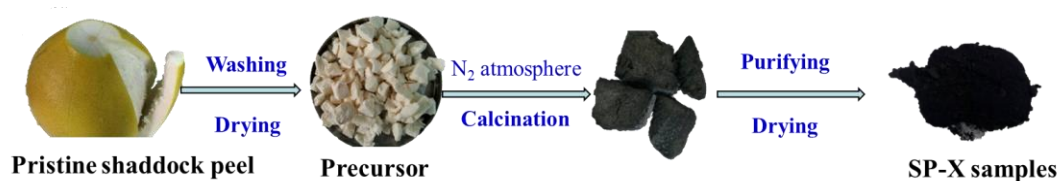


Supporting Information for

Facile synthesis of high performance hard carbon anode materials for sodium ion batteries

Ning Sun, Huan Liu and Bin Xu*



Scheme 1. Schematic diagram for the synthetic process of the shaddock peel-derived pyrolytic carbons.

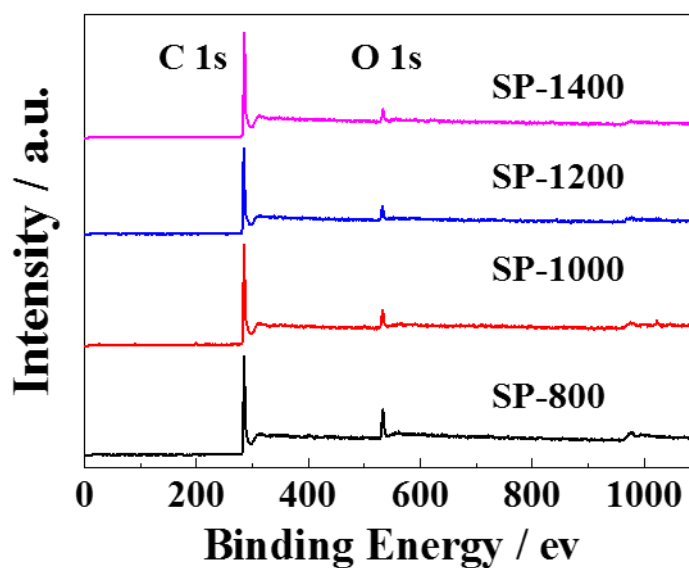


Figure S1 X-ray photoelectron spectroscopy survey spectra of the pyrolytic carbons.

