Coulometrics

Lower Cost Higher Performance Graphite for LIBs

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President and CEO
Coulometrics, LLC.

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PUREgraphite

Outline

- Company overview
- Review of natural graphite resources and flake quality from 12 different locations in the world
- Graphite process development for anode materials
- Full cell testing of new graphite anode materials

Company Overview

- Advanced Energy Storage Consulting
  - Started 2011
    - Basic materials R&D
    - Manufacturing / scale-up
    - Systems integration

Company Overview

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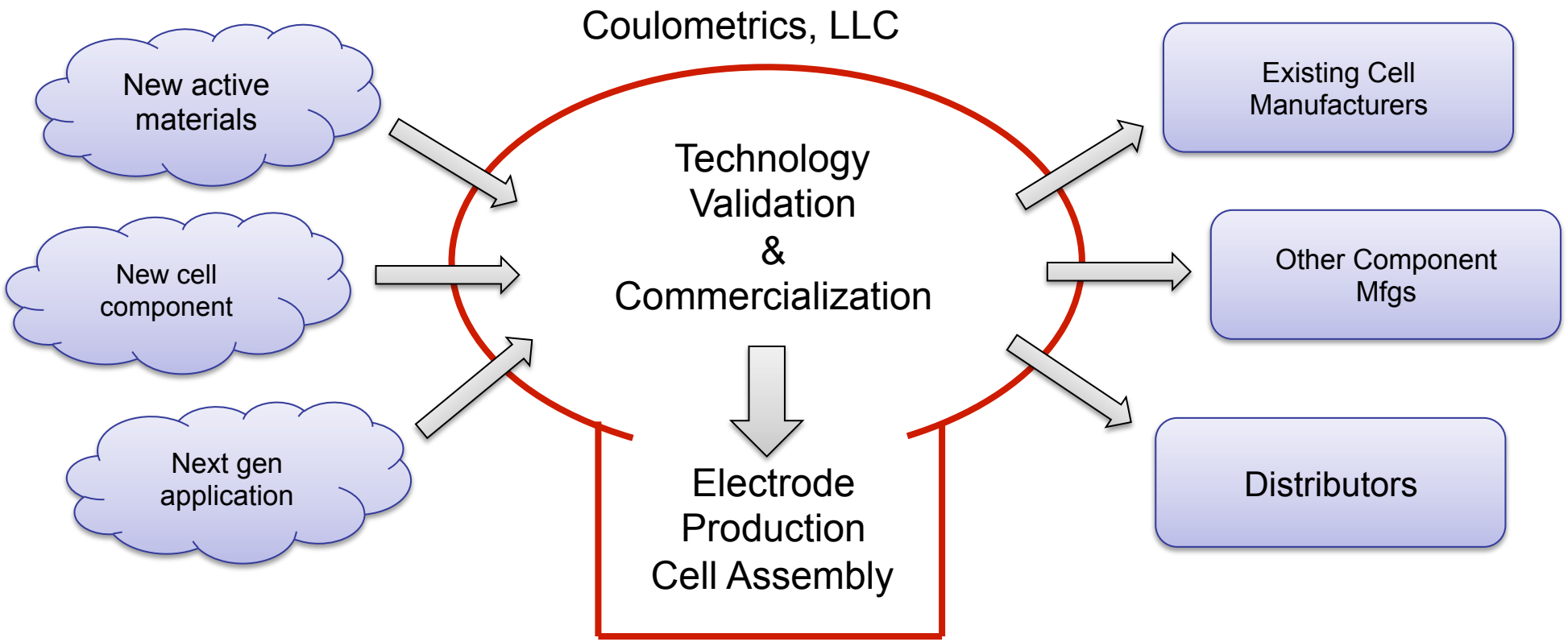
R&D → Scale Up → Market



Electrode Coating

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Pilot Scale Coating

Production Scale Coating

Calendering and Assembly

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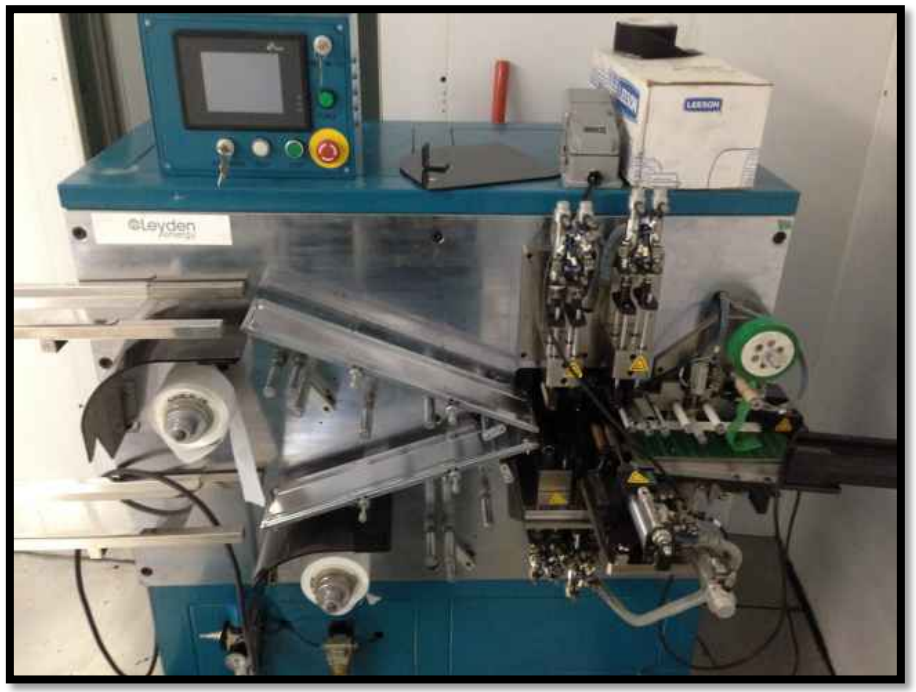
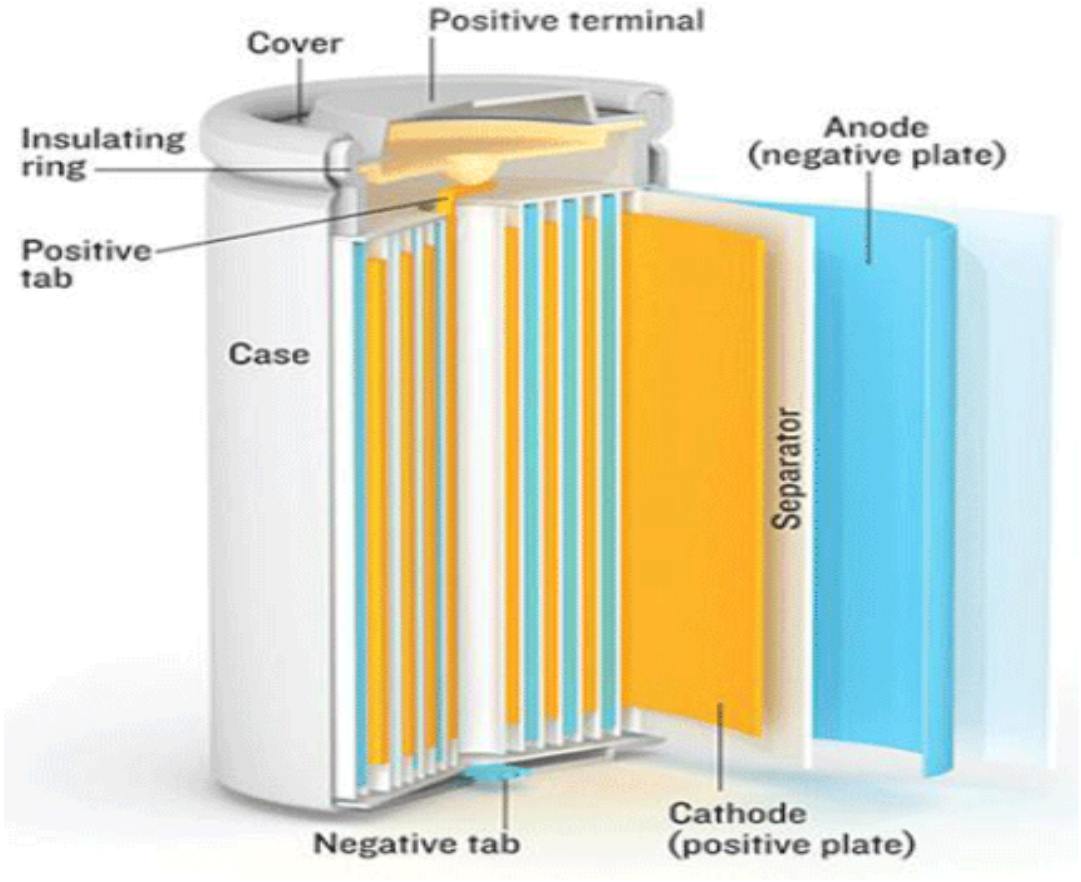
Electrode Roll Pressing

