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ELECTROCHEMICAL PERFORMANCE OF SILICON ENHANCED LAC KNIFE NATURAL FLAKE GRAPHITE FROM QUEBEC, CANADA IN LITHIUM ION BATTERIES

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Lac Knife Graphite Project

OUTLINE

- Lac Knife Flake Graphite Products
- Preparation of Silicon Enhanced Spherical Graphite
- Data from Oct. 9th Stuttgart, Germany EVS 30 Symposium
- Recent Performance Results on Silicon Enhanced Graphite
- Future Development Work

LAC KNIFE FLAKE GRAPHITE PRODUCTS

Flotation Concentrates from Pilot Plant Tests

- Coarse (+80 mesh) – 98.3%C
- Medium (-80x150 mesh) – 98.2%C
- Fine (-150x200 mesh) – 98.0%C

Purified Flake - 99.98^{+}%C

Carbon Coated Spherical Graphite (SPG)

- Standard D_{50} = 23.9 µm
- Fine D_{50} = 17.4 µm
- Superfine D_{50} = 11.9 µm

Sized Purified Graphites

- Flake Graphite D_{50} = 21, 16, 10 and 7µm
- Expanded Graphite D_{50} = 21, 15.8 and 3.5 µm

Grades Under Development

- Silicon Enhanced Carbon Coated Spherical Graphite
- High Rate Capability Graphite
- Oxidation Resistant Graphite

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Fig. 1 **PARTICLE SIZE DISTRIBUTIONS OF SUPERFINE, FINE AND STANDARD GRADES OF LAC KNIFE SPG**

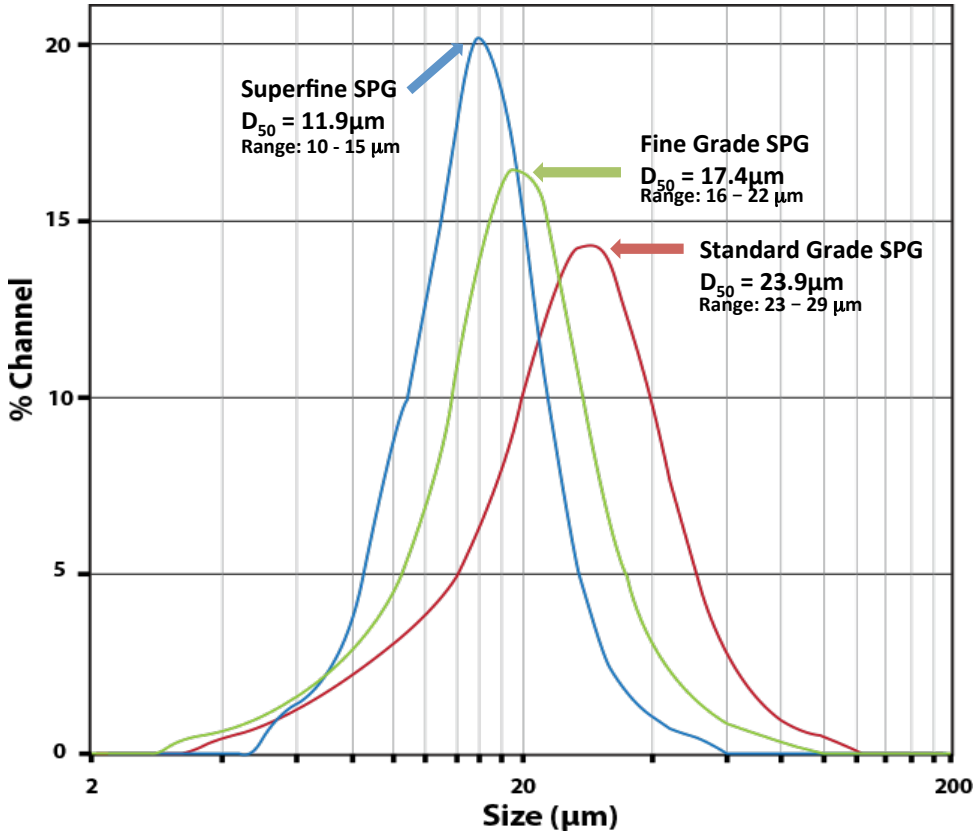

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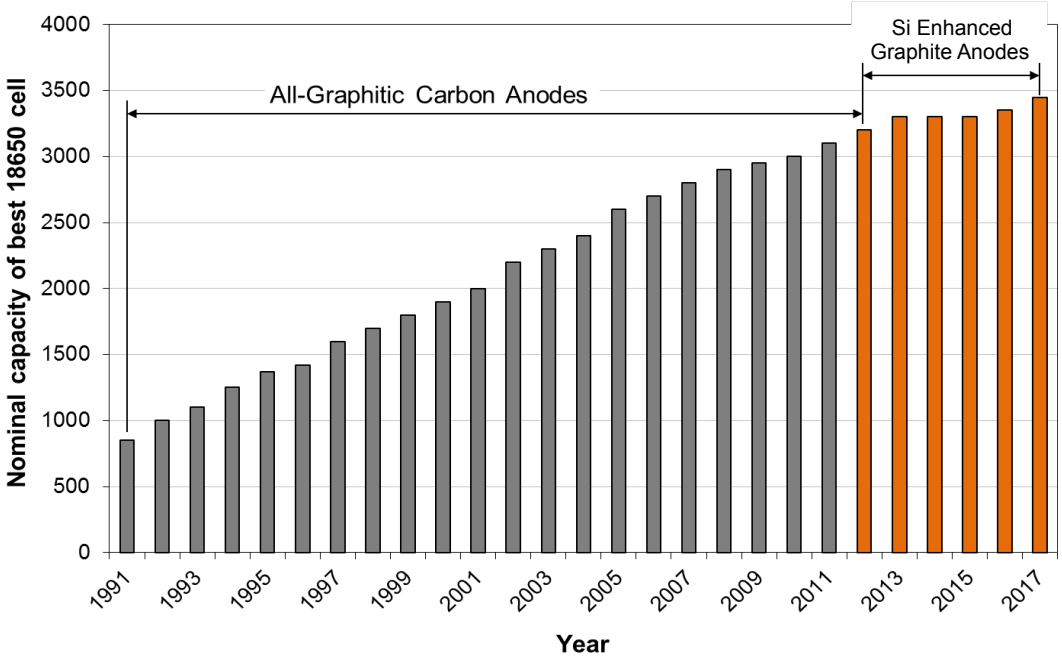
Fig. 2 WHY SILICON ENHANCED GRAPHITE?

