Electrode Architecture-Assembly of Battery Materials and Electrodes

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Project ID: ES222

Hydro Québec

Overview

Timeline

- Start date: October 2012
- End date: September 2016
- 68% completed

Barriers

- Low energy
- Poor cycle/calendar life

Budget

- Total project funding: $1460K
- FY13 funding: $365K
- FY14 funding: $365K
- FY15 funding: $365K
- FY16 funding: $365K

Partners

- LBNL (L. Gao, V. Battaglia)
- PNNL (J. Zhang, C. Wang)
- UT (J. Goodenough)

Objectives

- Develop *high-capacity, low-cost electrodes* with good cycle stability and rate capability.

- Identify a method to produce *new sources of Si*.

- Understand the *mechanism of electrode degradation* by using *in-situ tools* to improve the electrode composition and architecture.

Approach

- Design of *electrode architectures* by controlling tortuosity and porosity to achieve high ionic/electronic conductivity.

- Identify a method to produce *new sources of Si*.

- Utilize *in-situ and ex-situ SEM and TEM* to investigate the failure mode and SEI layer on the anode and cathode.

Milestones

- **Completed:**
  - Production of Si nanopowder : capacity fade < 20% @100 cycles
  - In-situ TEM analysis for Si nanopowder
  - Deliverables :
    - *Si powder* to LBNL (1kg), Stanford Univ.(1kg), Penn State Univ. (0.5kg)
    - *Electrode* : Si (Jun-2014, Sep-2014, Dec-2014), HV LMN (Sep-2014), HE NCM (Dec-2014), NCM-LMO (Dec-2014), Gr (Dec-2014)
    - *Electrolyte* : Sep-2014, Dec-2014
    - *Cell* : 20 Ah cells (ver.1 _Sep-2014), 60 Ah cells – 250 Wh/kg (ver.2_Dec-2014)

- **On going:**
  - Optimize particle size (200 ~ 50 nm) and process conditions of Si-nano-powder.
  - Study the effect of precursors : Si, SiH_4, SiO_x, Si-SiO_x
  - Continue to study SEI passivation, fracture of electrode and particles by in-situ SEM, TEM, dual-beam microscope.
  - Increase the energy density to meet the requirement of the BMR program
  - Increase the loading of Si electrode : development of binder and electrode architecture
  - Characterize the gas generation in slurry and cell.

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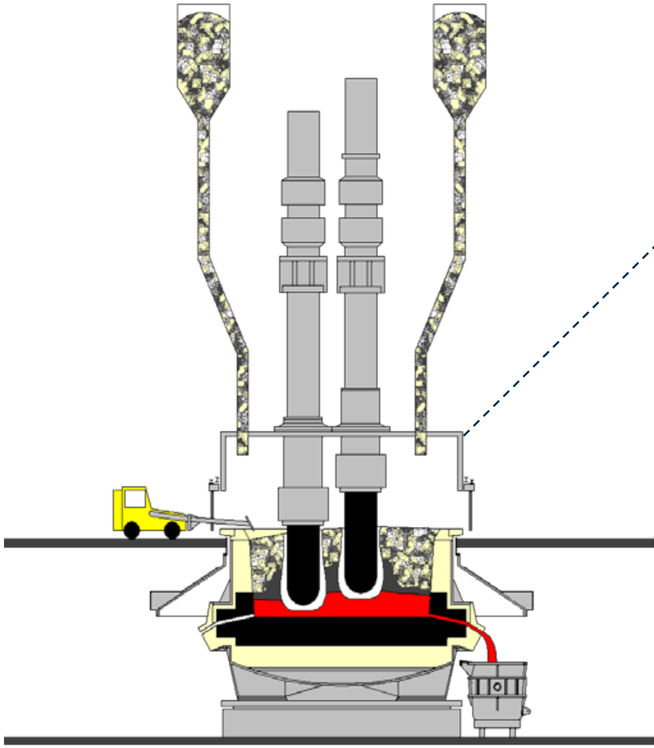
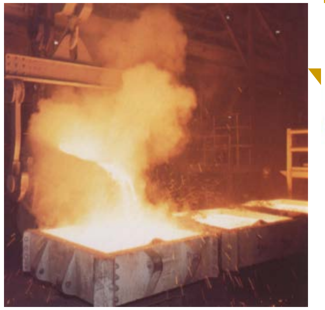
Si Production – Metallurgical Process