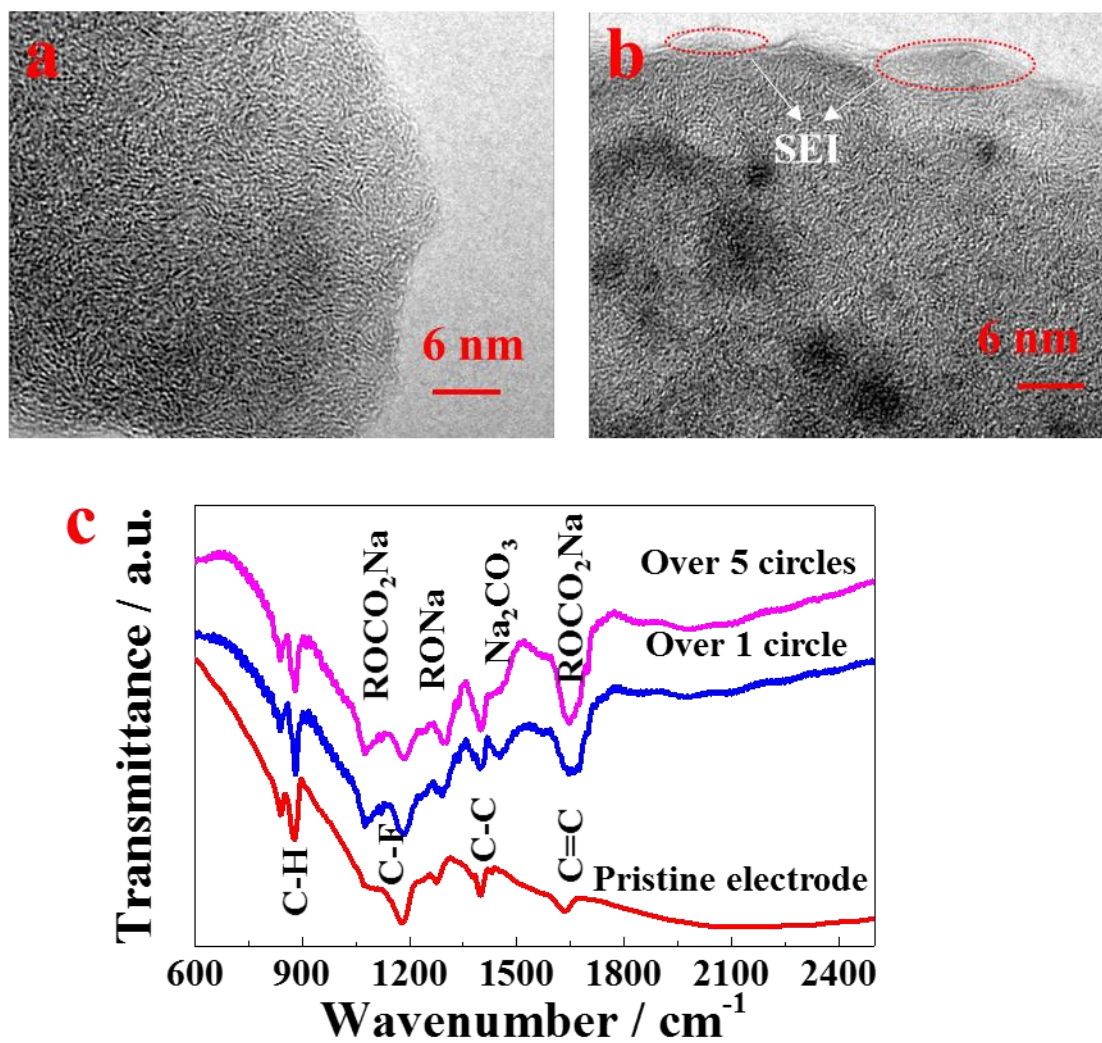


Figure S2 HRTEM images of the SP-800 sample before (a) and after initial discharge/charge cycling (b), and comparison of FTIR analysis of the SP-800 sample before and after cycling (c).

