Supporting Information for:

Sustainable Conversion of Lignocellulose to High Purity, Highly Crystalline Flake Potato Graphite

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Supporting Information contains 11 pages including 10 figures and 1 table.

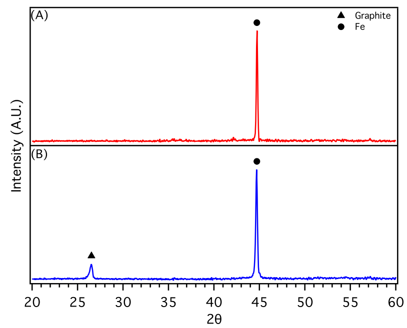

Figure S1. XRD patterns of bio-char/Fe pellet before (A, red) and after (B, blue) laser irradiation with graphite (triangle, JCPDS # 41-1487) and Fe (circle, JCPDS # 06-0696) peaks indicated.

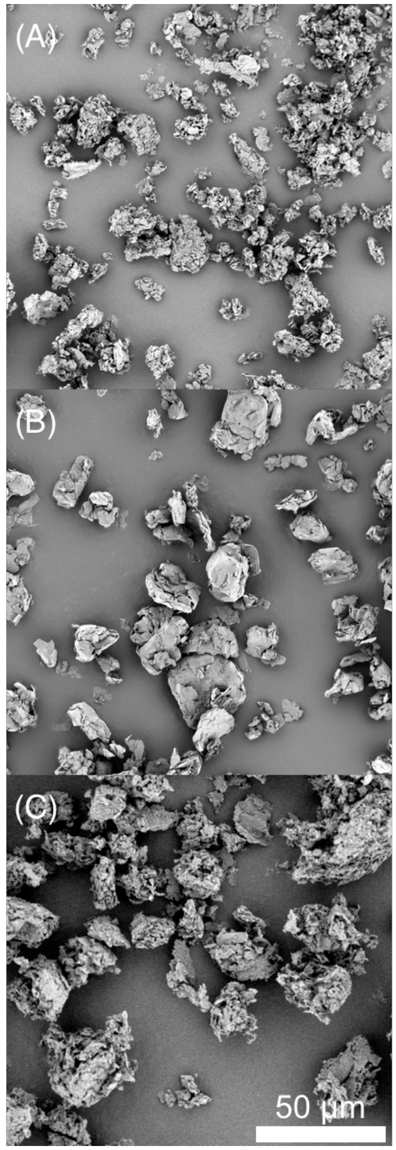

Figure S2. SEM images of purified BCG synthesized from (A) -325 mesh Fe and (C) Co showing that they have very similar morphology to (B) Hitachi MagE3 commercial potato graphite.

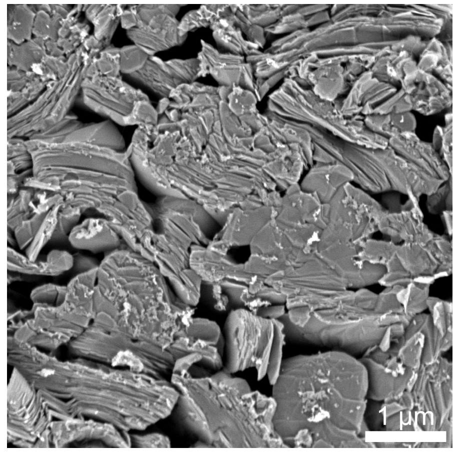

Figure S3. Cross section of a BCG agglomerate synthesized from Co showing its high packing density.

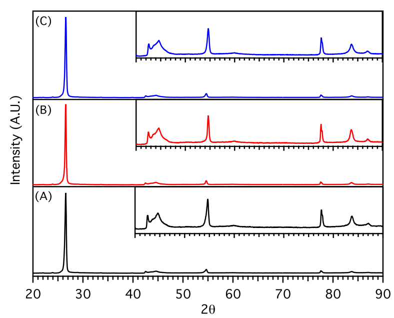

Figure S4. XRD patterns of BCG made with Fe (A), Ni (B) and Co(C).