Typical furnace power ~ 20 MW

Carbothermal reduction:

$$SiO_2 + 2C \longrightarrow Si + 2CO$$



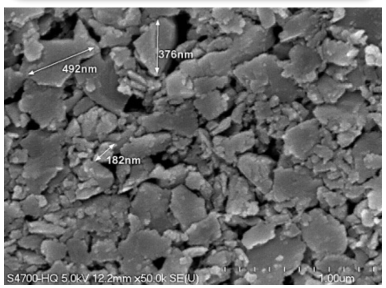
Price of MG-Si : ~ $3/kg

Si nano powder- 1. Metallurgical Process

Large Si chunk

- ❑ ***Low process cost***
  - ✓ ***Jet mill < $1/kg***
  - ✓ ***Wet mill < $3~4/kg***

Jaw crusher d_{50} < 13 mm → Roll crusher d_{50} < 1 mm → Jet mill d_{50} < 10 µm → Wet mill d_{50} < 1 µm



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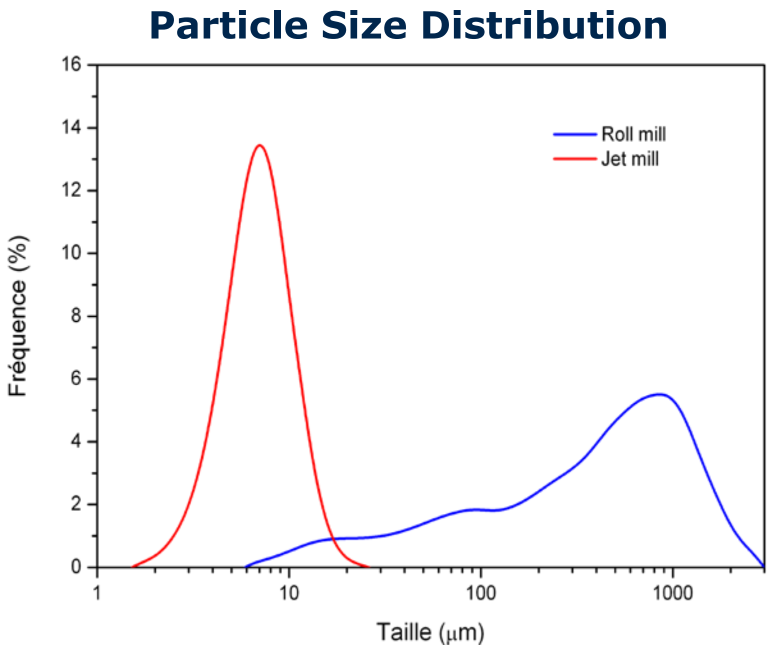
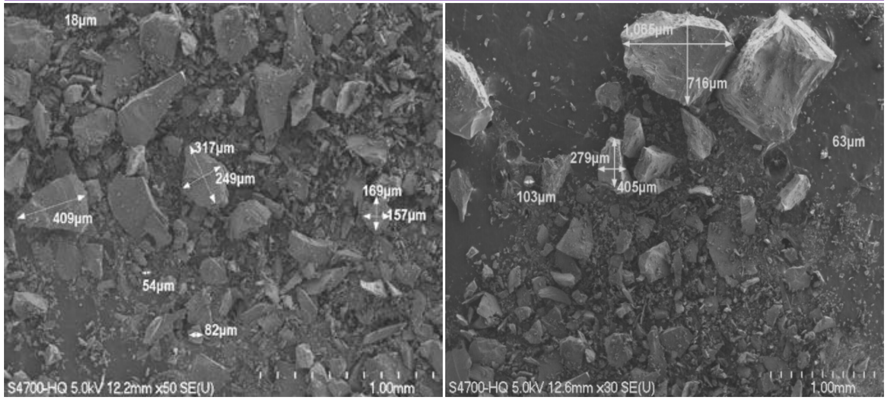
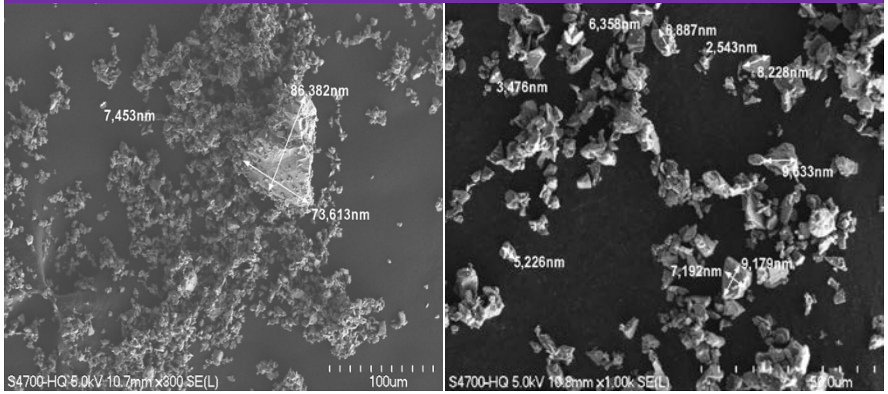
Jet Mill_Particle Size Distribution