Cell Winding

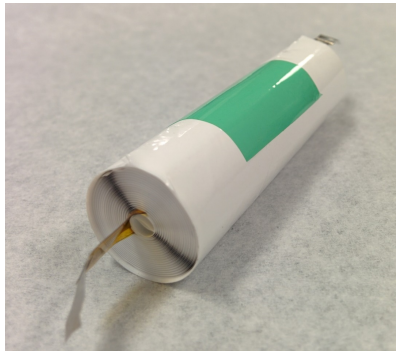


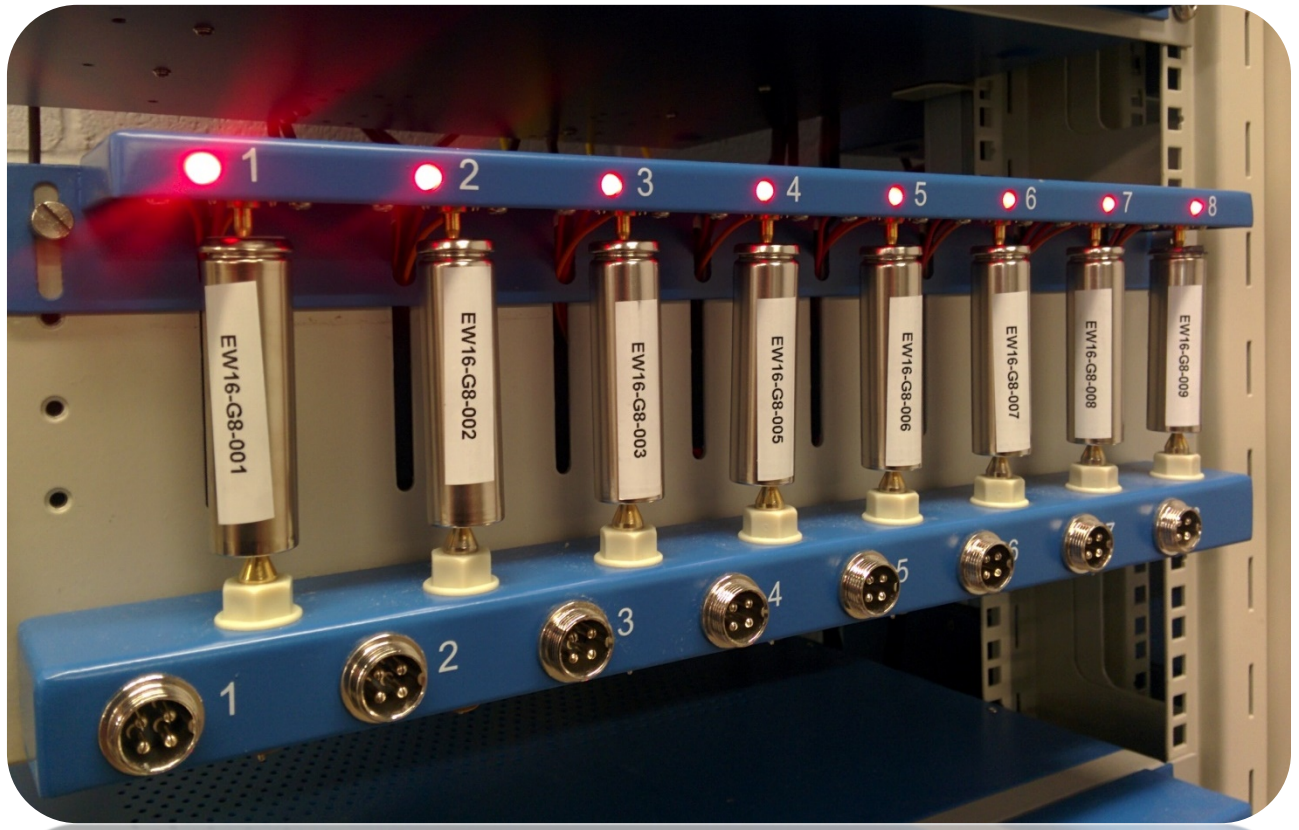
18650 Cell Assembly



Cell Testing

- 320 channels of Neware basic cyclers and formation
- 30 channels HPC
- 8 channels x 150A
- 2 channels x 500A





Natural Graphite Resources

- USGS:
  - World total inferred reserve of recoverably graphite: **800 Million Tonnes**
  - Current production: **1,200,000 tpy (flake and amorphous graphite)**
- Main uses
  - Refractory bricks and linings
  - Brake linings
  - Lubricants
  - Steel making
  - LIB anode materials
    - **70-80,000 tpy**

	Mine production 2014	2015[e]
United States	—	—
Brazil	80	80
Canada	30	30
China	780	780
India	170	170
Korea, North	30	30
Madagascar	5	5
Mexico	22	22
Norway	8	8
Russia	15	15
Sri Lanka	4	4
Turkey	29	32
Ukraine	5	5
Zimbabwe	7	7
Other countries	1	1
World total (rounded)	1,190	1,190

Natural Graphite Resources

- Large reserves of graphite with companies actively working to develop the resource
- Coulometrics has worked with about a dozen sources all over the world to sample and test the flake

Rigorous Flake Concentrate Analysis

- **FLAKE ANALYSIS TESTING:**
- Sieve samples to sizes shown in Table below.
  - +50, 50x100, 100x200, 200x400, 400x635, -635 mesh
  - Measure masses to get flake size distribution (Table 1)
  - Tap Density and LOI (Table 2)
  - Measure BET (Table 3)
- Grind samples to -635 mesh
  - Repeat BET
  - Add BET graph to report with both sieved and sieved/ground BET data
  - Complete XRD
  - Complete ash analysis on materials.
  - Send samples for PIXE Analysis.
  - EChem: Complete slurry, electrodes, coin cells, testing

Sieve the Graphite Flake Concentrate Into 6 Different Sizes

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Coulometrics Control #	Flake Size (mesh)	Particle Size (mm)	Mass in Sieve (g)	Size Fraction (%)
G16-0114	+50	0.300	0	0%
	50x100	0.300-0.150	0	0%
	100x200	0.150-0.075	7.66	3.4%
	200x400	0.074-0.037	56.76	25.4%
	400x635	0.037-0.020	98.98	44.2%
	-635	0.020	60.41	27.0%

G16-0114
GSP Ore, Graphite Concentrate
Tap & Ash Analysis

ID#	Flake Size (mesh)	Tap Density (g/cc)	**Size Fraction (%)**	**LOI – Ash Content** (% carbon)	**BET SA (As Received)**	**BET SA (Grnd to -635)**
				Average	Avg. (m^2/g)	Avg. (m^2/g)
G16-0114	As Received	0.53	NA	96.43	**5.36**	**6.04**
	+50	NA	0%		NA	
	50x100	NA	0%		NA	
	100x200	0.48	3.4%	97.80	**3.40**	**6.55**
	200x400	0.45	25.4%	97.53	**4.15**	**6.01**
	400x635	0.41	44.2%	96.95	**5.08**	**6.95**
	-635	0.40	27.0%	93.99	**6.33**	**N/A**

G16-0114
GSP Ore, Graphite Concentrate
PIXE Impurity Analysis

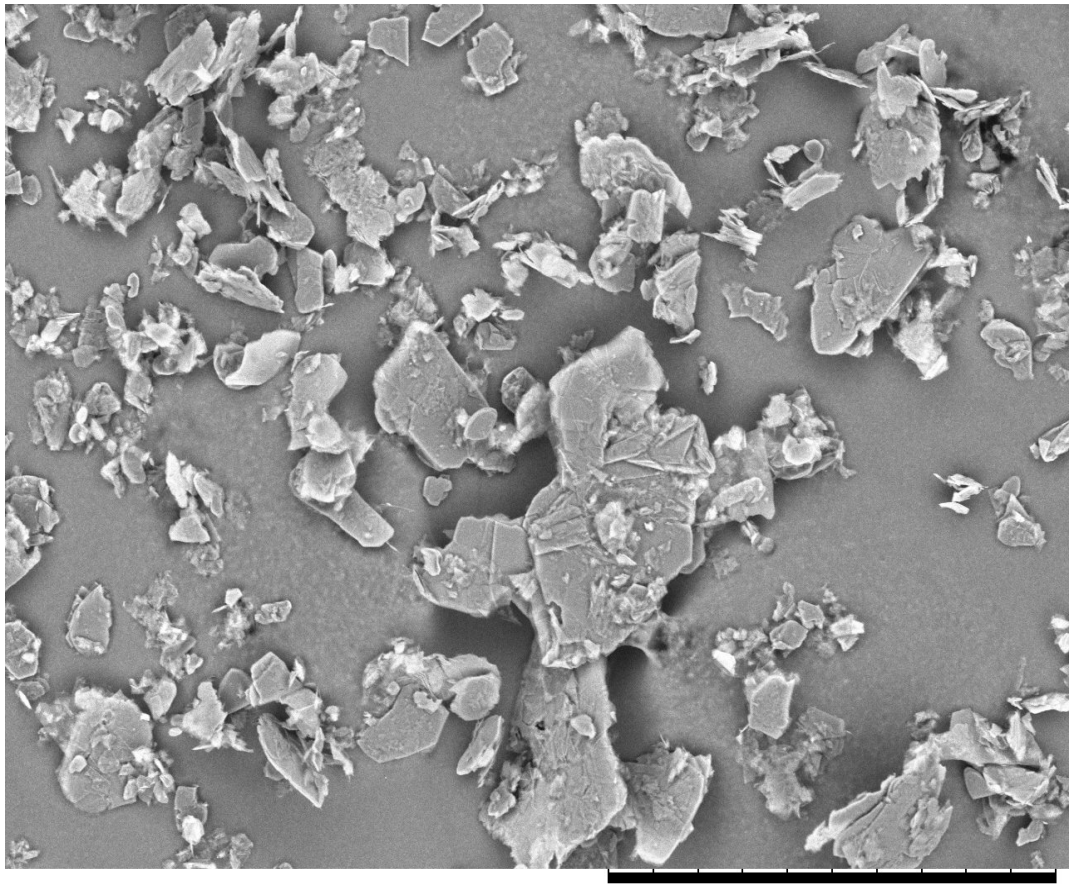
- Significant Impurities including:
  - S (4560ppm)
  - Si (7690ppm)
  - Fe (2400 ppm)
  - Al (3840ppm)

Carbon ID	Description	Na	Mg	Al	Si	P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
G16-0114	Graphite Corp	367	327	3840	7690		4560	62	976	167		156		37	6	2400		21	107

Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Tc	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb
10	1		3		5	10			8		36																					