18650 CELL NOMINAL CAPACITY ANALYSIS



M.L. BARSUKOV, et al. (2018) Silicon-Enhanced Graphite Anodes for Next-Generation Lithium-Ion Batteries: Product Concepts, Performance and Manufacturing Process Flowsheets. Materials for Li-ion Batteries: Advances and Applications with Silicon Anodes and Electrolytes. JAMES J. WU Eds. Pan Stanford Publishing Pte. Ltd, Chapter 2 (in press)

- By 2011 practical limit of capacity of 18650 cells has been reached with chemistries based on all-graphitic carbon anodes.
- Further capacity increases were made by seeding graphite anodes with transition metal dopants, which include Sn, Si, etc.

Fig. 3 PREPARATION OF CARBON COATED Si ENHANCED SPG

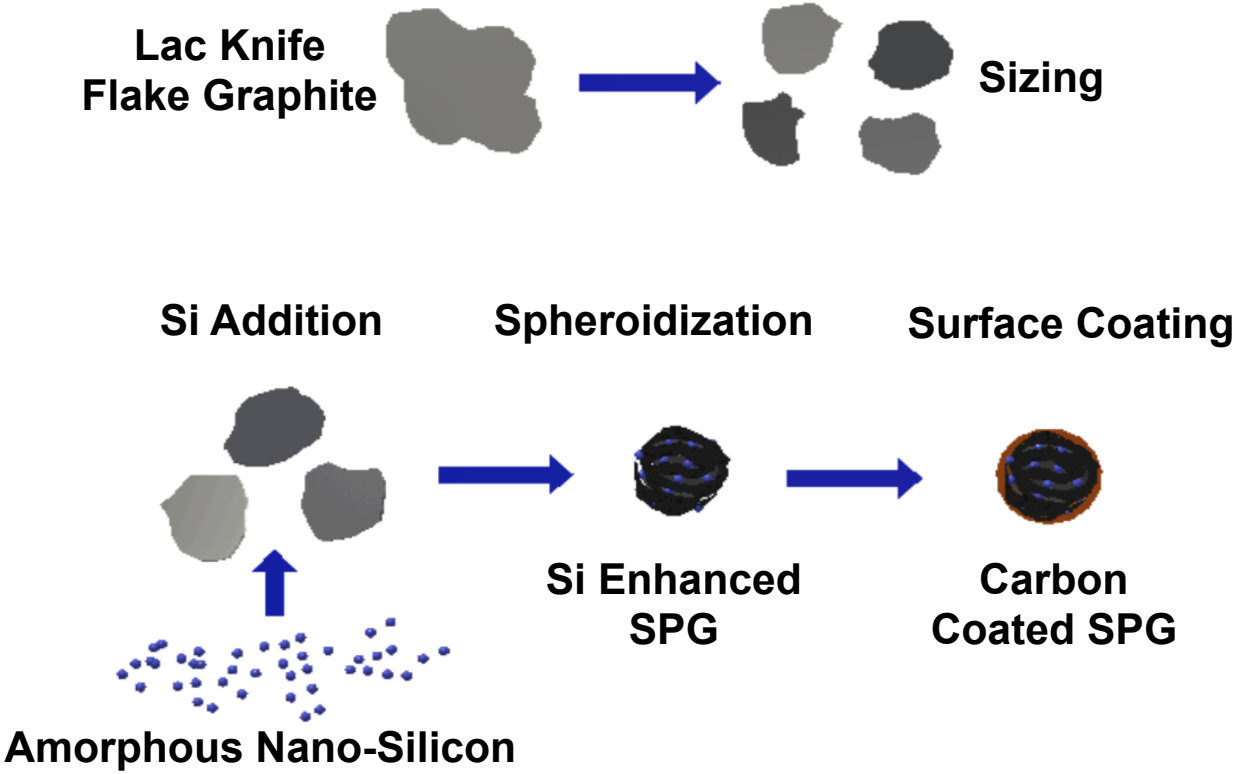


Fig. 4 CROSS SECTION OF CARBON COATED Si ENHANCED SPG

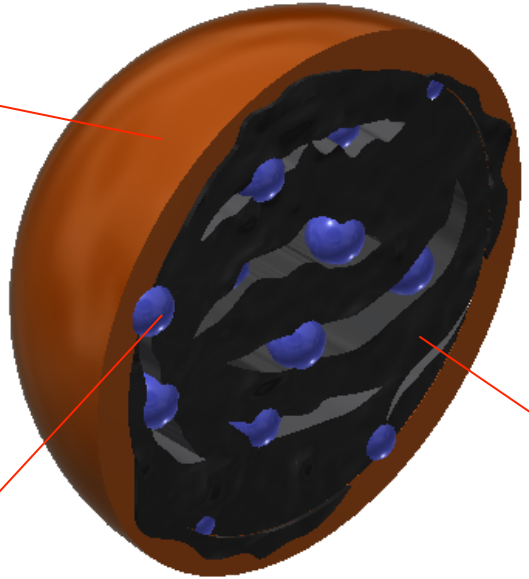
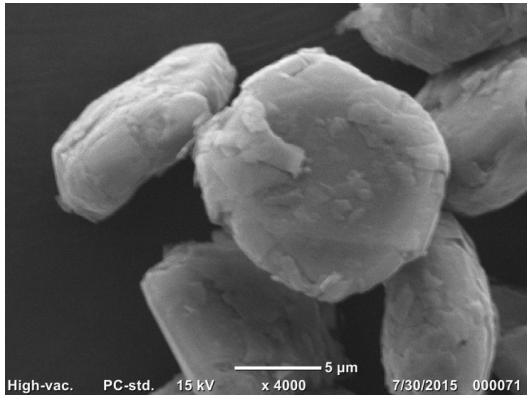


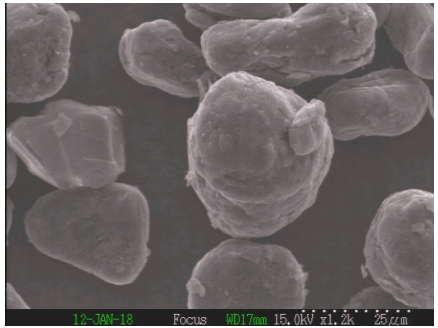
Fig. 5 SEMs OF STANDARD AND Si ENHANCED SPG