Jaw crusher + Roll crusher



Jet mill

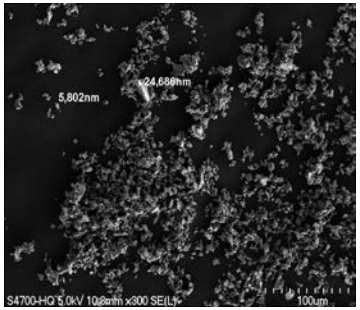


- ***Homogeneous particle size : D_{50} ~700 µm → D_{50} ~7 µm***
- ***Cleavage of crystalline particles***

Jet Mill_Chemical Analysis

Large Chunk

After Jet Mill



Element	Large Chunks (%)	After Jet mill (%)
B	0.0030	0.00029
Mg	0.0004	0.0004
Al	0.057	0.075
P	0.0034	0.0034
Ca	0.022	0.023
Ti	0.069	0.077
V	0.0019	0.0021
Cr	0.0012	0.0023
Mn	0.015	0.017
Fe	0.31	0.35
Ni	0.0015	0.0022
Cu	0.0018	0.0018
Zn	0.0006	0.0004
Zr	0.016	0.0180
C	0.011	0.015
O	**0.049**	**0.84**

- ***Oxygen content increases from 0.049% to 0.84% due to the higher surface area (formation of surface oxide).***

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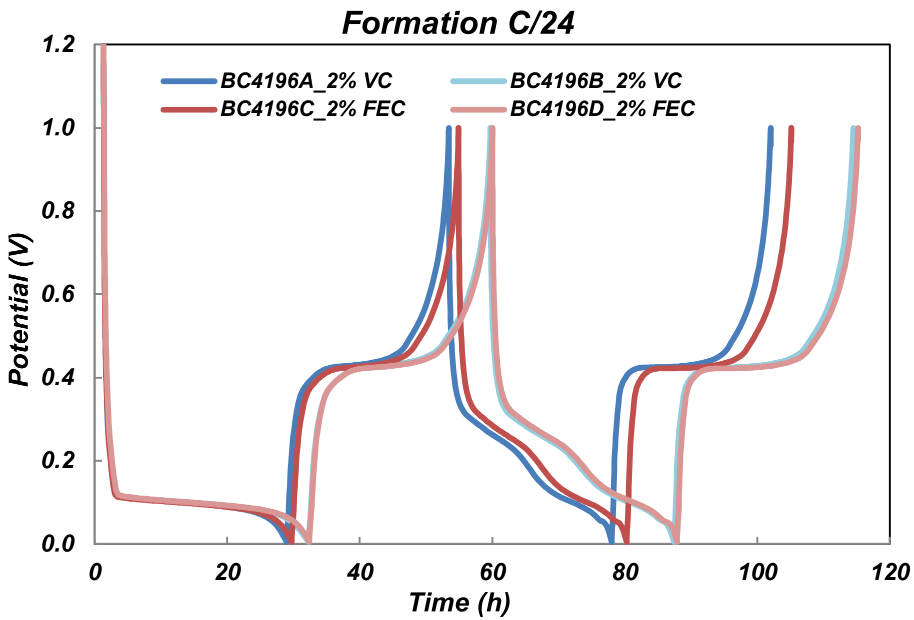
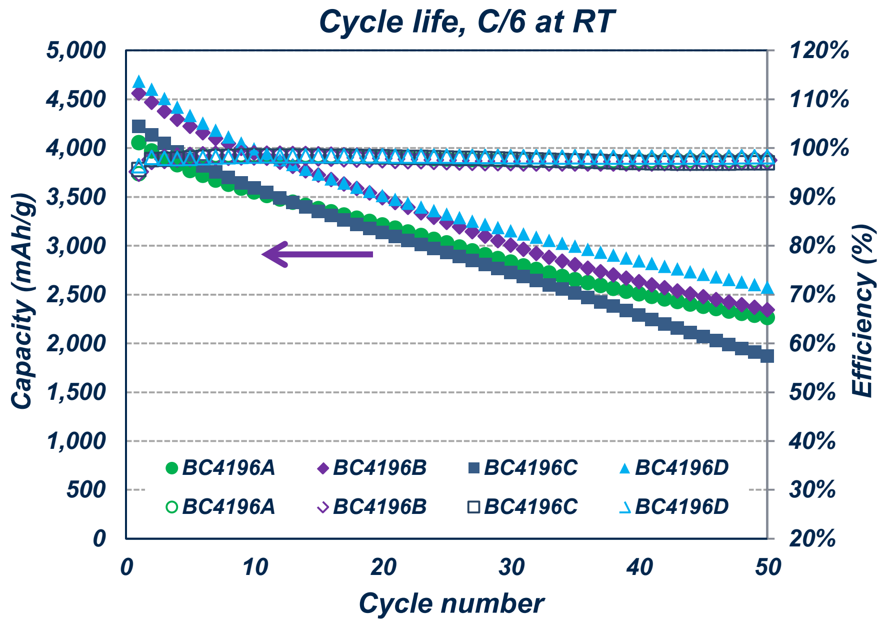
Jet Mill_Electrochemical Performance