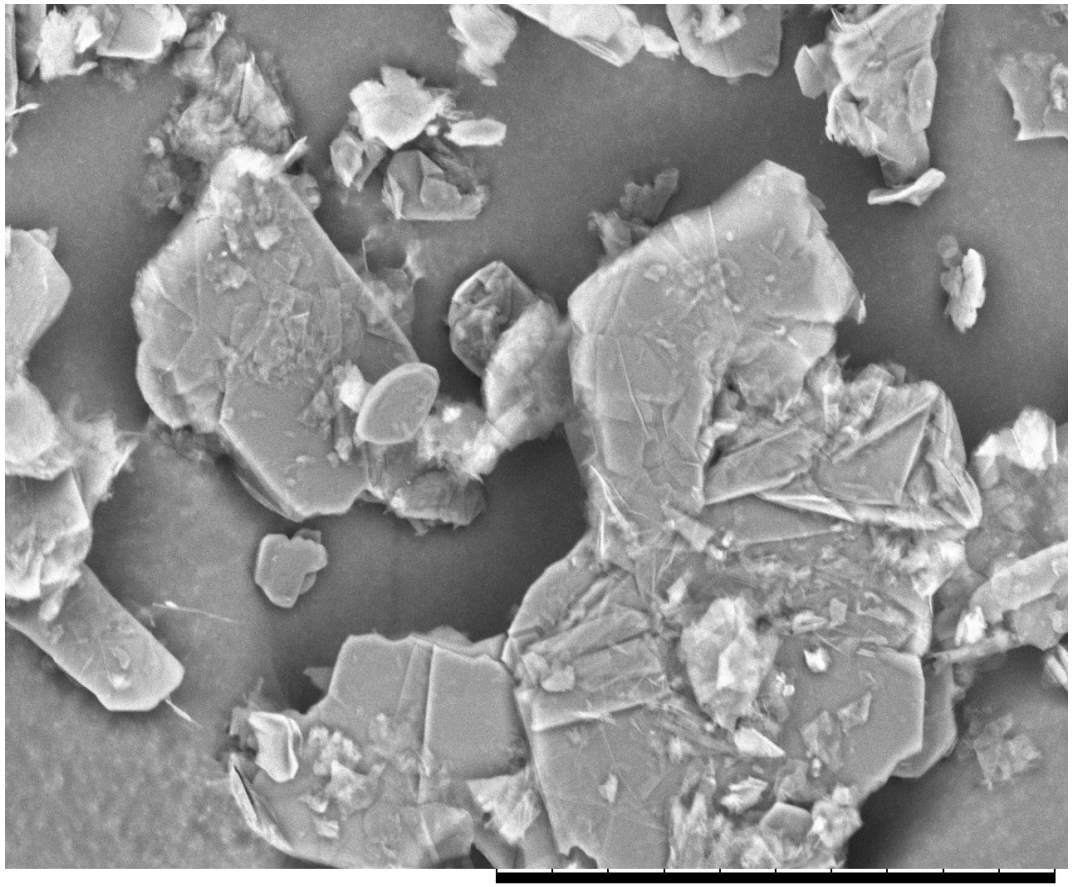
Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U	**Total - ppm**
																				20789

G16-0114
Graphitized GSP Ore
SEM Analysis – 1000X



G16-0159-0002 2016/12/15 14:28 D5.0 x400 200 um

Coulometrics, LLC.



G16-0159-0003 2016/12/15 14:29 D5.0 x1.0k 100 um

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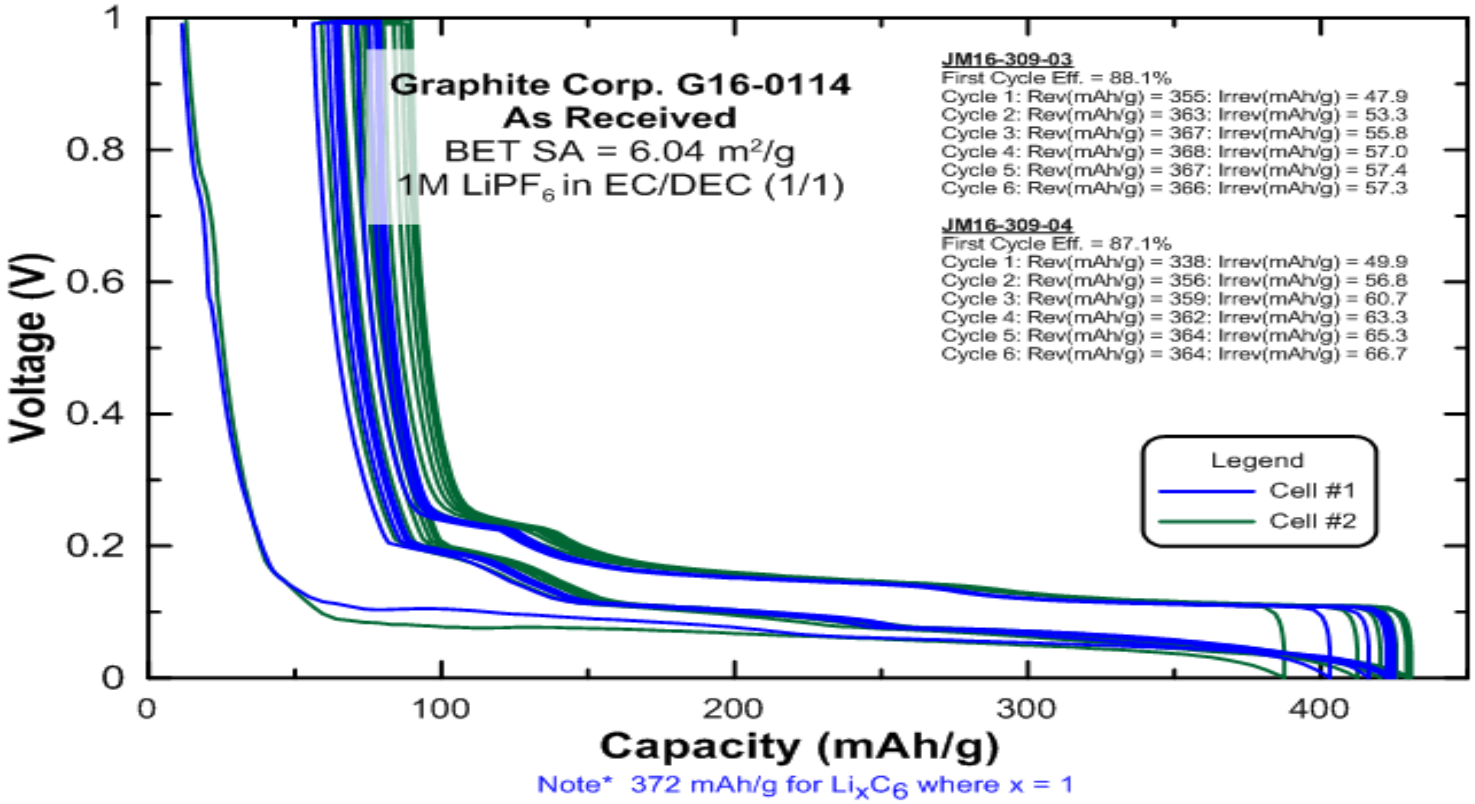
G16-0114: As Received Electrode Preparation

- Electrode Mixing Information:
  - Active material (G16-0114): 92.0%
  - Conductive carbon (SFG-6L): 2.0%
  - Binder (Kynar HSV900/NMP): 6.0%

- Electrode Properties
  - Active mass: 92.0%
  - Loading: 13.76 mg/cm^2
  - Calendered Density: 1.700 g/cc

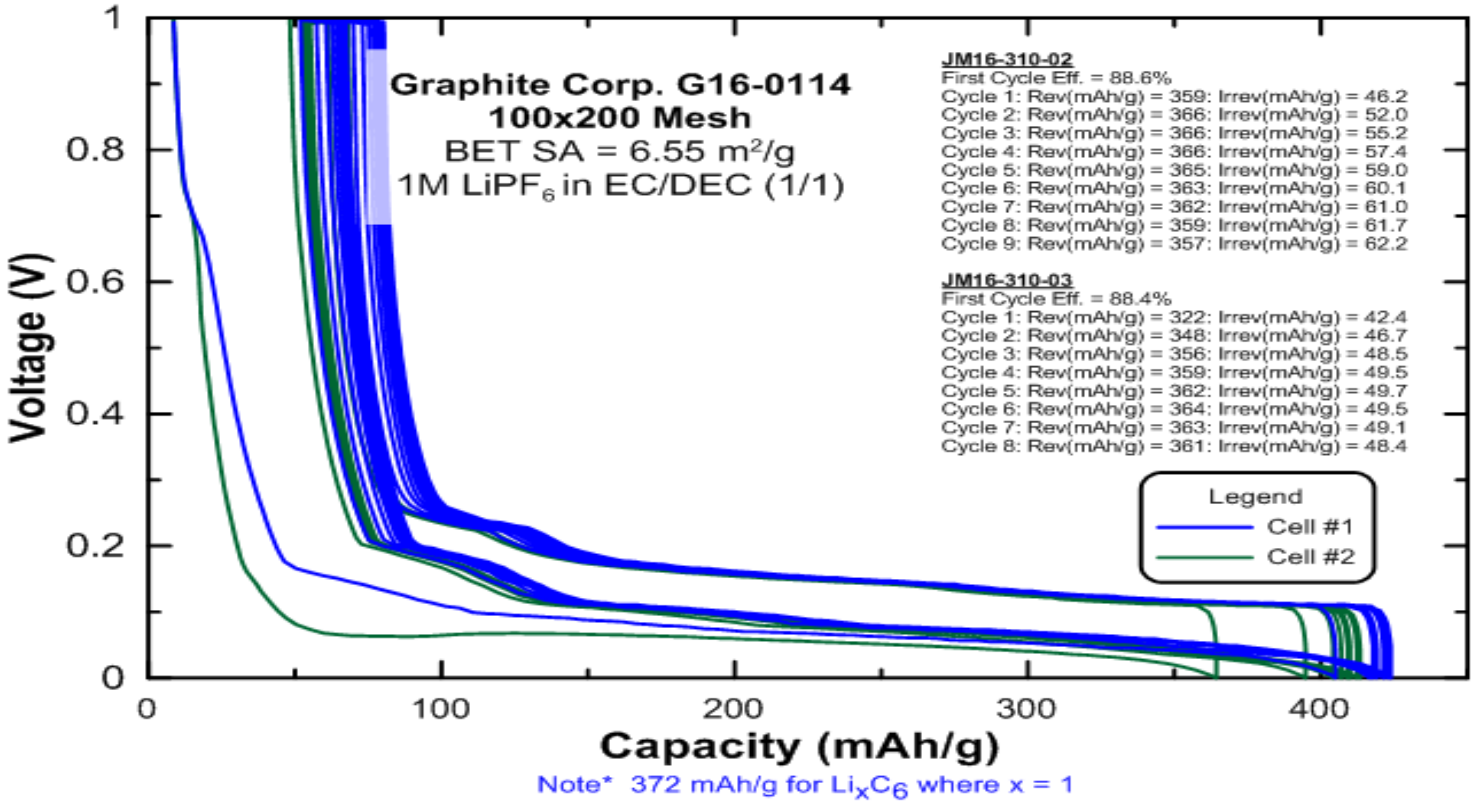
G16-0114: As Received
1M $LiPF_6$ in EC/DEC (1:1) Additives: None
Electrochemical Data