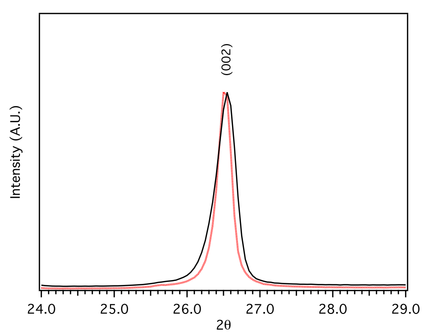

Figure S5. Overlay of the (002) reflections of the XRD patterns of BCG (black, solid) and SFG6 (red, dotted).

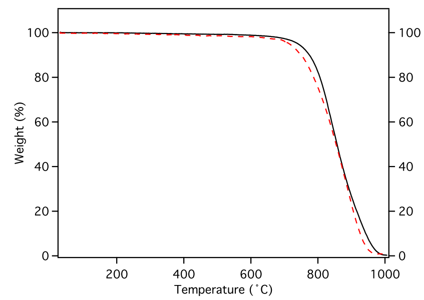

Figure S6. TGA thermogram of NGS (solid) and SFG6 (dashed).

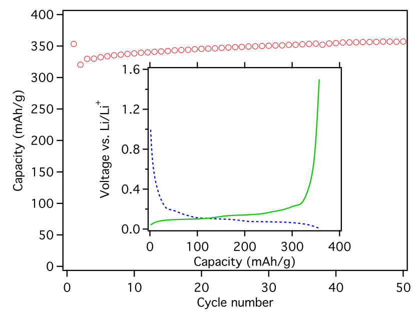

Figure S7. Gravimetric capacity of a ~ 5 µm BCG (made from -325 mesh Co) anode demonstrating excellent Li-ion capacity (~ 350 mA/g, red circles), comparable to that of commercial Li-ion battery grade graphite at a C/2 rate. Inset is its charge (blue dashed line) / discharge (green line) profile, again, nearly identical to commercial graphite.

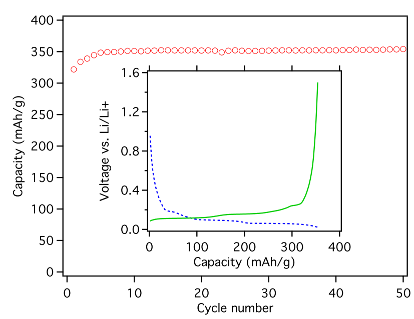

Figure S8. Gravimetric capacity of a ~ 5 µm BCG (made from -325 mesh Ni) anode demonstrating excellent Li-ion capacity (~ 350 mA/g, red circles), comparable to that of commercial Li-ion battery grade graphite at a C/2 rate. Inset is its charge (blue dashed line) / discharge (green line) profile, again, nearly identical to commercial graphite.

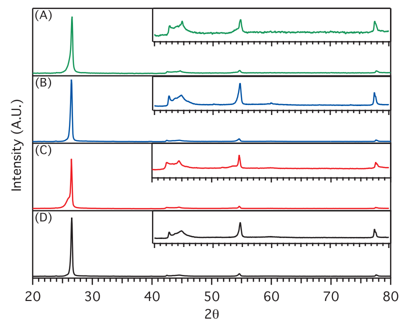

Figure S9. XRD patterns of BCG made with -325 mesh Fe and (A, green) Lignin, (B, blue) wood flour, (C, red) corn cob, and (D, black) cellulose.

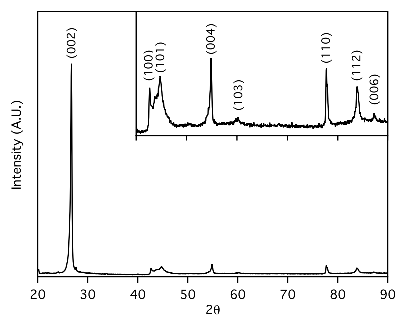

Figure S10. XRD patterns of BCG made with -325 mesh Fe and lignite coal. Inset scaled to show lower intensity reflections.