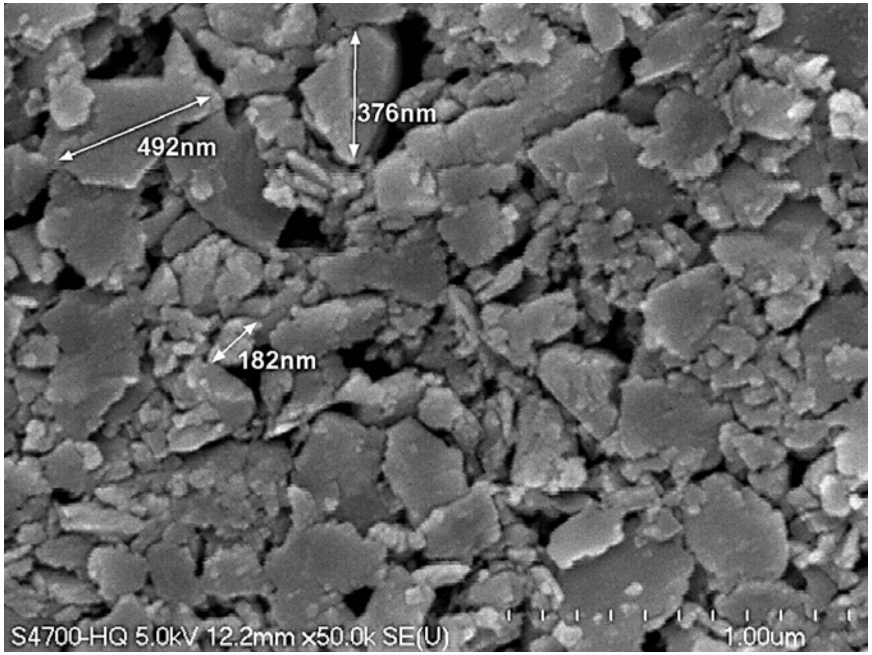
Sample	Charge (mAh/g)	Discharge (mAh/g)	Efficiency (%)	Charge (mAh/g)	Discharge (mAh/g)	Efficiency (%)
BC4196A	4840	4283	88.5%	4300	4205	97.8%
BC4196B	5423	4802	88.6%	4847	4741	97.8%
BC4196C	4976	4406	88.5%	4438	4351	98.0%
BC4196D	5440	4836	88.9%	4872	4789	98.3%