Lac Knife SPG – 0 wt% Si

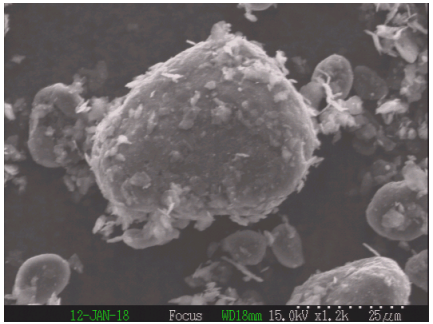


As the wt% of Si addition increases, more Si particles appear on the surface of the SPG. Nevertheless, spheroidal shape of core graphite particle is retained within broad spectrum of Si additions.

9 wt% Si



13.5 wt% Si



18 wt% Si

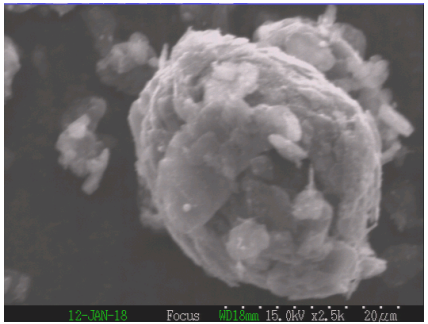


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Fig. 6 TEMs OF STANDARD AND Si ENHANCED SPG

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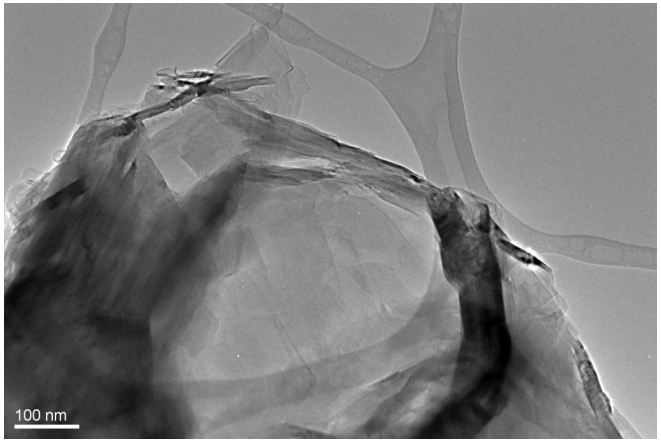
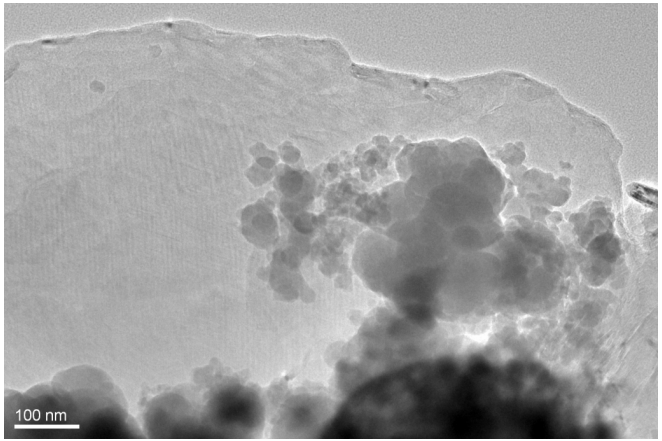
Standard SPG



9 wt% Si Enhanced SPG



- Spheroidized edges of basal plane on graphite are clearly evident.
- No foreign inclusions are visible in SPG, attesting to its ultra-high purity level
- Nano-scale particles of Silicon are clearly visible in the Si-enhanced SPG structure;
- Most of the Si is trapped inside the spheroidal shell of SPG.