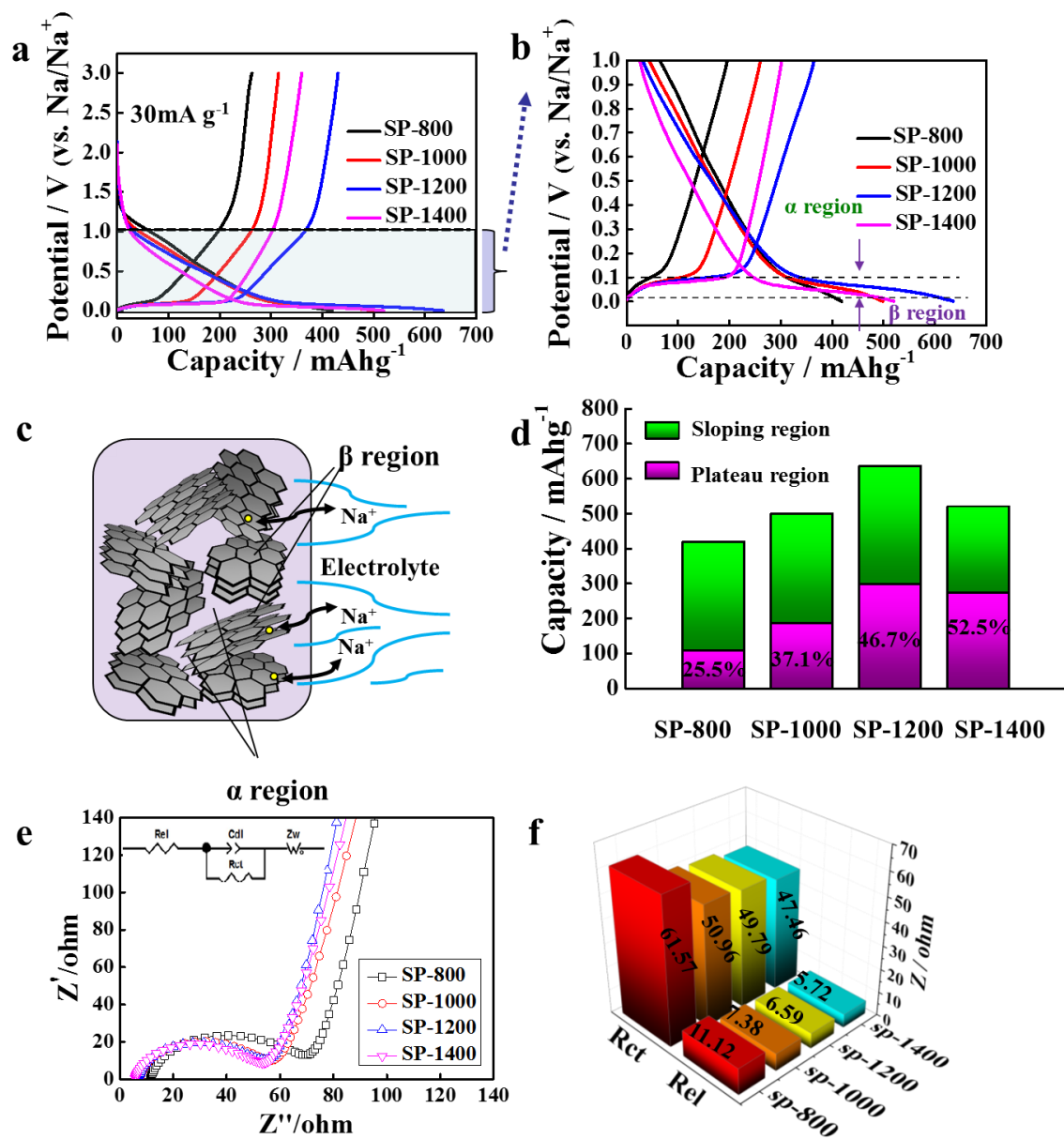


Figure S3 The initial discharge/charge profiles of the pyrolytic carbons at 30mA g⁻¹ (a-b), schematic illustration of the sodium ion insertion mechanism (c), and summary of discharge capacity above and below 0.1 V of the SP-X samples in the initial cycle at 30 mA g⁻¹ (d), EIS of the as-prepared SP-X electrodes with the equivalent circuit diagram in the inset (e), and comparison of impedance of the SP-X electrodes collected from Nyquist diagram (f).

