2013, 52, 5997-6001.
- 7. F.-W. Yuan and H.-Y. Tuan, *Chemistry of Materials*, 2014, **26**, 2172-2179.
- 8. M.-H. Park, K. Kim, J. Kim and J. Cho, Advanced Materials, 2010, 22, 415-418.
- 9. K. H. Seng, M.-H. Park, Z. P. Guo, H. K. Liu and J. Cho, *Angewandte Chemie* International Edition, 2012, **51**, 5657-5661.
- 10. M. I. Bodnarchuk, K. V. Kravchyk, F. Krumeich, S. Wang and M. V. Kovalenko, *ACS Nano*, 2014, **8**, 2360-2368.
- F.-S. Ke, K. Mishra, L. Jamison, X.-X. Peng, S.-G. Ma, L. Huang, S.-G. Sun and X.-D. Zhou, *Chemical Communications*, 2014, **50**, 3713-3715.
- 12. D. J. Xue, S. Xin, Y. Yan, K. C. Jiang, Y. X. Yin, Y. G. Guo and L. J. Wan, *Journal of the American Chemical Society*, 2012, **134**, 2512-2515.
- 13. L. P. Tan, Z. Lu, H. T. Tan, J. Zhu, X. Rui, Q. Yan and H. H. Hng, *Journal of Power Sources*, 2012, **206**, 253-258.
- 14. C. Yao, J. Wang, H. Bao and Y. Shi, *Materials Letters*, 2014, **124**, 73-76.
- 15. M.-H. Seo, M. Park, K. T. Lee, K. Kim, J. Kim and J. Cho, *Energy & Environmental Science*, 2011, **4**, 425-428.
- 16. L. C. Yang, Q. S. Gao, L. Li, Y. Tang and Y. P. Wu, *Electrochemistry Communications*, 2010, **12**, 418-421.
- 17. Y. Hwa, C.-M. Park, S. Yoon and H.-J. Sohn, *Electrochimica Acta*, 2010, **55**, 3324-3329.
- A. M. Chockla, K. C. Klavetter, C. B. Mullins and B. A. Korgel, *Chemistry of Materials*, 2012, 24, 3738-3745.
- 19. Y.-M. Lin, K. C. Klavetter, P. R. Abel, N. C. Davy, J. L. Snider, A. Heller and C. B. Mullins, *Chem. Commun.*, 2012, **48**, 7268-7270.
- C. K. Chan, R. N. Patel, M. J. O'Connell, B. A. Korgel and Y. Cui, *ACS Nano*, 2010, 4, 1443-1450.
- 21. N. Liu, H. Wu, M. T. McDowell, Y. Yao, C. Wang and Y. Cui, *Nano Lett.*, 2012, **12**, 3315-3321.
- A. M. Chockla, J. T. Harris, V. A. Akhavan, T. D. Bogart, V. C. Holmberg, C. Steinhagen, C. B. Mullins, K. J. Stevenson and B. A. Korgel, *Journal of the American Chemical Society*, 2011, **133**, 20914-20921.
- T. H. Hwang, Y. M. Lee, B.-S. Kong, J.-S. Seo and J. W. Choi, *Nano letters*, 2011, 12, 802-807.
- 24. N. Liu, Z. Lu, J. Zhao, M. T. McDowell, H. W. Lee, W. Zhao and Y. Cui, *Nature nanotechnology*, 2014, **9**, 187-192.

- H. Wu, G. Chan, J. W. Choi, I. Ryu, Y. Yao, M. T. McDowell, S. W. Lee, A. Jackson,
 Y. Yang, L. Hu and Y. Cui, *Nature nanotechnology*, 2012, 7, 310-315.
- 26. C. Wang, H. Wu, Z. Chen, M. T. McDowell, Y. Cui and Z. Bao, *Nature chemistry*, 2013, **5**, 1042-1048.
- 27. H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, *Nat Commun*, 2013, **4**, 1943.
- 28. N. Liu, K. Huo, M. T. McDowell, J. Zhao and Y. Cui, *Scientific reports*, 2013, **3**, 1919.
- 29. W. Li, Z. Yang, J. Cheng, X. Zhong, L. Gu and Y. Yu, *Nanoscale*, 2014, **6**, 4532-4537.
- W. Li, M. Li, Z. Yang, J. Xu, X. Zhong, J. Wang, L. Zeng, X. Liu, Y. Jiang, X. Wei, L. Gu and Y. Yu, *Small*, 2015, **11**, 2762-2767.
- 31. R. Mo, D. Rooney, K. Sun and H. Y. Yang, Nat. Commun., 2017, 8, 13949.
- 32. C. J. Peng, L. Wang, Q. W. Li, Y. Y. Li, K. Huo and P. K. Chu, *ChemElectroChem*, 2017, **4**, 1002-1006.