- C/20 cycling
  - Rev. Cap
    - 359 mAh/g
  - Irrev. Cap.
    - 48 mAh/g
  - First cycle efficiency
    - 87.6%



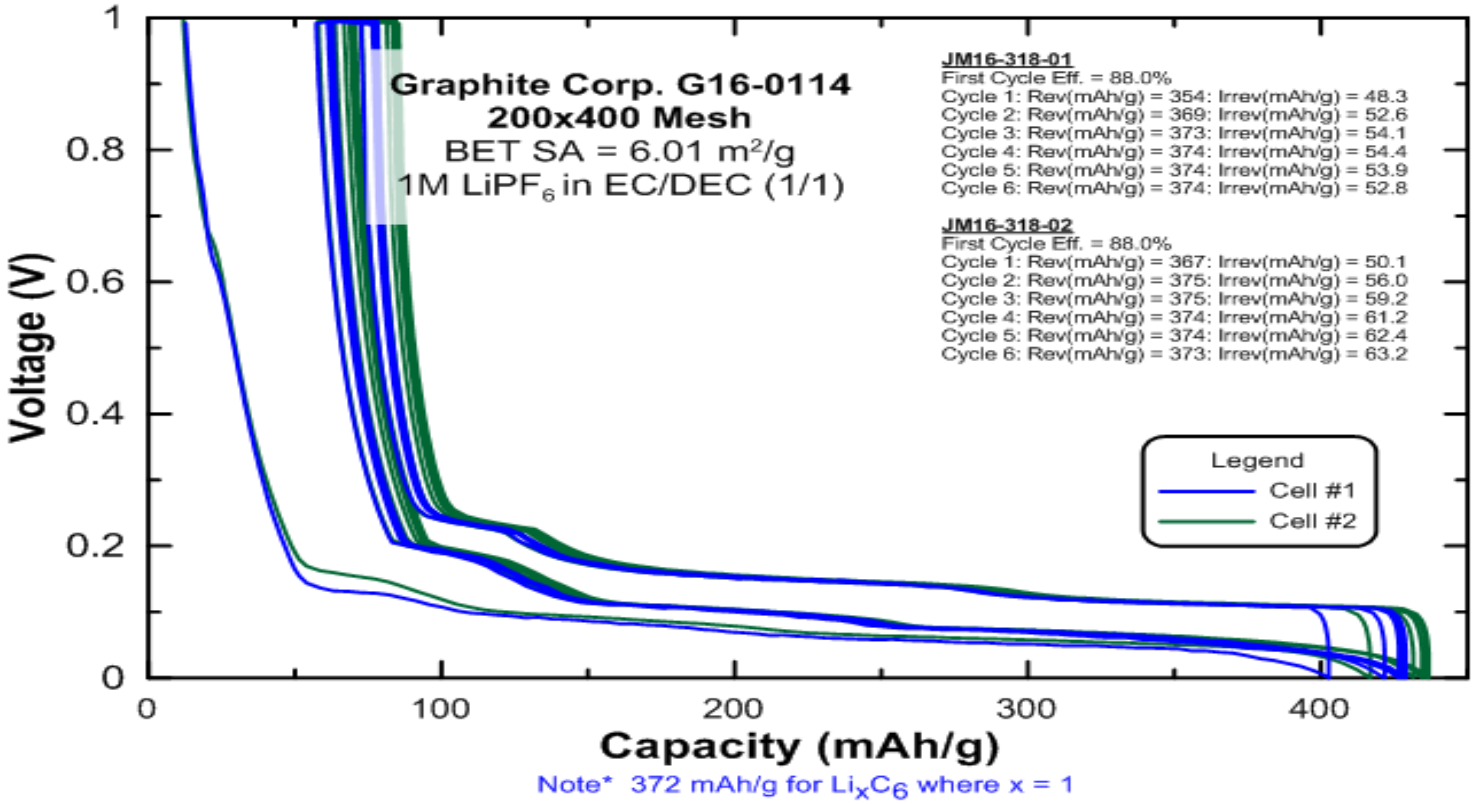
G16-0114: 100x200 Mesh
1M $LiPF_6$ in EC/DEC (1:1) Additives: None
Electrochemical Data

- C/20 cycling
  - Rev. Cap
    - 358 mAh/g
  - Irrev. Cap.
    - 42.4 - 46.2 mAh/g
  - First cycle efficiency
    - 88.5%



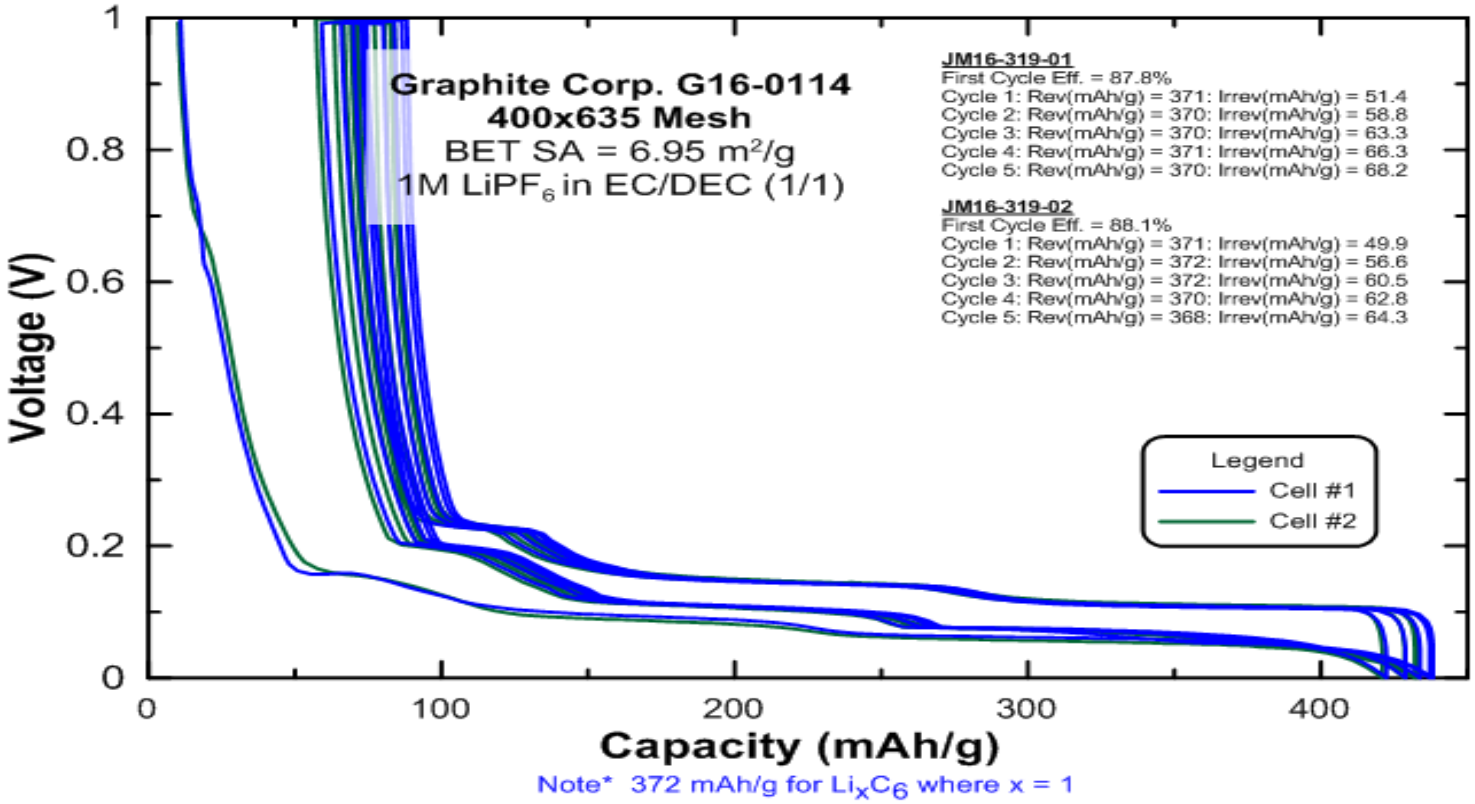
G16-0114: 200x400 Mesh
1M $LiPF_6$ in EC/DEC (1:1) Additives: None
Electrochemical Data

- C/20 cycling
  - Rev. Cap
    - 367 mAh/g
  - Irrev. Cap.
    - 48.3 - 50.1 mAh/g
  - First cycle efficiency
    - 88.0%



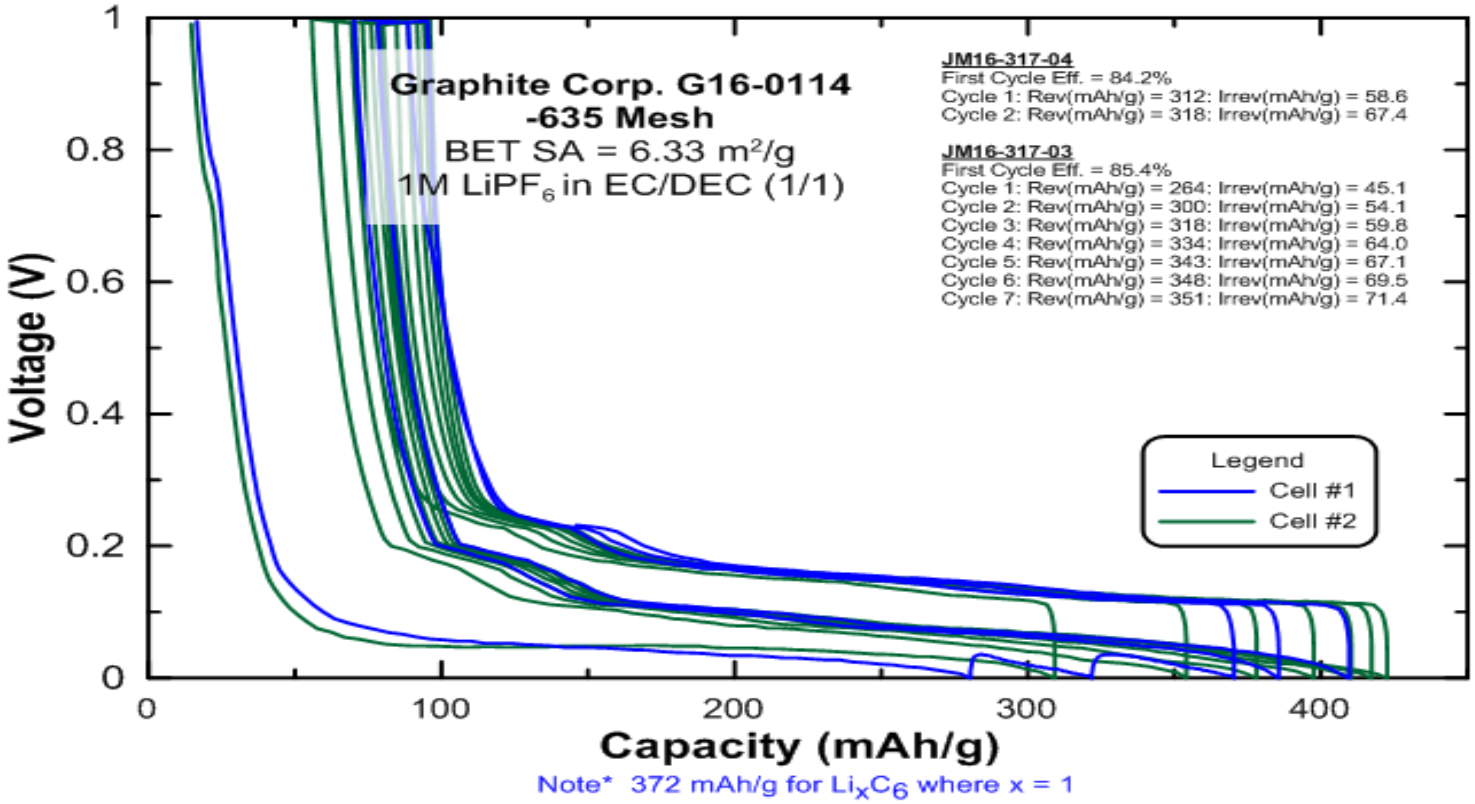
G16-0114: 400x635 Mesh
1M $LiPF_6$ in EC/DEC (1:1) Additives: None
Electrochemical Data