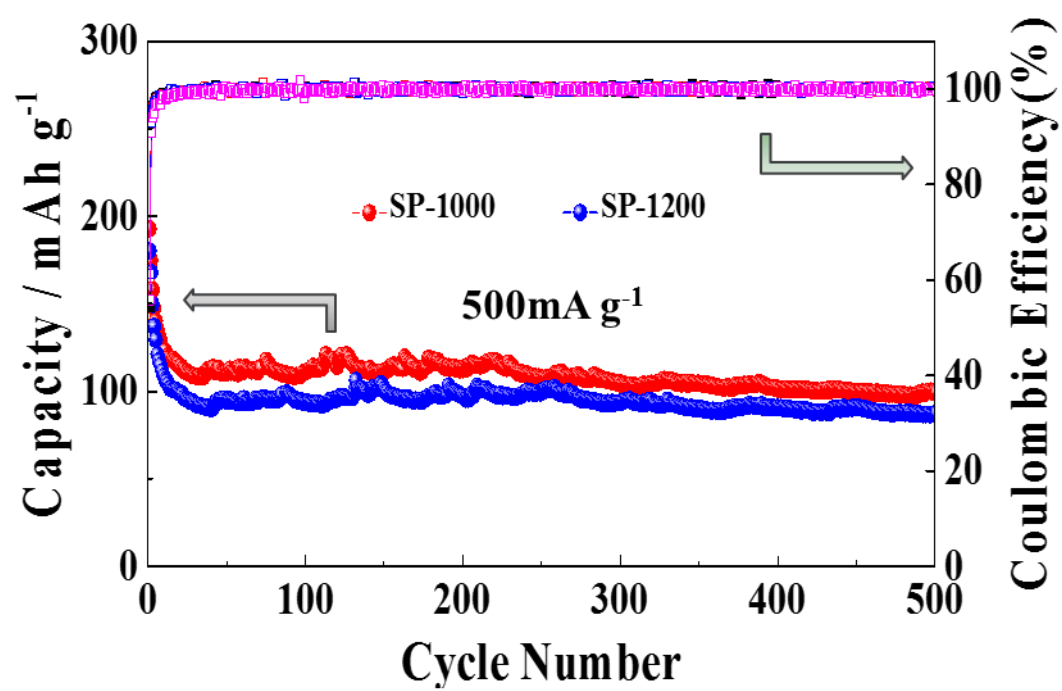
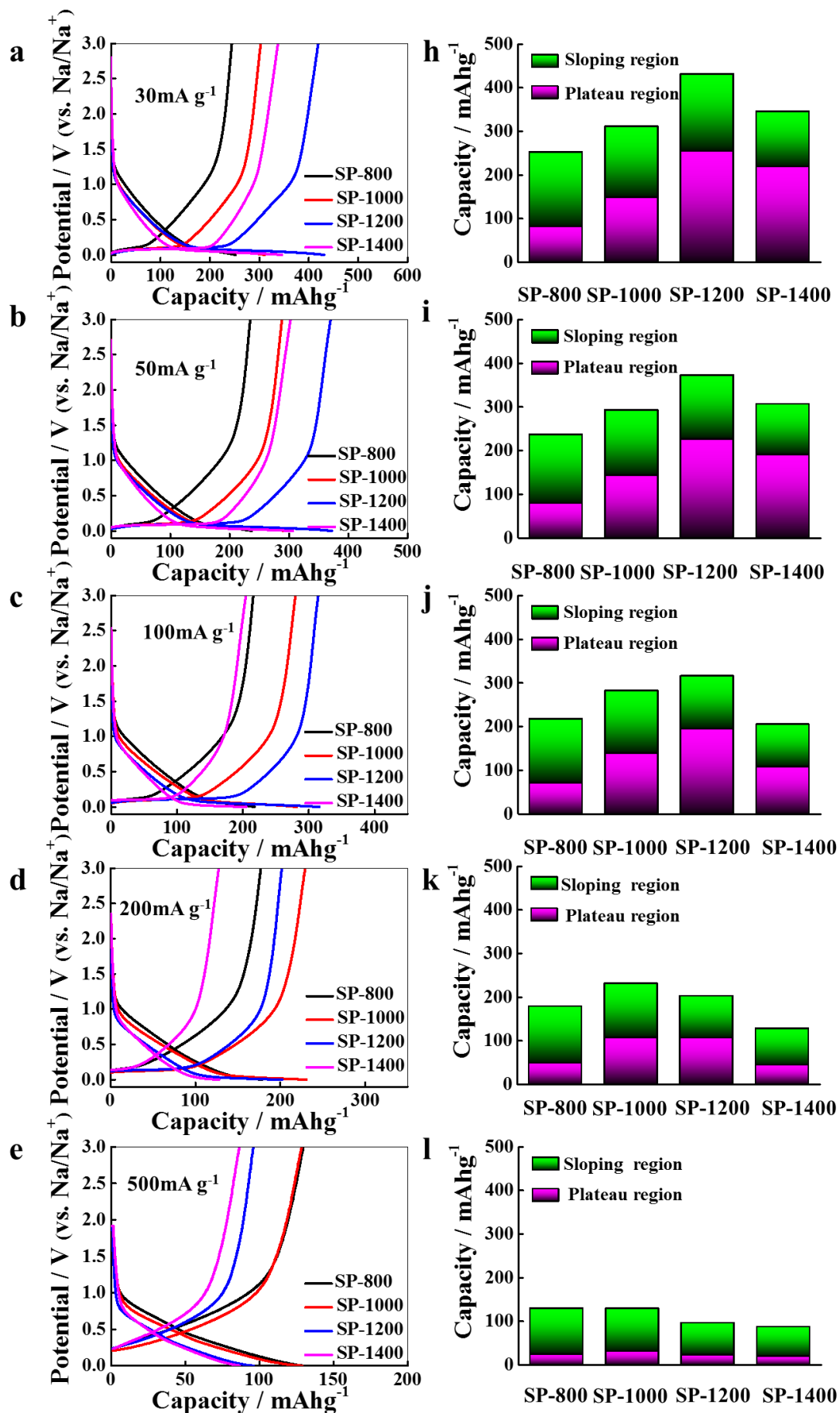


Figure S4 Cycle performance of the pyrolytic carbons at a current load of 500 mA g⁻¹.