Element	Concentration [ppm wt]	Element	Concentration [ppm wt]
Li	0.08	Pd	< 0.1
Be	< 0.05	Ag	< 0.1
B	9.1	Cd	< 0.5
C	Matrix	In	Binder
N	-	Sn	< 0.5
O	-	Sb	< 0.1
F	=< 100	Te	< 0.5
Na	76	I	=< 10
Mg	2.8	Cs	< 0.5
Al	2.3	Ba	1.4
Si	67	La	=< 1
P	0.62	Ce	< 0.5
S	3.5	Pr	< 0.5
Cl	130	Nd	< 0.05
K	2.6	Sm	< 0.05
Ca	13	Eu	< 0.05
Sc	< 0.05	Gd	< 0.05
Ti	0.34	Tb	< 0.05
V	< 0.05	Dy	< 0.05
Cr	< 0.5	Ho	< 0.05
Mn	0.43	Er	< 0.05
Fe	210	Tm	< 0.05
Co	0.14	Yb	< 0.05
Ni	3.5	Lu	< 0.05
Cu	2.2	Hf	< 0.05
Zn	< 0.5	Ta	< 100
Ga	< 0.5	W	< 0.05
Ge	< 0.1	Re	< 0.05
As	=< 1	Os	< 0.05
Se	< 0.5	Ir	< 0.05
Br	< 0.5	Pt	< 0.1
Rb	< 0.1	Au	< 0.5
Sr	0.72	Hg	< 0.5
Y	< 0.05	Tl	< 0.05
Zr	< 0.1	Pb	< 0.1
Nb	< 0.1	Bi	< 0.05
Mo	< 0.1	Th	< 0.05
Ru	< 0.5	U	< 0.05
Rh	< 0.1		

Table S1. Glow Discharge Mass Spectrometry (GDMS) elemental analysis data of BCG performed by EAG Laboratories.

Supporting Discussion

Economic Model

BCG Production Costs

The calculated results in the table below are based on our current yield of 0.25 g/Wh of laser output and do not include the cost (~ \$20 - 40/t for sawdust) of the biomass (it is accounted for in the cost of electricity generation from the bio-oil co-product, see *Effect of Biochar to BCG Upgrading on Biomass Pyrolysis Economics* section below for discussion). This number is likely to increase with optimization of parameters such as laser residence time, sample dimensions and metal to biochar ratio, decreasing production costs. IR laser power efficiencies have been rapidly increasing in past decade, now exceeding 50% in some cases (fiber lasers). An efficiency of 35% (including cooling) is assumed for the calculations here. In order to be consistent with the maize residue study used below, electricity is valued at \$80/MWh.[30] The price of fiber lasers have also sharply decreased over this same time frame, with module cost thought to soon be less than \$10/W. For the purpose of these calculations, we use the current, undiscounted, complete laser cost of \$47/W, but it should be noted that anticipated decreases in this cost would result in a significant decrease in production costs. At a 90% capacity factor, graphite production rate of 1.00 t/y would require a 0.507 kW laser, thus the capital cost for the laser is \$47/W x 0.507 kW = \$23,829 depreciated over its 15 year life expectancy. Cost of iron, the most abundant and cheapest of all metals, is expected to be nominal with removal by HCl to produce the chloride, a product made by an analogous process industrially and profitably sold for use as a coagulant in waste water treatment. Other capital costs, other utilities, personnel, maintenance and overhead are assumed to be similar to those for bio-oil production.[1] Financing of the capital costs is assumed to be by a US SBA 504 loan at the highest allowable interest rate (4.54%) and the costs averaged over 15 years.