- C/20 cycling
  - Rev. Cap
    - 365 mAh/g
  - Irrev. Cap.
    - 49.9 - 51.4 mAh/g
  - First cycle efficiency
    - 88.0%



G16-0114: -635 Mesh
1M $LiPF_6$ in EC/DEC (1:1) Additives: None
Electrochemical Data

- C/20 cycling
  - Rev. Cap
    - 344 mAh/g
  - Irrev. Cap.
    - 59.6 mAh/g
  - First cycle efficiency
    - 84.2 %



G16-0114
GSP Ore, Graphite Concentrate
Electrochemical Data Summary

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ID#	Flake Size Ground to -635 mesh	eChem Results		
		Rev. Capacity (mAh/g)	Irrev. Capacity (mAh/g)	First Cycle Efficiency (%)
G16-0114	As Received	359	47.9	88.1
	+50	Not enough material after sieving		
	50x100	Not enough material after sieving		
	100x200	358	42.4	88.6
	200x400	367	48.3	88.0
	400x635	365	49.9	88.1
	-635	344	58.6	85.4

Note: Numbers subject to change as cells cycle more.

Natural Graphite Resources

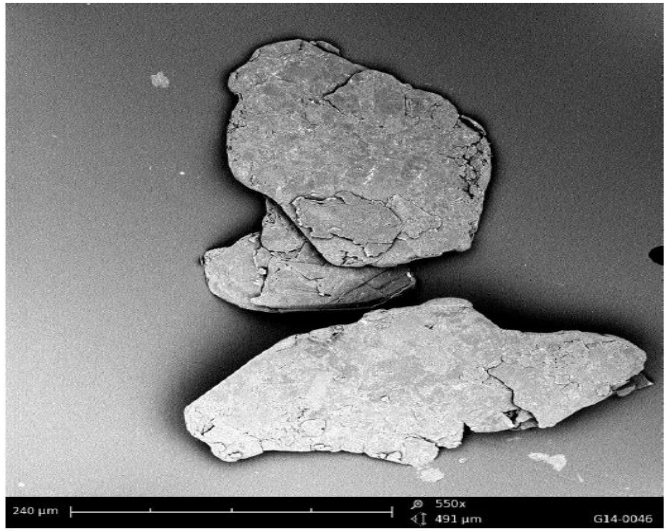
- Repeated for 12 different deposits from junior mines all over the world
- All deposits showed similar results
  - 94-98% purity
  - Rev capacity 355-365 mAh/g
  - Range of flake sizes

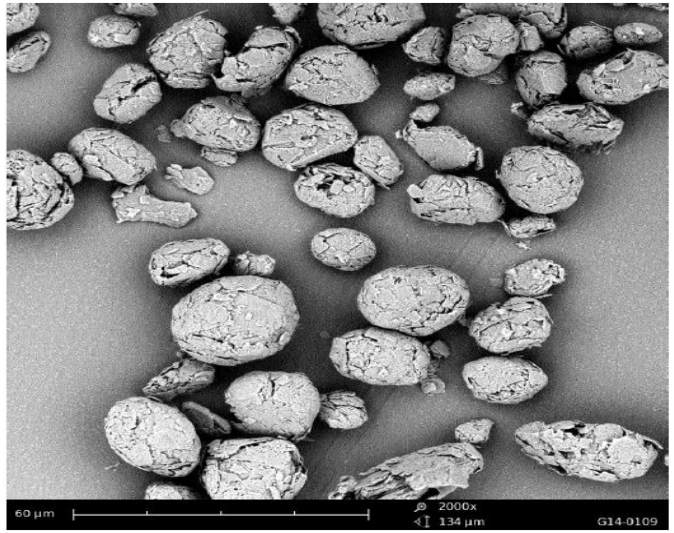
Graphite Process Development

- Standard Process used in China Today (95% of worlds Natural Graphite)
  - Flake Concentrate
  - Spheronize Graphite
  - Acid purification process
    - $HF/HCl/H_2SO_4$
  - Pitch coating
  - Calcination
- New Process (more suitable for use in the United State)
  - Flake Concentrate
  - Spheronize Graphite
  - Thermal Purification
  - CVD Coating

Spherical Carbon Process Development

- Spheronizing
- Purification
- Coating





Thermal Purification Temperature: 2600-2950°C PIXE Analysis

- Significant Impurities including:
  - Al, Si, and Mo : 15 - 50ppm
  - Al (50ppm), Si (22ppm), Mo (15ppm)
  - Fe <10ppm
  - Ni <5ppm
  - V <10ppm

Ash Test = 99.99% Carbon

Before:

After:

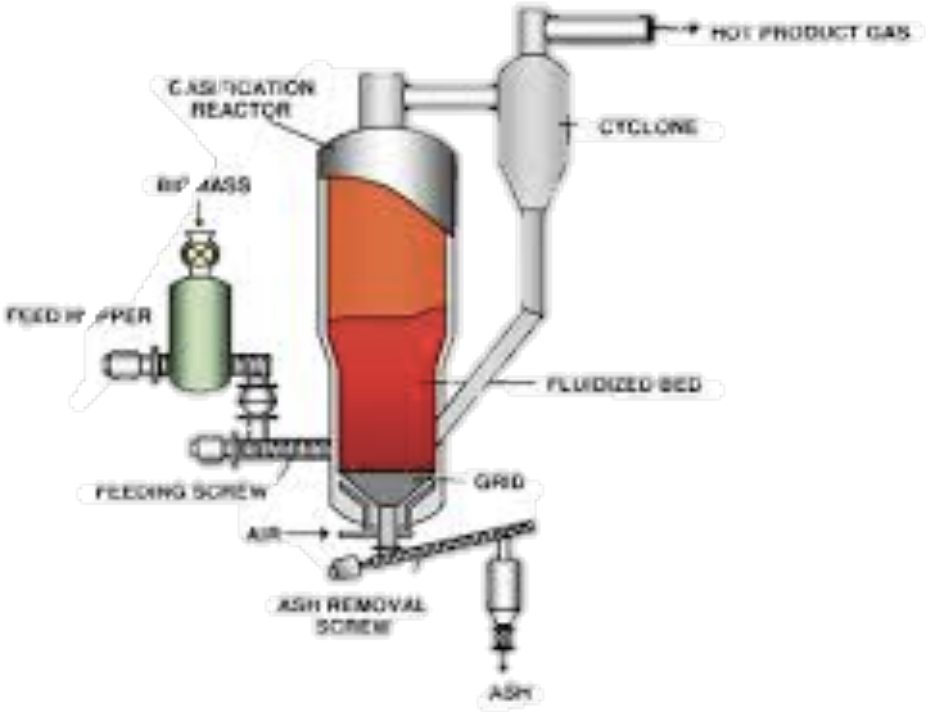
Carbon ID	Description	Na	Mg	Al	Si	P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
G16-0159	Graphite Corp PF			50	22								8			5		1.8	

Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Tc	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb
											15																					

Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U	Total - ppm
																				101.8

CVD Coating

- Reduce surface area
- Eliminate functional groups



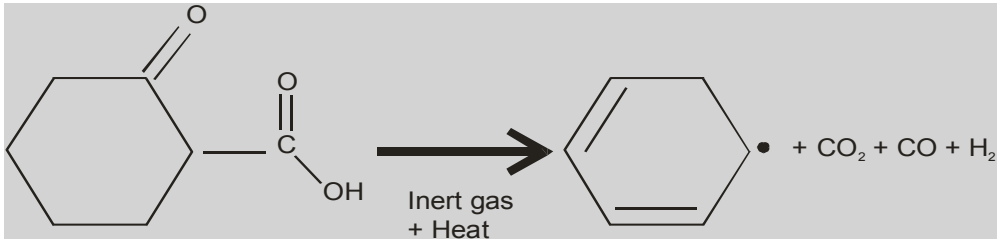


Figure 1: Heat treatment process used to eliminate surface functional

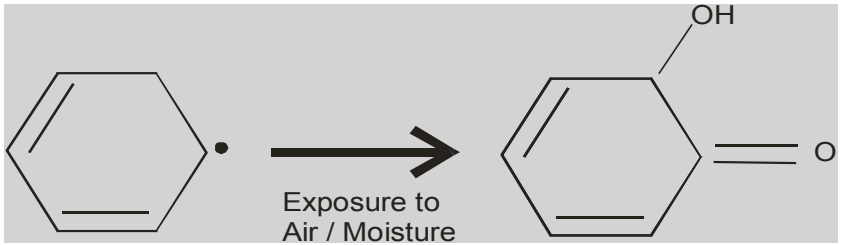
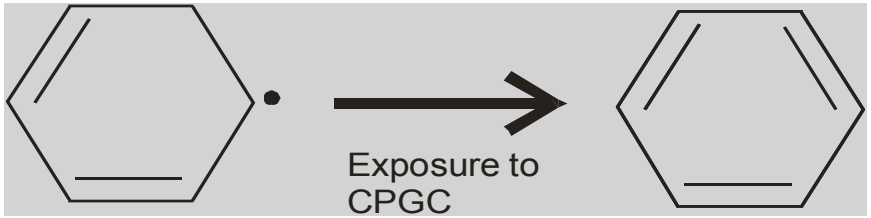


Figure 2: Residual carbon radicals react to form OH and O containing and are the source of H_2O in the cell.