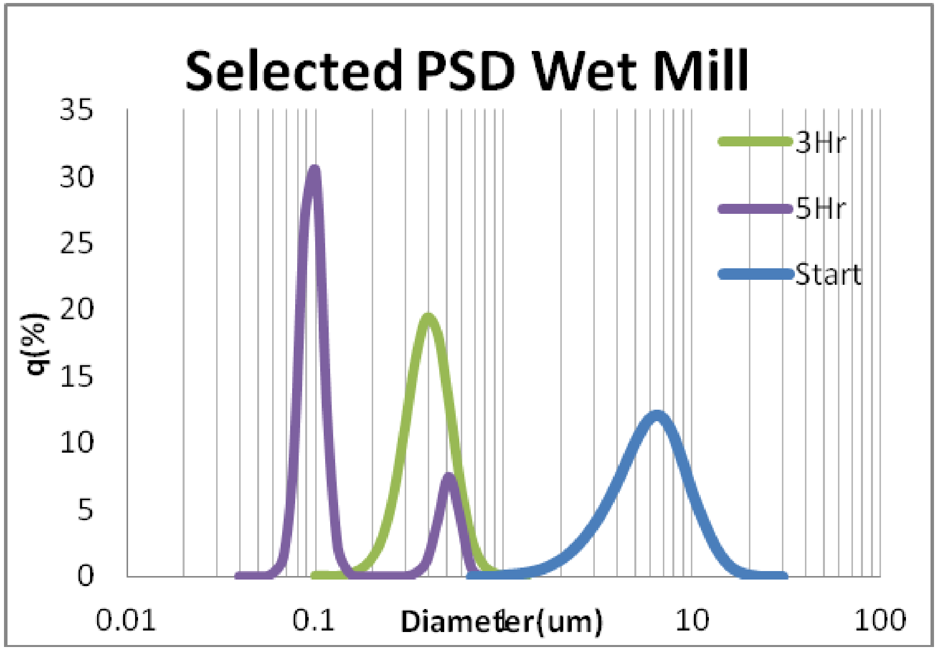
❑ ***Cycle life test @ SOC/DOD 100 %***

- ***Charge : CC(C/6)/CV(5mV for 15min)***
- ***Discharge : CC(C/6) to 1.0V***

- ***Capacity : > 4200 mAh/g with C/24 at RT***
- ***Initial Coulombic efficiency > 88%***
- ***Capacity retention : ~50% at 50th cycle***

Wet Mill_ Particle Distribution





Ball diameter: 2 mm

- ***Crystalline particles without impurity***
- ***Particle size : D_{50} ≈ 100 nm***
- ***Particle size can be controlled by ball size and process time***

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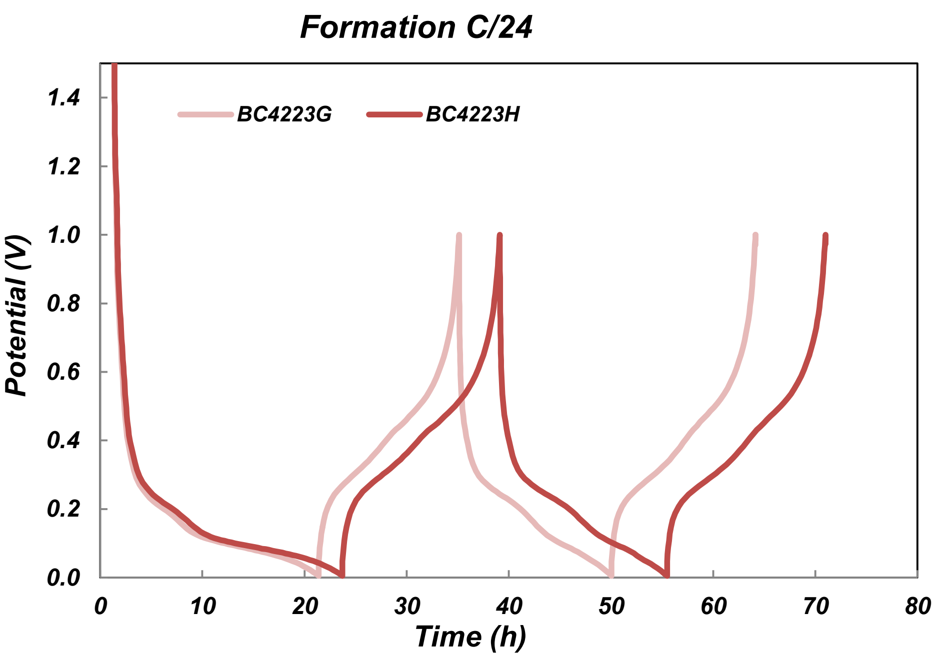
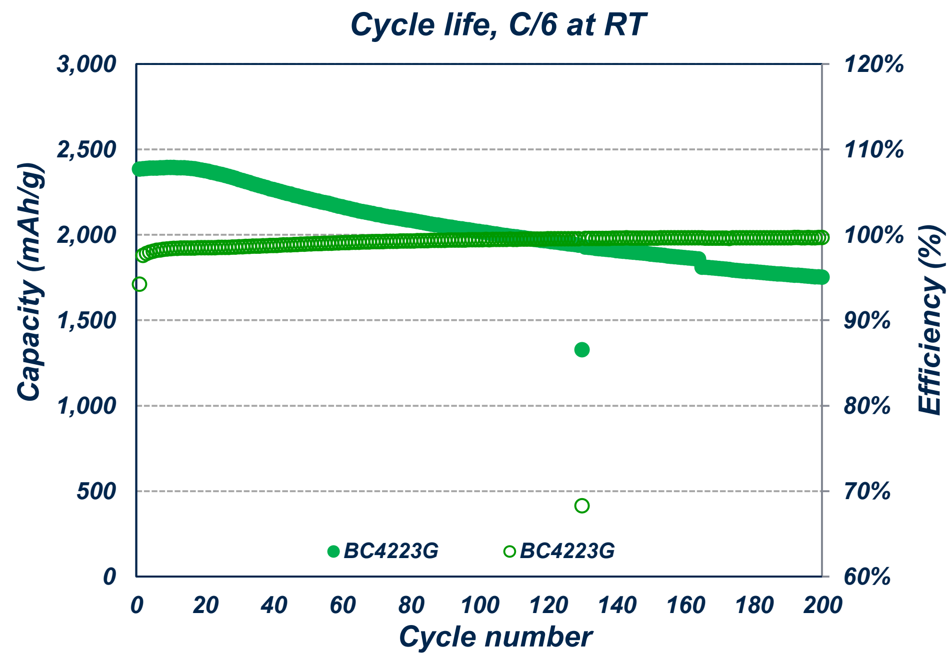
Wet Mill_Electrochemical Performance