Production Costs	Costs per ton graphite produced (USD, $)
Electricity (laser)	$914
Other utilities	$55
Laser (depreciation)	$1,589
Other facilities (depreciation)	$21
Interest	$613
Personnel	$16
Maintenance	$8
Overhead	$8
Total Production Cost BCG/t	$3,224

Table: Line item estimate of total production cost of BCG.

BCG Value

The price of graphite depends strongly on its purity. The purity level (99.95%), crystallinity and electrochemical performance of BCG is that of graphite for Li-ion battery anodes (> 99.9+ %). The average prices for battery grade natural and synthetic graphite are $14,870 and $18,000 in the United States, respectively,[2] more that 4.5 – 5.5 times greater than the BCG production cost estimate.

Effect of Biochar to BCG Upgrading on Biomass Pyrolysis Economics

The simplest analysis of the valorization potential of BCG production is to simply take the difference between the net value of the BCG (after production costs) and the biochar. Estimates of the value of biochar range from ~ $10 to 50 /t based on its combustion value at the lower end and soil amendment at the high end.[1, 3] On this basis, BCG upgrading could add ~ $11,500 – 14,500 per ton to the value of biochar. However, this estimate assumes that a market and sufficient supply of biochar is already available, which is not the case. Thus, a more relevant model upon which to estimate the economic potential of BCG should also include the production of biochar, for instance, the combination of BCG and biomass pyrolysis energy production.

Regional costs differences play a major factor in the economic outlook of electricity, bio-oil and heat production from biomass pyrolysis. The primary differences are in the costs of raw materials (processed/delivered biomass) and the market price for electricity. Areas with active forest product industries and high electricity or heating oil costs are particularly well suited for economically competitive pyrolysis energy production. We have based our calculations on the results of a case study of maize residue pyrolysis in the United States Corn Belt,[1] to demonstrate that conversion of low value biochar into high value graphite could make a process found to be unprofitable highly profitable. The case study for fast pyrolysis found a net loss of \$47.91 per ton of feedstock with a yield of 0.045 t and a net income from the biochar of \$1.61. At the demonstrated BCG from biochar yield of 84%, 0.045 t of biochar could be converted to 0.0378 t BCG. At a sale price of \$14,870 – 18,000 /t and a production cost of \$3,224 /t BCG, upgrading the biochar could net \$440 – 559, transforming a \$47.91 loss to a \$392 – 510 profit per ton of feedstock. Optimizing for char production by using slow rather than fast pyrolysis yields 0.350 t of biochar and a loss of \$70.08 per t feedstock,[1] but the larger loss could be more than offset by the value of the addition graphite produced. It should be noted that the scale of the maize residue pyrolysis plant model (12.52 MW) is small enough that the BCG produced should have little effect on the overall Li-ion graphite price; ~ 2650 t BCG would be produced per year if all of the biochar produced was converted, a small fraction of the market estimated to be at least 250,000 tons per year by 2020.[4] It should also be noted that the potential gross value of the BCG produced, \$39.4 – 47.7 million, is ~ 4.7 – 5.7 times greater than the gross value of the electricity produced by the plant (100% capacity factor, \$8.4 million at \$80 /MWh).

1. McCarl, B. A.; Peacoke, C.; Chrisman, R.; Kung, C.-C.; D. Sands, R., *Economics of biochar production, utilization and greenhouse gas offsets*. 2009; p 341-358.
2. Chung, D.; Elgqvist, E.; Santhanagopalan, S., Automotive Lithium-ion Battery Supply Chain and US Competitiveness Considerations. Clean Energy Manufacturing Analysis Center, C., Ed. 2015.
3. Wright, M.; E. Daugaard, D.; Satrio, J.; Brown, R., Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *Fuel* **2010,** *89*, S2-S10.
4. Graphite Demand From Lithium Ion Batteries to More than Treble in 4 Years. *Benchmark Mineral Intelligence* **2016**.