TEM data by ISI, 200 kV EM-002B Ultra-high resolution Transmission Electron Microscope

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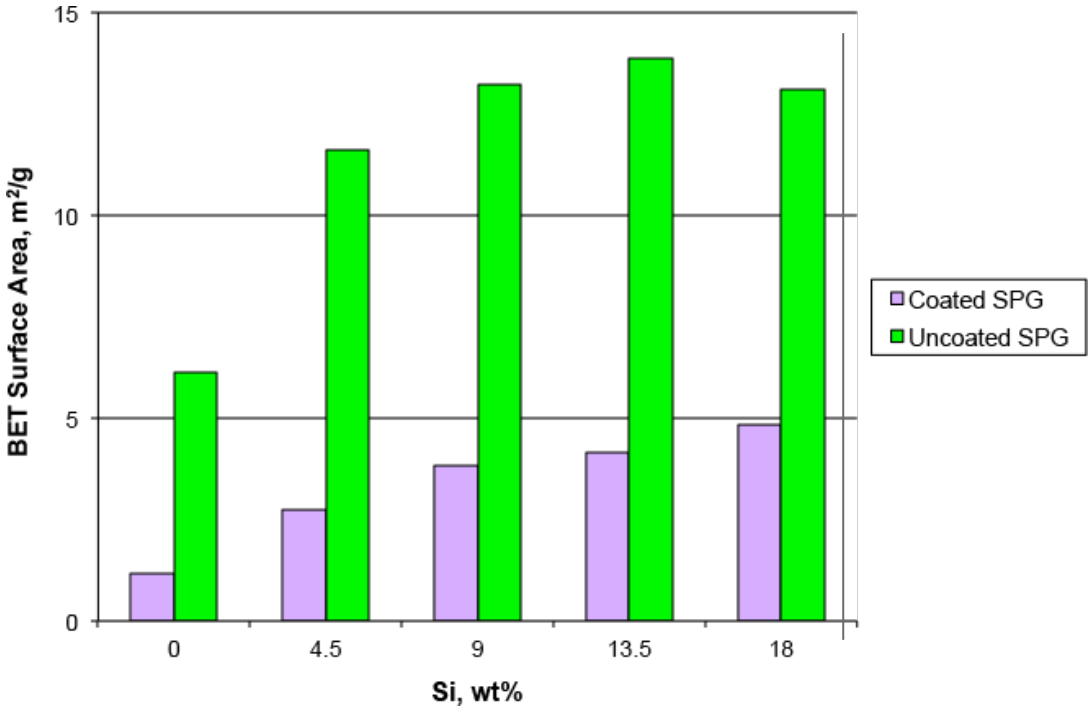
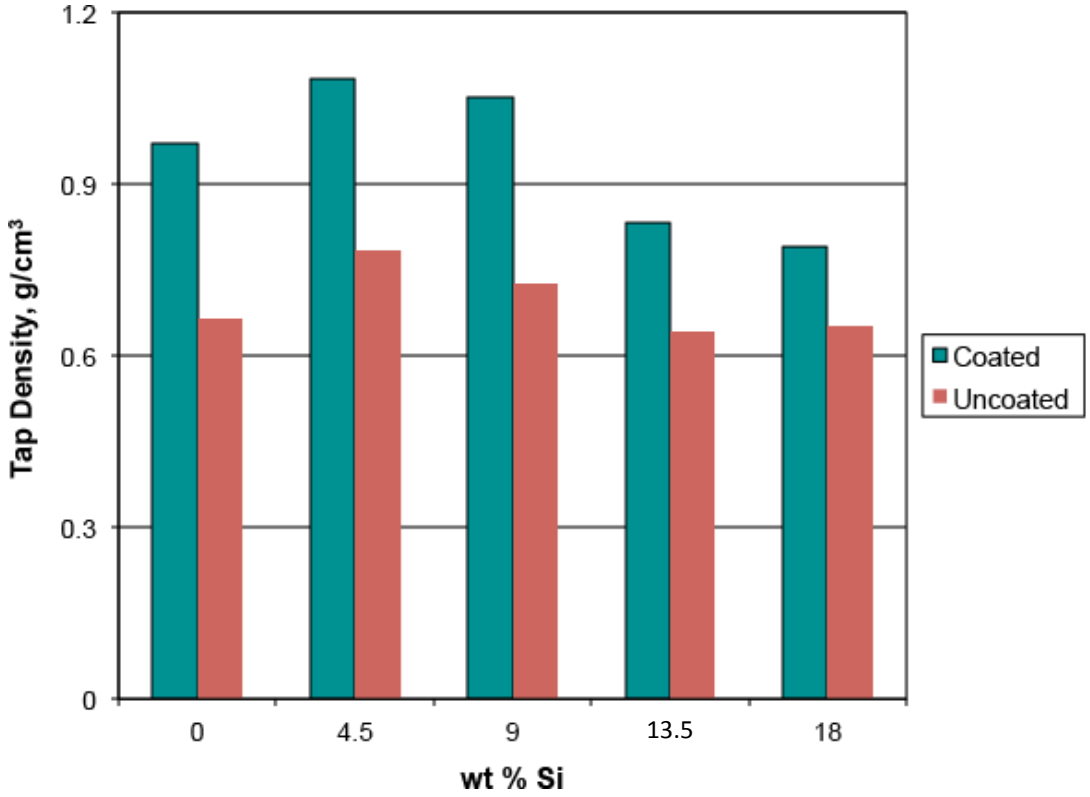
Fig. 7 EFFECT OF CARBON COATING ON SURFACE AREA OF Si ENHANCED SPG