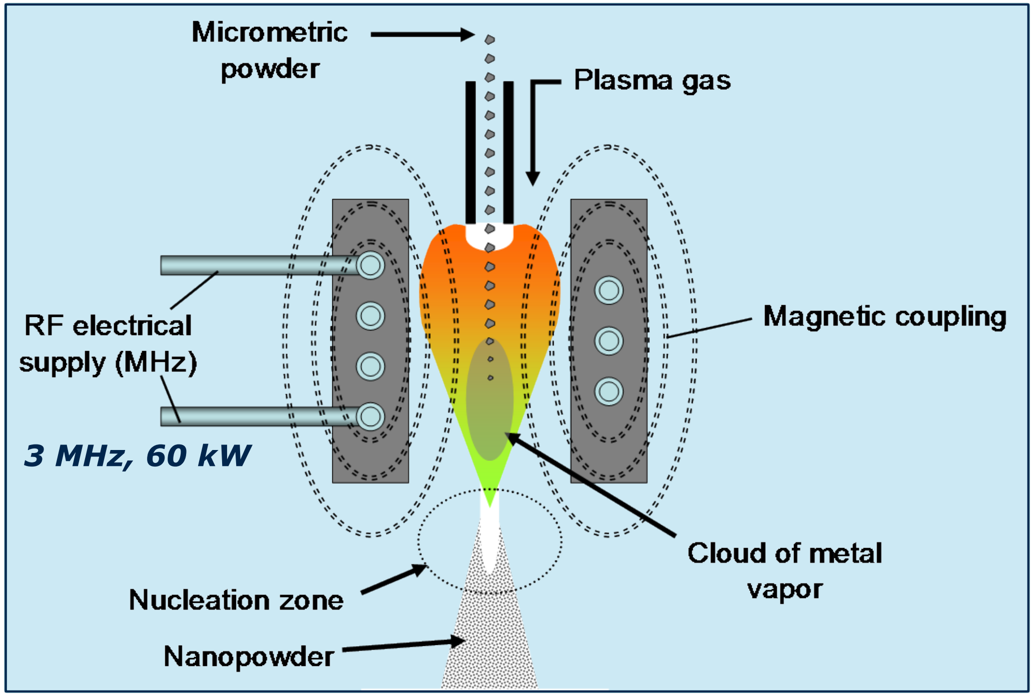
Cell#	Charge (mAh/g)	Discharge (mAh/g)	Efficiency (%)	Charge (mAh/g)	Discharge (mAh/g)	Efficiency (%)
BC4223G	3509	2408	68.6%	2610	2469	94.6%
BC4223H	3917	2699	68.9%	2863	2716	94.9%