Natural Graphite Product

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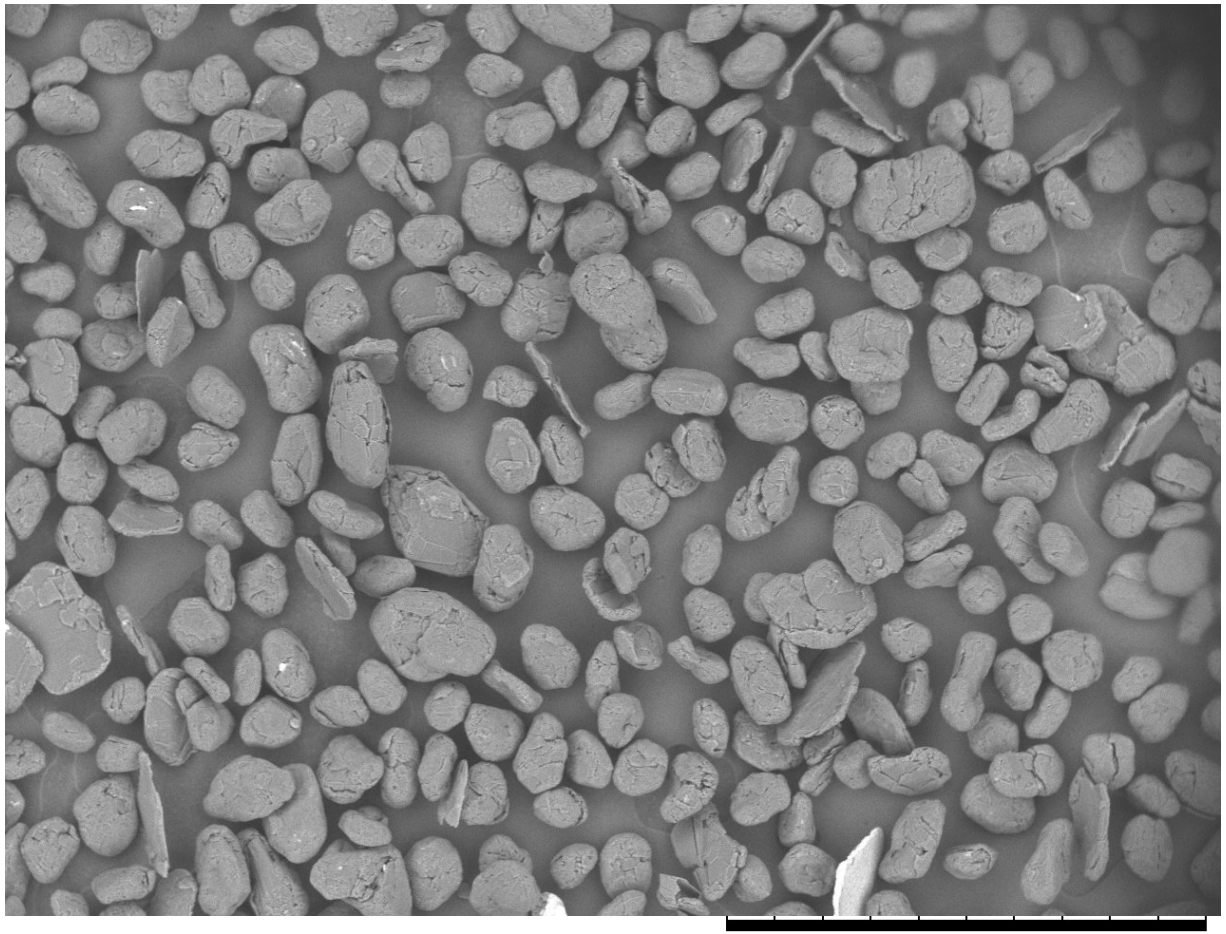
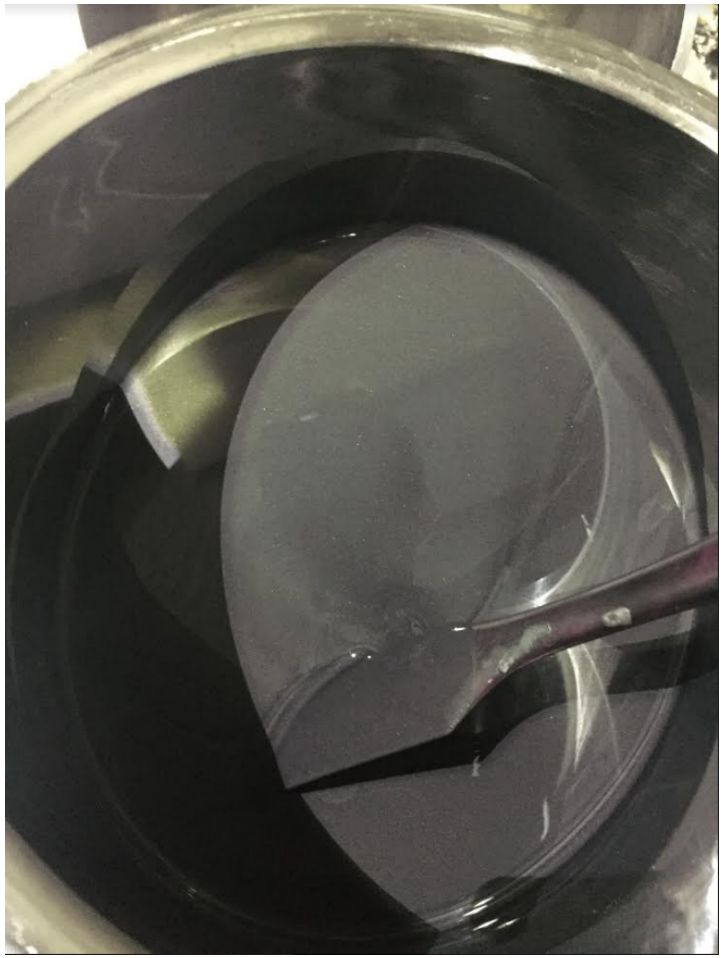
ID	Analysis	Value	Units
G16-0114	Tap Density	1.06	g/cc
	BET Avg.	3.73	m^2/g
	D_{10}	11.09	µm
	D_{50}	20.38	
	D_{90}	32.17	
	LOI – Ash Content	>99.995	% Carbon
	Capacity	365	mAh/g
	1st Cycle Efficiency	94	%



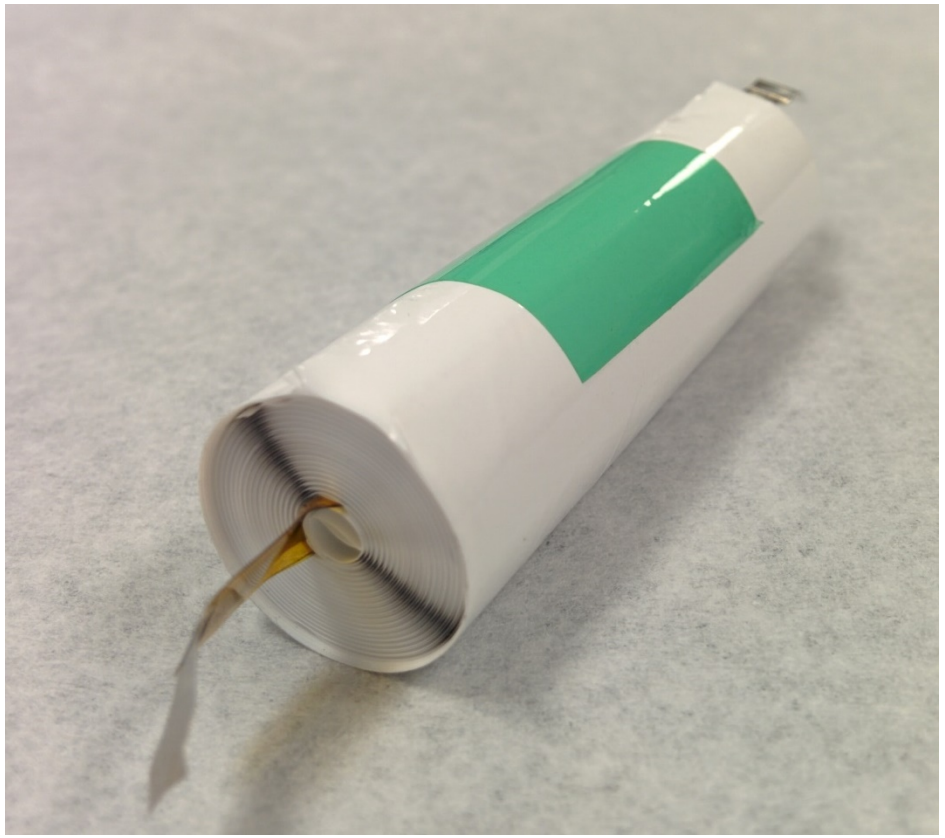
Slurry Development

- Mix graphite with conductive additives to develop a slurry suitable for slot-die coating
- Properties:
  - Carbon black must be well dispersed
  - Good stable dispersion
  - No agglomeration
- **Stable dispersions** are developed for each graphite material regardless of how long it takes