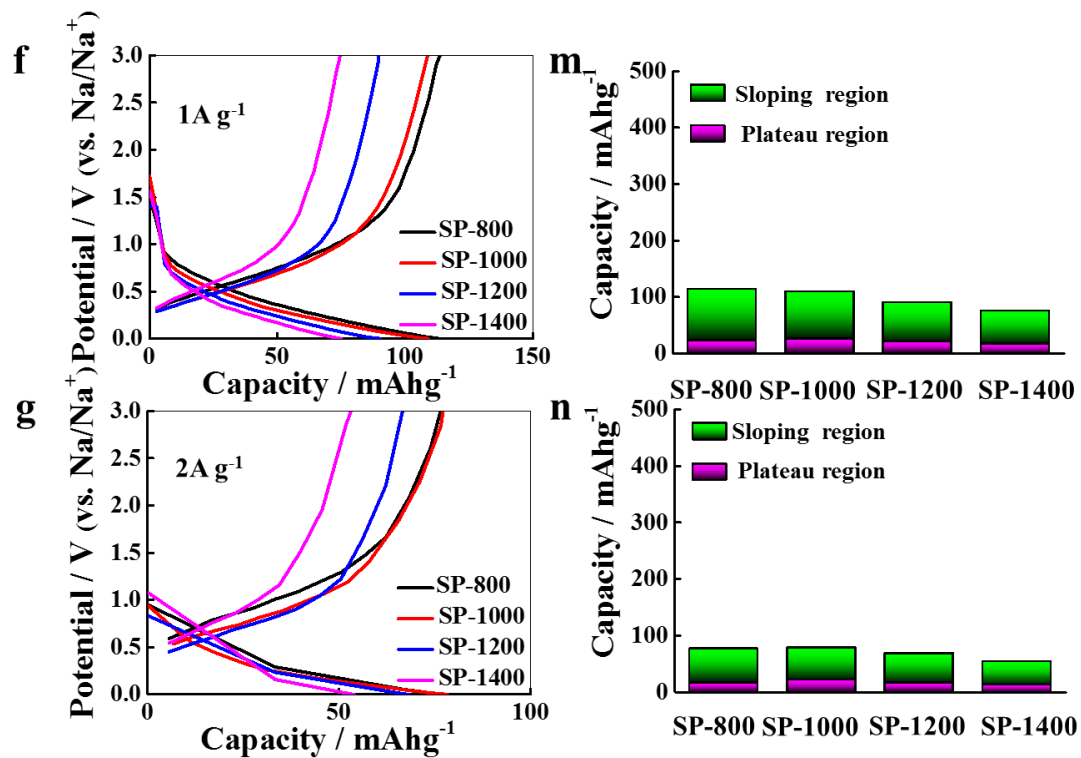


Figure S5 Charge/discharge profiles (a-g) and summary of discharge capacity above and below 0.1 V of the pyrolytic carbons (h-n) in the fifth cycle at different current densities.

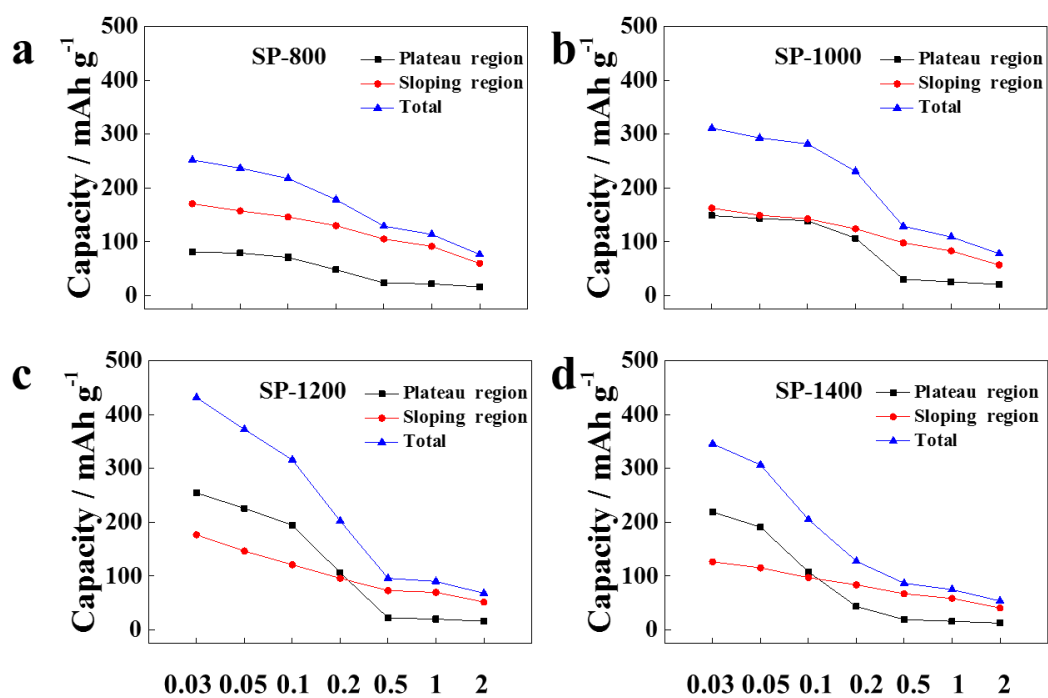


Figure S6 Comparison of the capacity change of the plateau and sloping region of the pyrolytic carbons at different current densities.