❑ ***Cycle test @ 100% SOC/DOD***

- ***Charge : CC(C/6)/CV(0.005V for 15min)***
- ***Discharge : CC(C/6) to 1.0V***

- ***Capacity : ~2500 mAh/g with C/24 at RT***
- ***Initial Coulombic efficiency : < 67%***
- ***Capacity retention : ~73% at 200th cycle***

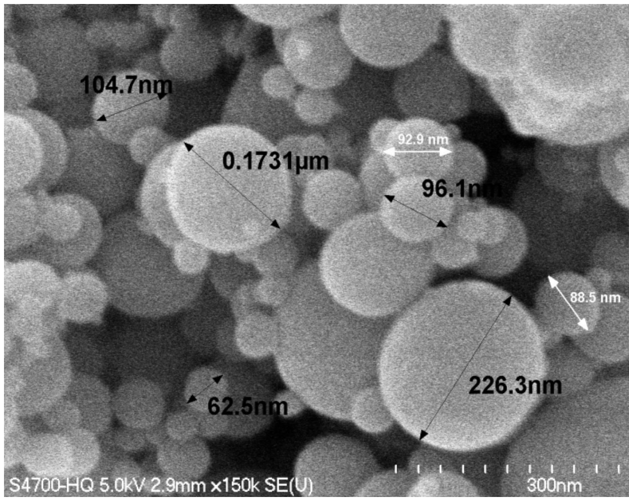
Si nano powder - 2. Plasma Process

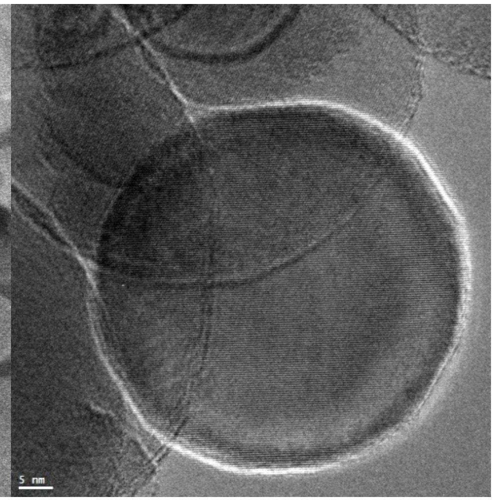


Silicone powder (µm size, 99.999wt%) —*Heat*→ ***Metal vapor*** —*Quenching*→ ***Si nanopowder***

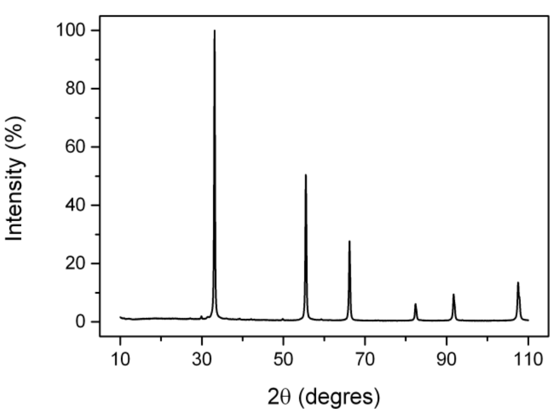
- ***High process cost > $50/kg***

Characterization of Plasma-Nano Si

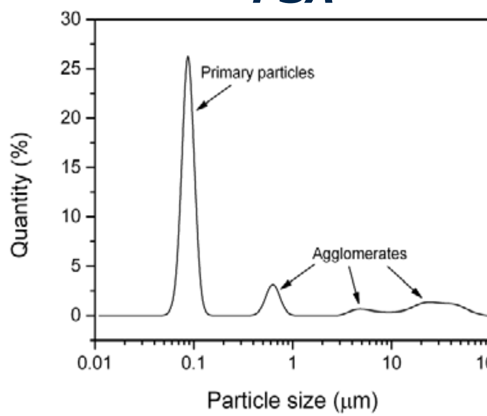




XRD



PSA



SEM
- ✓ *Spherical shape*
- ✓ *Dia. 50 to 200 nm*

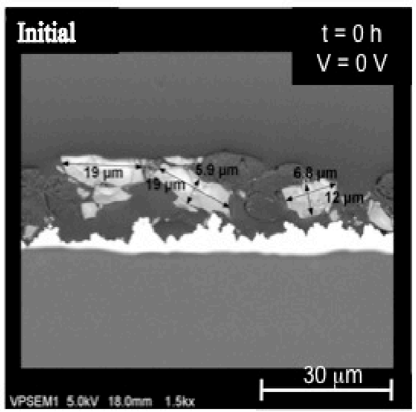
TEM
- ✓ *Crystalline lattice in the silicon nanoparticles*
- ✓ *Contamination-free atomic surface*