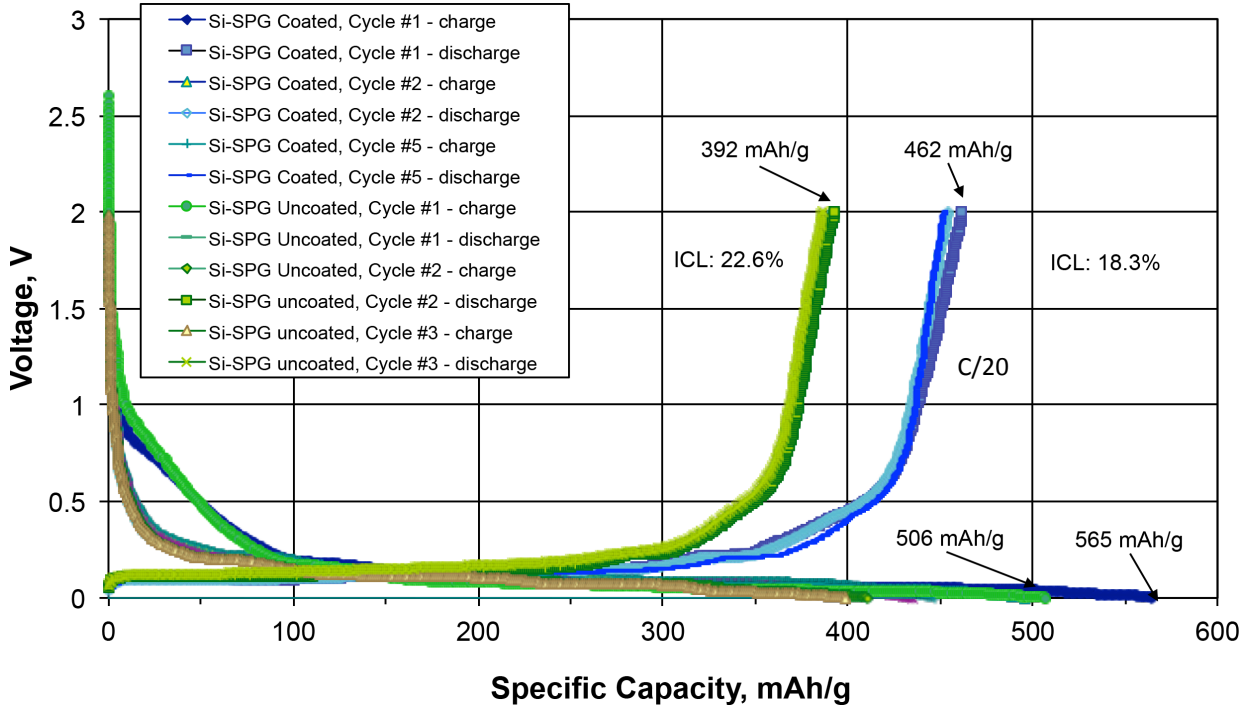
- Applying a carbon coating reduces the surface area of the SPG
- Target SA for graphite used in Li ion batteries is generally less than 4 m^2/g