Table S1 Element composition of the pyrolytic carbons by XPS

Samples	C / at %	O / at %	N / at %	Cl / at %
SP-800	91.08	6.32	1.97	0.63
SP-1000	94.89	3.83	1.28	-
SP-1200	96.98	3.02	-	-
SP-1400	97.53	2.47		-

Table S2 Performance comparison of SP-1200 *versus* state-of-the-art anode carbons of SIBs reported in literature.

Material	Initial coulombic efficiency(%)	Initial reversible capacity	Cyclability (reversible capacity)	Citation
SP-1200	67.7	430 mA h g ⁻¹ at 30 mA g ⁻¹ ; 370 mA h g ⁻¹ at 50 mA g ⁻¹	352 mA h g ⁻¹ at 50 mA g ⁻¹ over 200 cycles	This work
Templated carbon	~14	180 mAh g ⁻¹ at 74.4 mA g ⁻¹	130 mAh g ⁻¹ over 40 cycles	[1]
Hollow carbon nanowires	50.5	251 mAh g ⁻¹ at 50 mA g ⁻¹	206.3 mAh g ⁻¹ over 400 cycles	[2]
Hollow carbon nanospheres	41	223 mAh g ⁻¹ at 50 mA g ⁻¹	~160 mAh g ⁻¹ at 100mA g ⁻¹ over 100 cycles	[3]
Carbon nanofiber	58	255 mAh g ⁻¹ at 40 mA g ⁻¹	176 mAh g ⁻¹ at 200 mA g ⁻¹ over 600 cycles	[4]
Nitrogen-Doped Porous Carbon Nanosheets	34.8	349 mAh g ⁻¹ at 50 mA g ⁻¹	200 mAh g ⁻¹ over 50 cycles	[5]
Reduced graphene oxide	~25	~400 mAh g ⁻¹ at 40 mA g ⁻¹	174.3 mAh g ⁻¹ over 250 cycles	[6]
Carbon nanosheet frameworks	54	298 mAh g ⁻¹ at 50 mA g ⁻¹	255 mAh g ⁻¹ at 100 mA g ⁻¹ over 200 cycles	[7]
Expanded graphite	49.5	284 mAh g ⁻¹ at 20 mA g ⁻¹	184 mAh g ⁻¹ at 100mA g ⁻¹ over 2000 cycles	[8]
Carbon fiber	58.2	250 mAh g ⁻¹ at 50 mA g ⁻¹	233 mAh g ⁻¹ over 200 cycles	[9]
Sphere carbon	62	160 mA h g ⁻¹ at 150 mA g ⁻¹	90 mAh g ⁻¹ over 50 cycles	[10]
Highly Disordered Carbon	57.6	246 mAh g ⁻¹ at 100mA g ⁻¹	225 mAh g ⁻¹ over 180 cycles	[11]
Mesoporous carbon	39.9	164 mAh g ⁻¹ at 100 mA g ⁻¹	125 mAh g ⁻¹ over 100cycles	[12]
Carbon microspheres	30~40	202 mAh g ⁻¹ at 30 mA g ⁻¹	183 mAh g ⁻¹ over 50cycles	[13]
Hard Carbon/Carbon Nanotube Composites	61	300 mAh g ⁻¹ at 20 mA g ⁻¹	280 mAh g ⁻¹ over 50 cycles	[14]
Hierarchically Porous Carbon/Graphene Composite	~30	670 mA h g ⁻¹ at 50 mA g ⁻¹	400 mAh g ⁻¹ over 100 cycles	[15]
Hard carbon derived from Banana	68	~360 mA h g ⁻¹ at 50 mA g ⁻¹	330 mAh g ⁻¹ at 100mA g ⁻¹ over 50 cycles	[16]
Porous hard carbon	27	287 mA h g ⁻¹ at 50 mA g ⁻¹	181 mA h g ⁻¹ at 200mA g ⁻¹ over 220cycles	[17]
Hard carbon micro-spherules	83	311 mA h g ⁻¹ at 30 mA g ⁻¹	290 mA h g ⁻¹ over 220 cycles	[18]
Graphene oxide doped hard carbon	83	289 mA h g ⁻¹ at 20 mA g ⁻¹	220 mA h g ⁻¹ over 200 cycles	[19]
Mesoporous carbon	36	~330 mAh g ⁻¹ at 50mA g ⁻¹	260 mAh g ⁻¹ over 100cycles	[20]