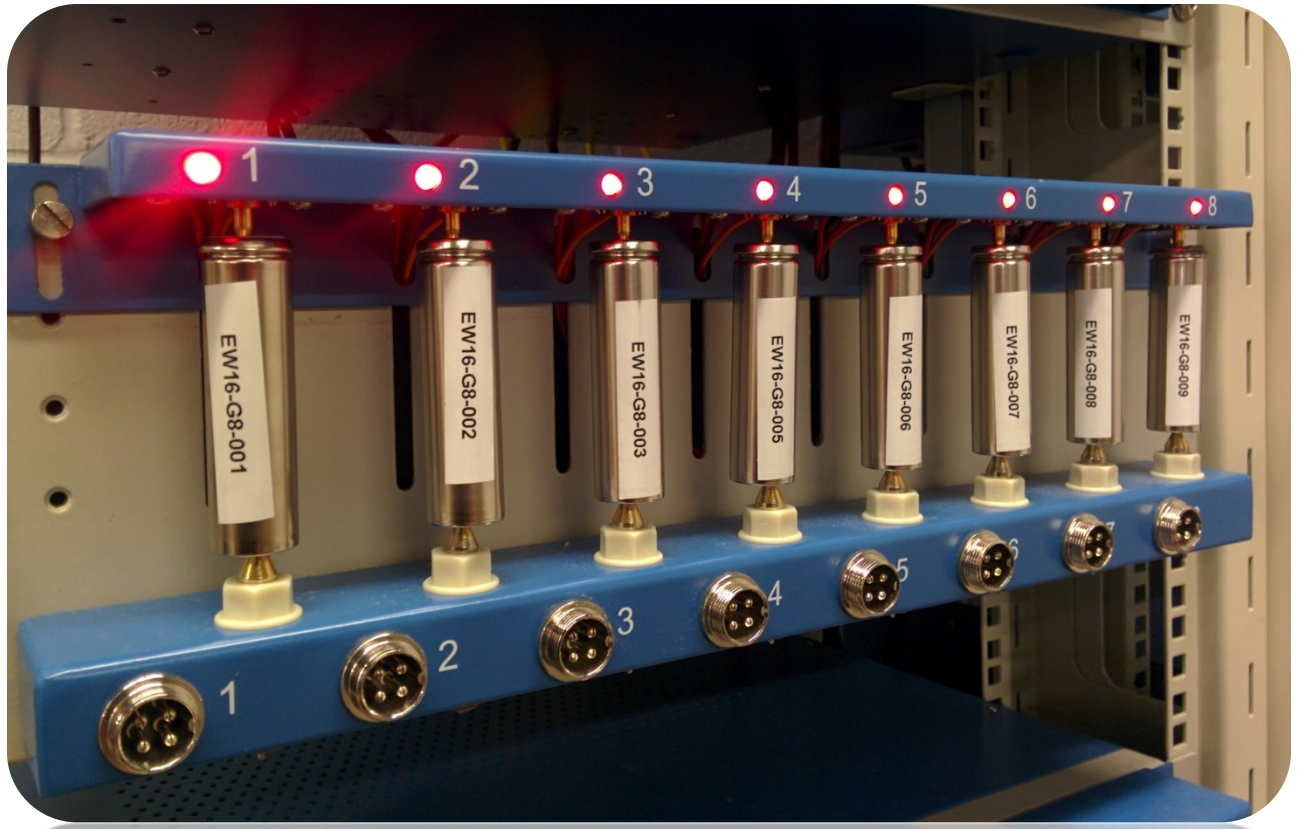
Cell Assembly and Testing

- 18650 batteries are assembled
- Cathode:
  - NMC 111
- Electrolyte
  - EC/EMC 3:7 + 1M $LiPF_6$
  - Additives:
    - Standard LIB Additives
    - Coulometrics proprietary additives for improved SEI layer formation and improved life
- Typical capacity:
  - 2.2-2.4 Ah



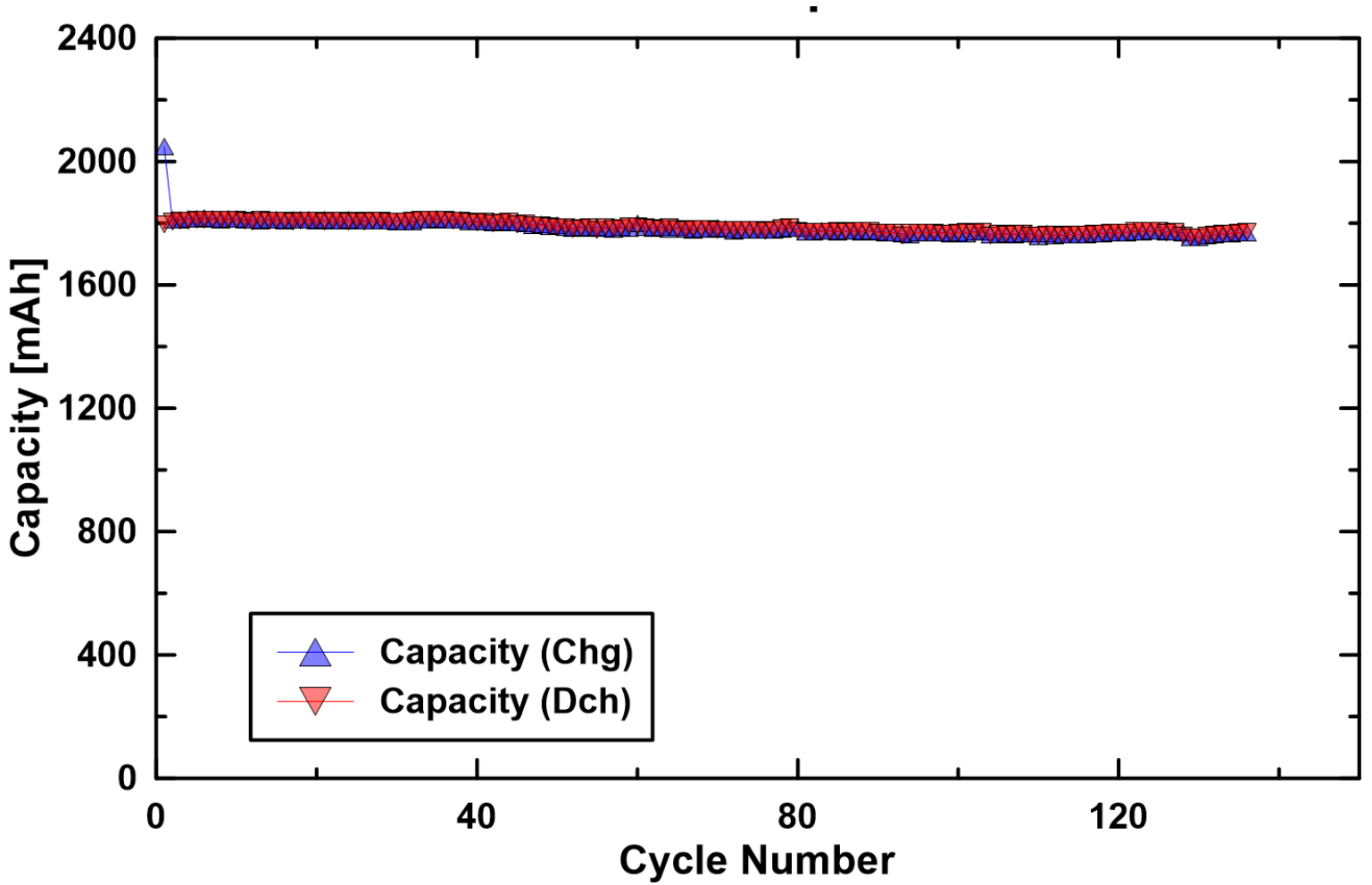
Cell Testing

- Initial formation is completed using Neware system
- Cell capacity is measured
- Cell is cycled 5-10 times