Fig. 8 EFFECT OF Si ADDITION ON TAP DENSITY OF SPG



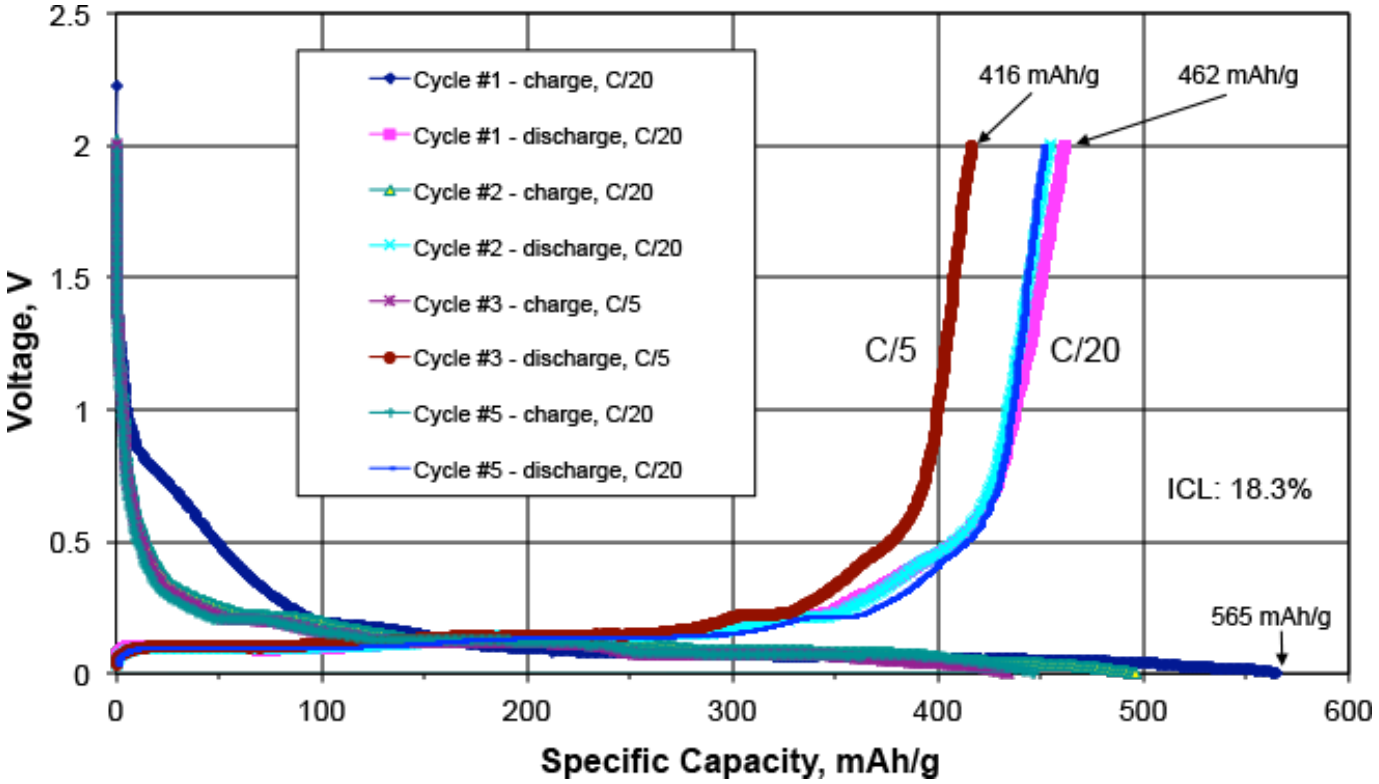
- Carbon Coating increases the tap density of both the Standard and Si-enhanced SPG
- Targeted tap density of 0.9 to 1.0 g/cc for coated SPG was achieved at Si levels up to 9 wt% Si

Fig. 9 GALVANOSTATIC CHARGE/DISCHARGE CURVES FOR CARBON COATED AND UNCOATED SPG AT 4.5 wt% Si ADDITION



- Coating the SPG with carbon increases the reversible capacity from 392 to 462 mAh/g which is 24% higher than the theoretical capacity of graphite alone.
- Carbon Coating also reduces the Irreversible Capacity Loss (ICL) from 22.6% to 18.3%

Fig. 10 GALVANOSTATIC CURVES FOR CARBON COATED SPG AT C/20 & C/5 RATES AT 4.5 wt% Si ADDITION



- Data shows highly stable cycling performance while changing cycling rates between C/20 and C/5