References

1. S. Wenzel, T. Hara, J. Janek and P. Adelhelm, *Energy & Environmental Science*, 2011, **4**, 3342-3345.
2. Y. Cao, L. Xiao, M. L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z. Nie, L. V. Saraf, Z. Yang and J. Liu, *Nano letters*, 2012, **12**, 3783-3787.

3. K. Tang, L. Fu, R. J. White, L. Yu, M.-M. Titirici, M. Antonietti and J. Maier, *Advanced Energy Materials*, 2012, **2**, 873-877.
4. W. Luo, J. Schardt, C. Bommier, B. Wang, J. Razink, J. Simonsen and X. L. Ji, *Journal of Materials Chemistry A*, 2013, **1**, 10662-10666.
5. H. G. Wang, Z. Wu, F. L. Meng, D. L. Ma, X. L. Huang, L. M. Wang and X. B. Zhang, *ChemSusChem*, 2013, **6**, 56-60.
6. Y.-X. Wang, S.-L. Chou, H.-K. Liu and S.-X. Dou, *Carbon*, 2013, **57**, 202-208.
7. H. Jia Ding, Zhi Li Alireza Kohandehghan, Kai Cui, Zhanwei Xu, *ACS Nano*, 2013, **7**, 11104-11015.
8. Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, Y. Ishii, J. Cumings and C. Wang, *Nature communications*, 2014, **5**, 4033-4042.
9. T. Chen, Y. Liu, L. Pan, T. Lu, Y. Yao, Z. Sun, D. H. C. Chua and Q. Chen, *Journal of Materials Chemistry A*, 2014, **2**, 4117-4121.
10. V. G. Pol, E. Lee, D. Zhou, F. Dogan, J. M. Calderon-Moreno and C. S. Johnson, *Electrochimica Acta*, 2014, **127**, 61-67.
11. X. Zhou and Y.-G. Guo, *ChemElectroChem*, 2014, **1**, 83-86.
12. J. Liu, H. Liu, T. Yang, G. Wang and M. O. Tade, *Chinese Science Bulletin*, 2014, **59**, 2186-2190.
13. T. Chen, L. Pan, T. Lu, C. Fu, D. H. C. Chua and Z. Sun, *J. Mater. Chem. A*, 2014, **2**, 1263-1267.
14. R. Suresh Babu and M. Pyo, *Journal of the Electrochemical Society*, 2014, **161**, A1045-A1050.
15. Y. Yan, Y. X. Yin, Y. G. Guo and L. J. Wan, *Advanced Energy Materials*, 2014, **4**, 1301584.
16. E. M. Lotfabad, J. Ding, K. Cui, A. Kohandehghan, W. P. Kalisvaart, M. Hazelton and D. Mitlin, *ACS Nano*, 2014, **8**, 7115-7129.
17. K. L. Hong, L. Qie, R. Zeng, Z. Q. Yi, W. Zhang, D. Wang, W. Yin, C. Wu, Q. J. Fan, W. X. Zhang and Y. H. Huang, *Journal of Materials Chemistry A*, 2014, **2**, 12733-12738.
18. Y. Li, S. Xu, X. Wu, J. Yu, Y. Wang, Y.-S. Hu, H. Li, L. Chen and X. Huang, *J. Mater. Chem. A*, 2015, **3**, 71-77.
19. W. Luo, C. Bommier, Z. Jian, X. Li, R. Carter, S. Vail, Y. Lu, J. J. Lee and X. Ji, *ACS Applied Materials & Interfaces*, 2015, **7**, 2626-2631.
20. Z. Guan, H. Liu, B. Xu, X. Hao, Z. Wang and L. Chen, *J. Mater. Chem. A*, 2015, **3**, 7849-7854.