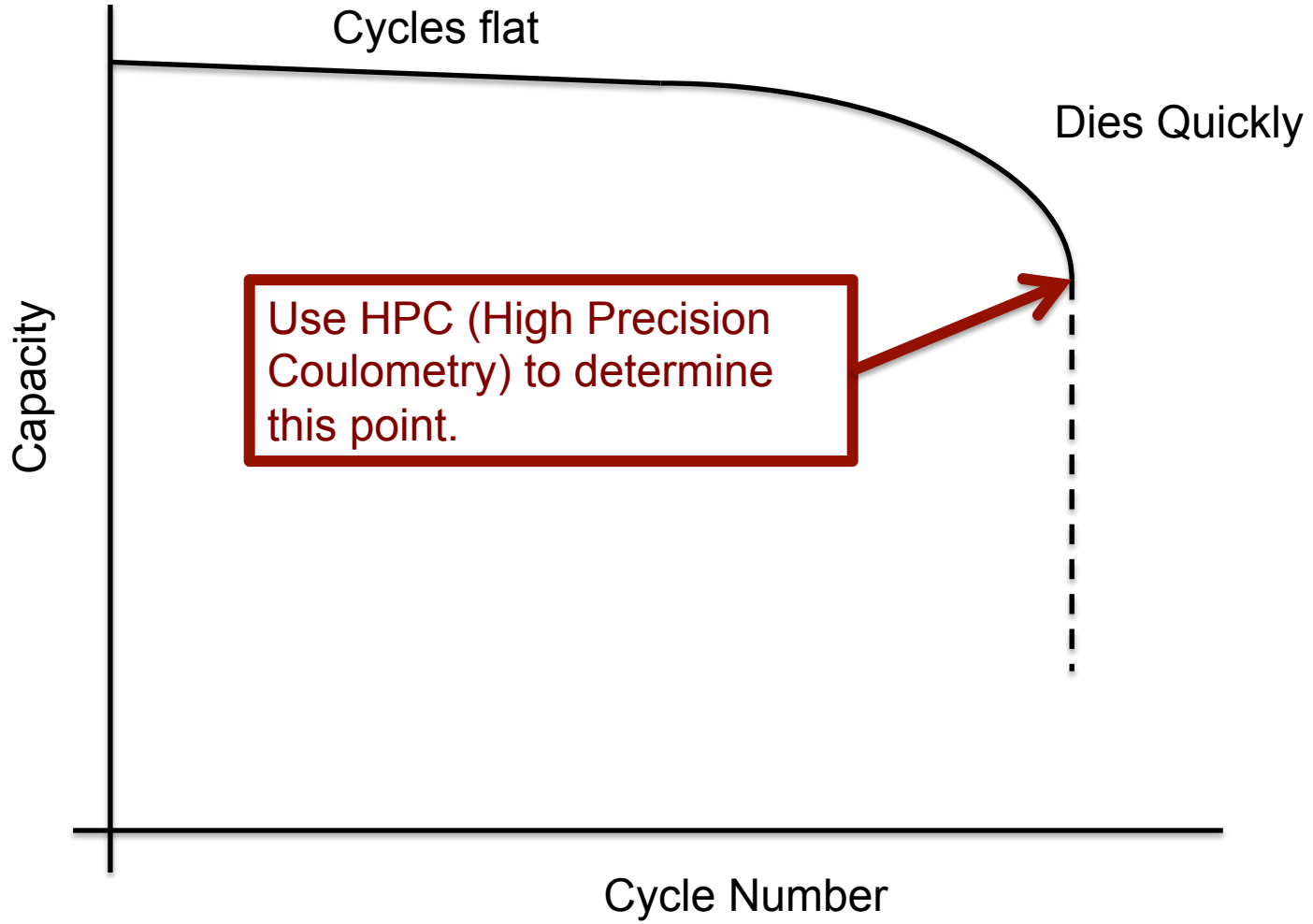
Standard Cell Cycling at 21°C

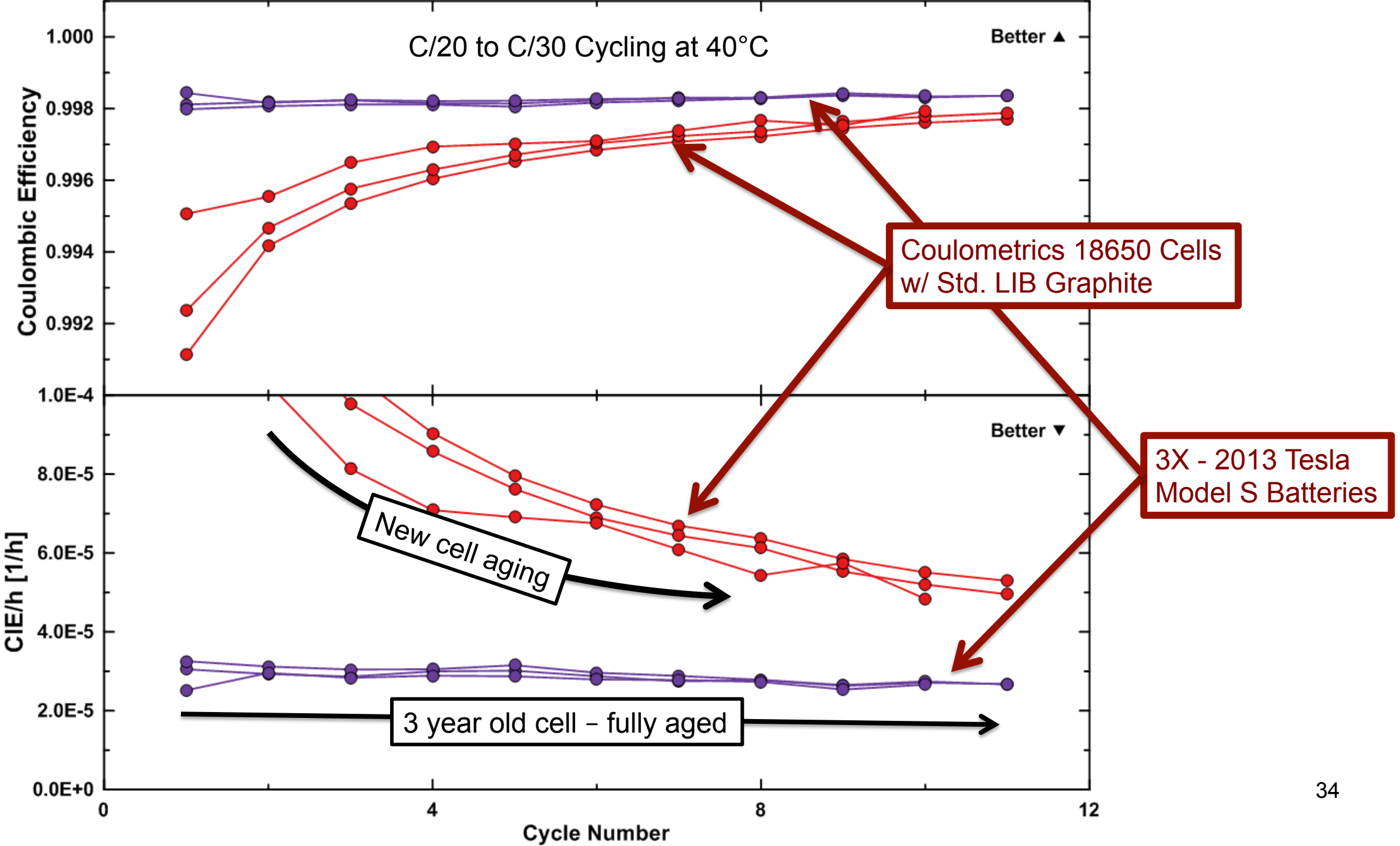
- Cells cycle with limited capacity loss
- Variation in cell capacity are more a reflection of temperature stability than cell capacity loss

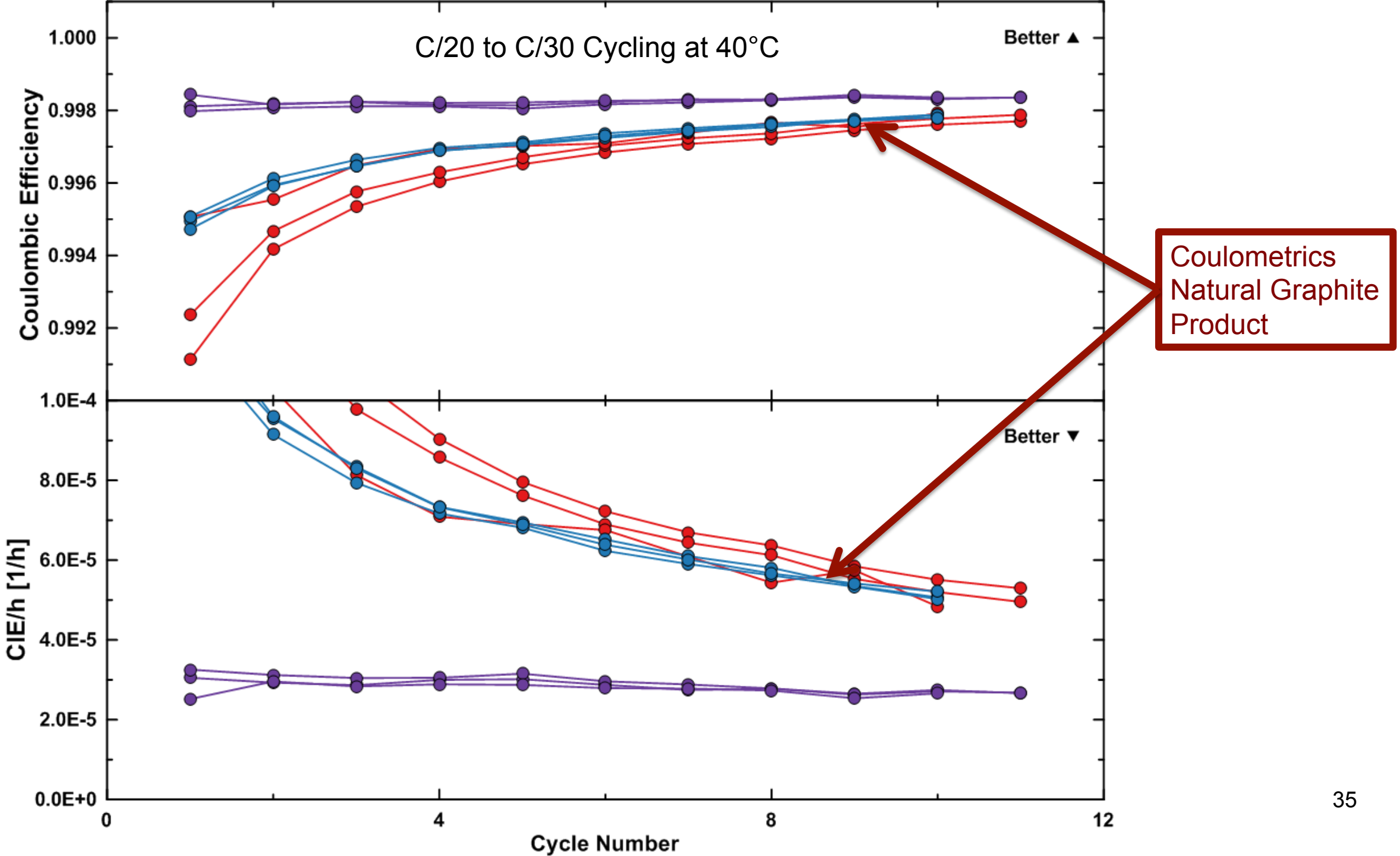


Cell Cycling

- How do you test for cell life?
  - If you cathode / anode are good (and they should be) then the same amount of lithium
  - Cell will cycle with almost constant capacity and then die quickly
  - Can take 1-2 years to cycle a cell at 40°C
  - Higher temperatures can lead to new failure mechanisms
- What can you do?
  - High Precision Coulometry
    - Measure loss of electrons per cycle due to oxidation/ reduction of the electrolyte




C/20 to C/30 Cycling at 40°C
Better ▲
Coulombic Efficiency
1.000
0.998
0.996
0.994
0.992
1.0E-4
Better ▼
CIE/h [1/h]
8.0E-5
6.0E-5
4.0E-5
2.0E-5
0.0E+0
0
4
8
12
Cycle Number
Coulometrics 18650 Cells w/ Std. LIB Graphite
3X - 2013 Tesla Model S Batteries
New cell aging
3 year old cell – fully aged


C/20 to C/30 Cycling at 40°C
Better ▲
Coulombic Efficiency
1.000
0.998
0.996
0.994
0.992
1.0E-4
Better ▼
CIE/h [1/h]
8.0E-5
6.0E-5
4.0E-5
2.0E-5
0.0E+0
0
4
8
12
Cycle Number
Coulometrics
Natural Graphite
Product

GRAPHITE CORPS COULOMETRICS JOINT VENTURE

Coulometrics

- **Coulometrics and Graphite Corps have agreed to develop new graphite materials for LIBs under a new company called: PUREGraphite**

  + Environmentally friendly process
    - 2018 → 1,000 tpy
    - Easily scalable to over 100,000 tpy

PUREgraphite

Coulometrics

National Science Foundation
WHERE DISCOVERIES BEGIN

This work was supported by:
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Thank You!

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