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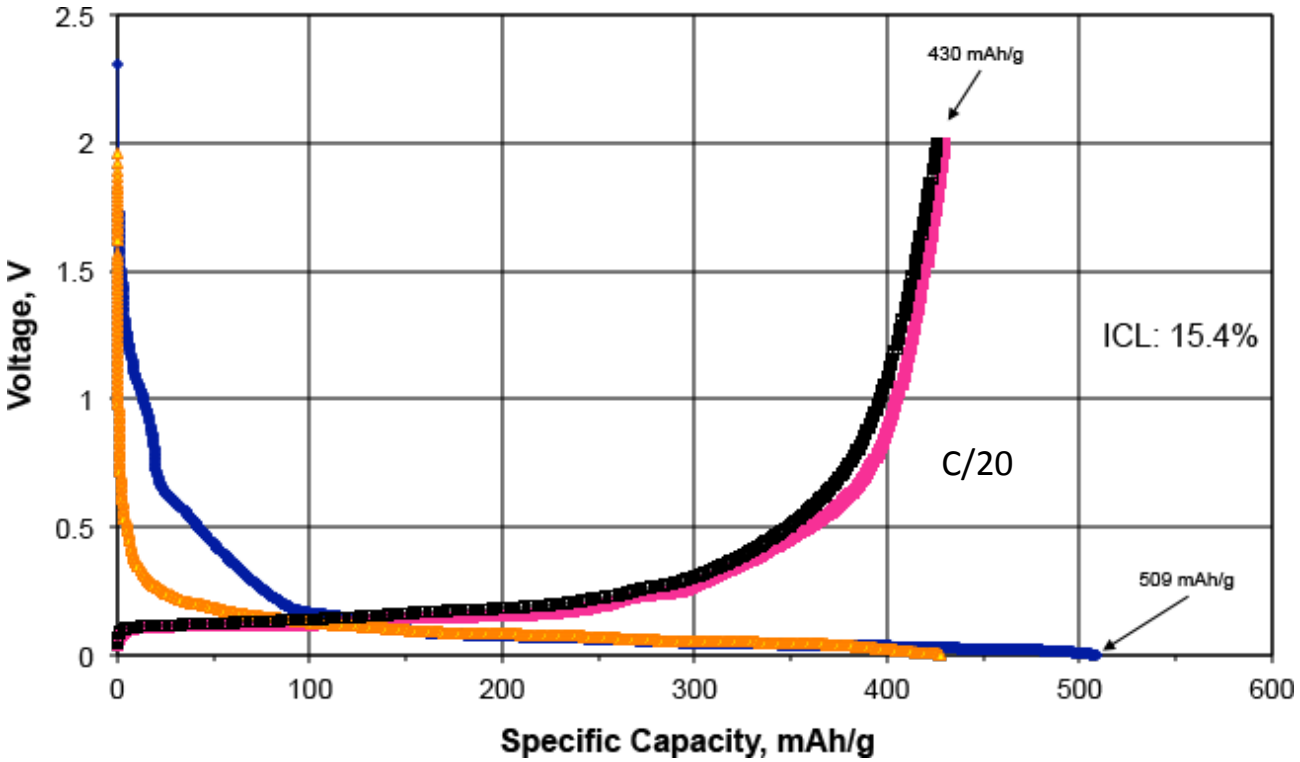
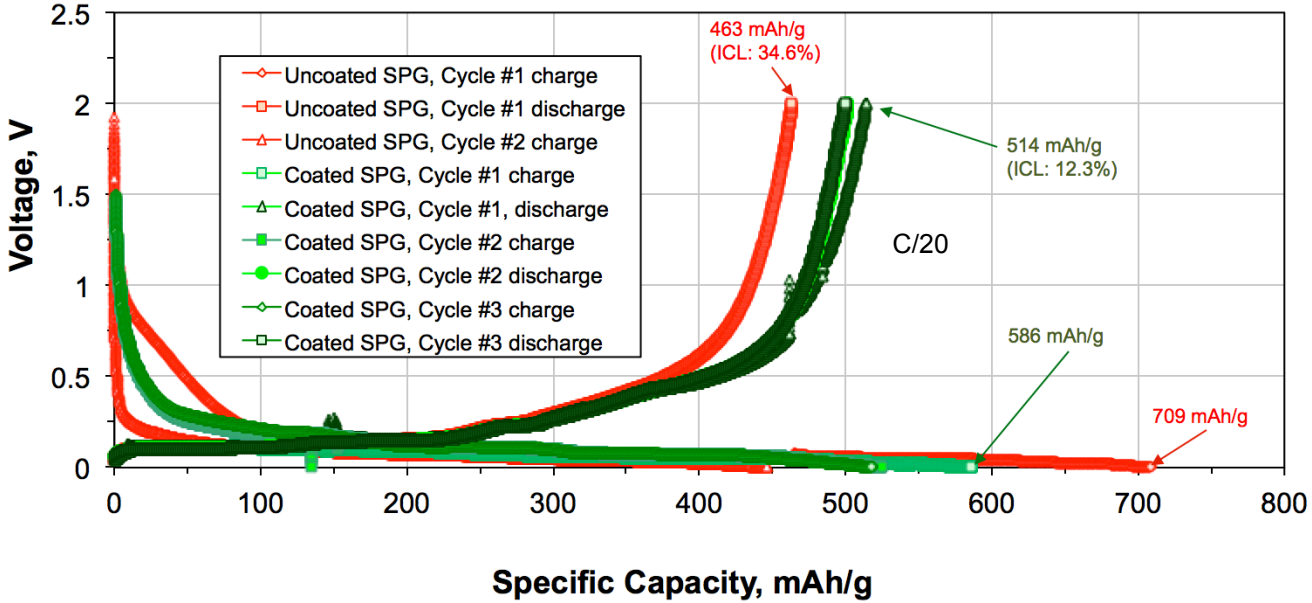
Fig. 11 GALVANOSTATIC CURVES FOR CARBON COATED SPG at 9 wt% Si ADDITION



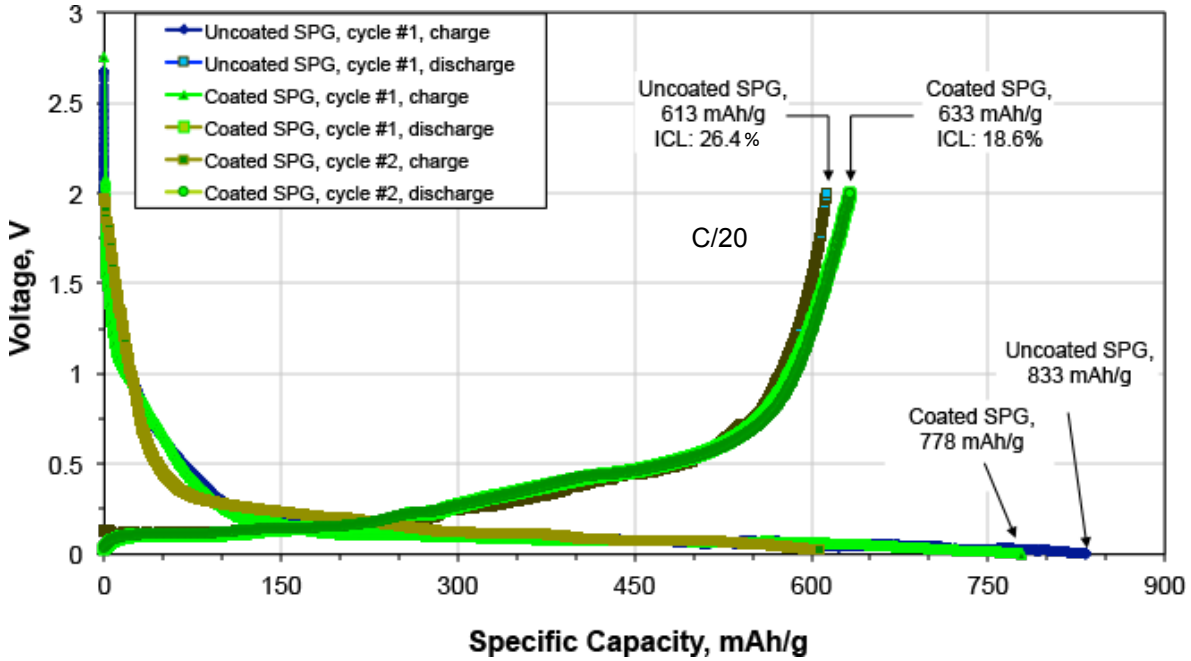
- Irreversible Capacity Loss (ICL) has been reduced to 15.4% compared with 18.3% for 4.5 wt% Si SPG

Fig. 12 GALVANOSTATIC CURVES FOR CARBON COATED AND UNCOATED SPG AT 13.5 wt% Si ADDITION



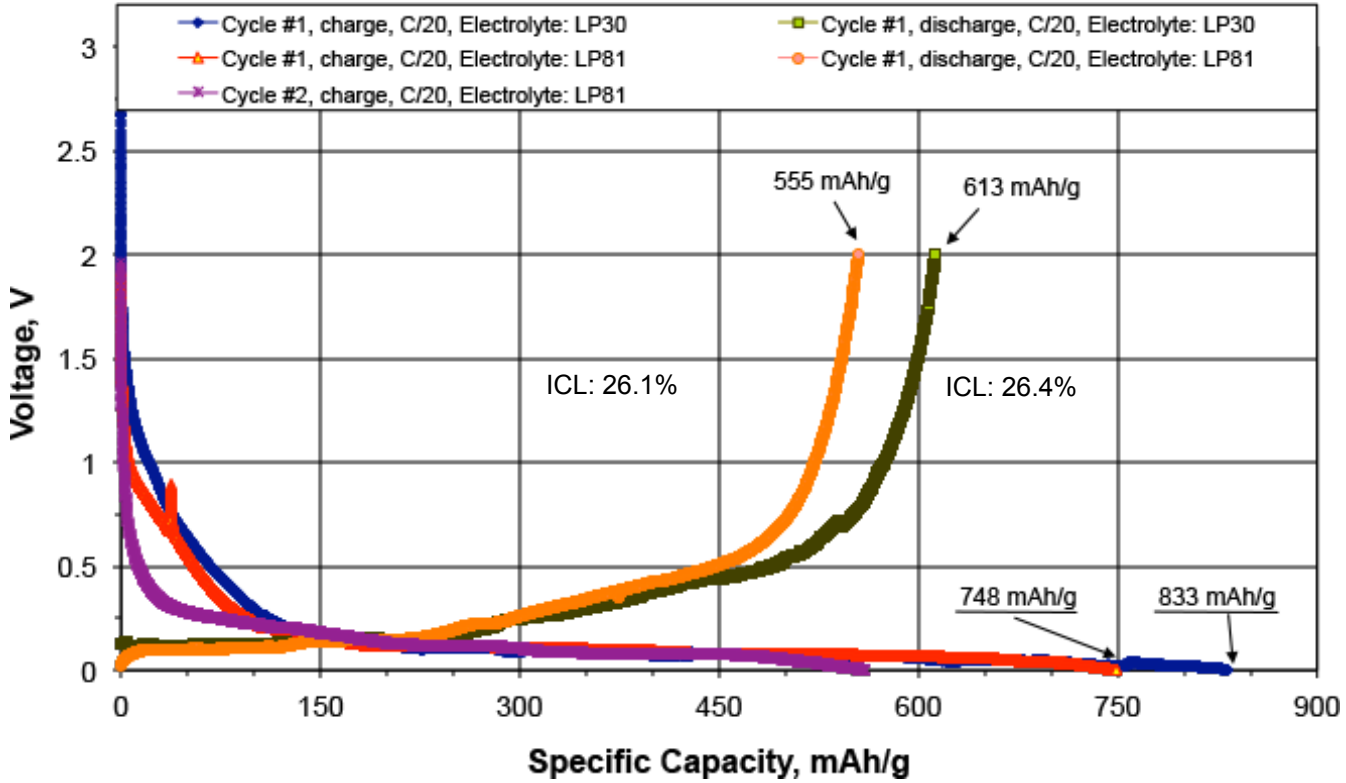
- Coating the SPG with carbon increases the Reversible Capacity from 463 to 514 mAh/g which is 38% higher than the theoretical capacity of graphite alone.
- Carbon coating also reduces the Irreversible Capacity Loss (ICL) from 34.6% to 12.3%

Fig. 13 GALVANOSTATIC CURVES FOR CARBON COATED AND UNCOATED SPG AT 18 wt% Si ADDITION



- Coating the SPG with carbon increases the Reversible Capacity from 613 to 633 mAh/g which is 70% higher than the theoretical capacity of graphite alone.
- Carbon coating also reduces the Irreversible Capacity Loss (ICL) from 26.4% to 18.6%

Fig. 14 EFFECT OF ELECTROLYTE ON THE GALVANOSTATIC CURVES FOR UNCOATED SPG AT 18 wt% Si ADDITION



- The use of LP 30 electrolyte increased the reversible capacity of the uncoated SPG from 555 to 613 mAh/g

FUTURE DEVELOPMENT WORK

- Alternative sources of silicon
- Optimize process for adding silicon to the SPG
- Optimize spheroidizing process
- Classifying and Sizing of SPG
- Alternative sources of carbons for coating the SPG
- Determine best electrolytes to use with Lac Knife SPG

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THANK YOU

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