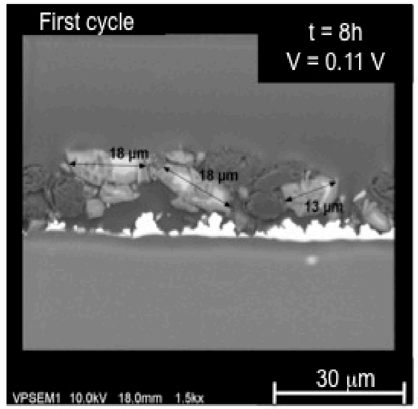
XRD
- ✓ *c-Si with diamond cubic lattice (a = 5.43 Å)*
- ✓ *No impurity phase detected*

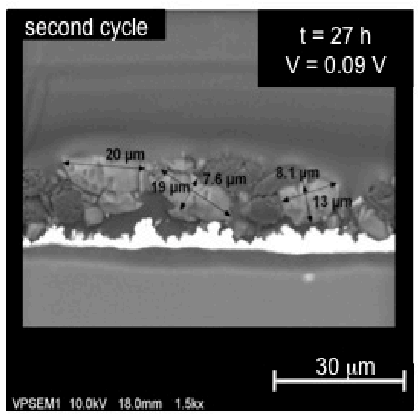
PSD : *D_{50} = 85 nm*

BET : *30 m^2/g*

Micro-Si (electrode)

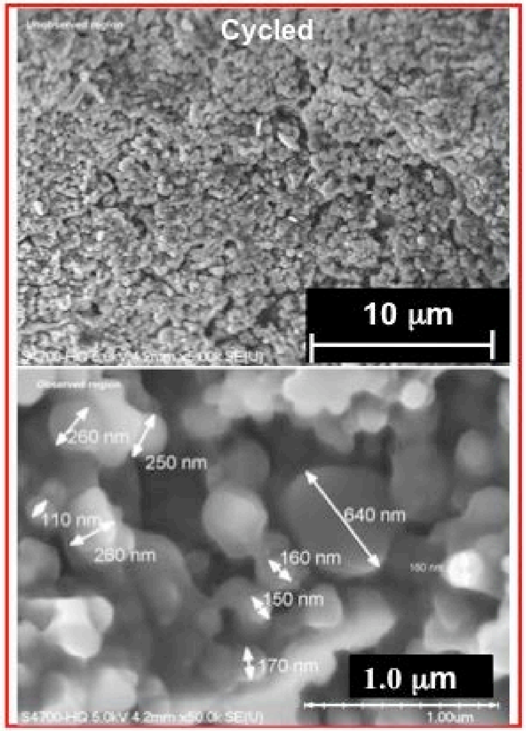


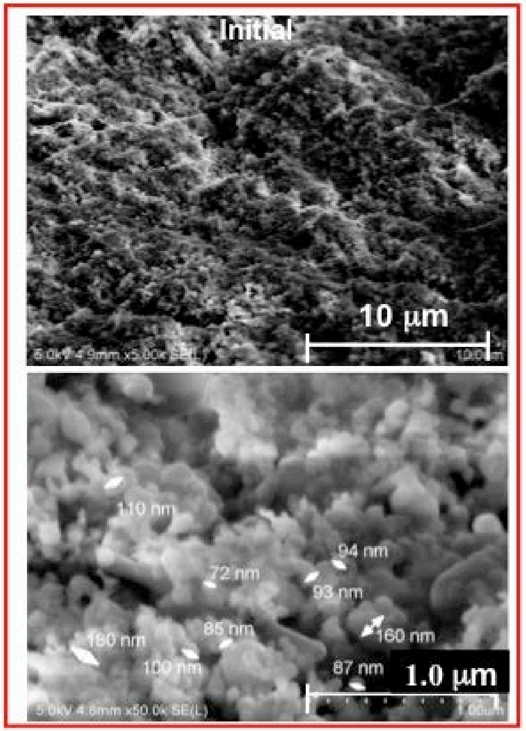


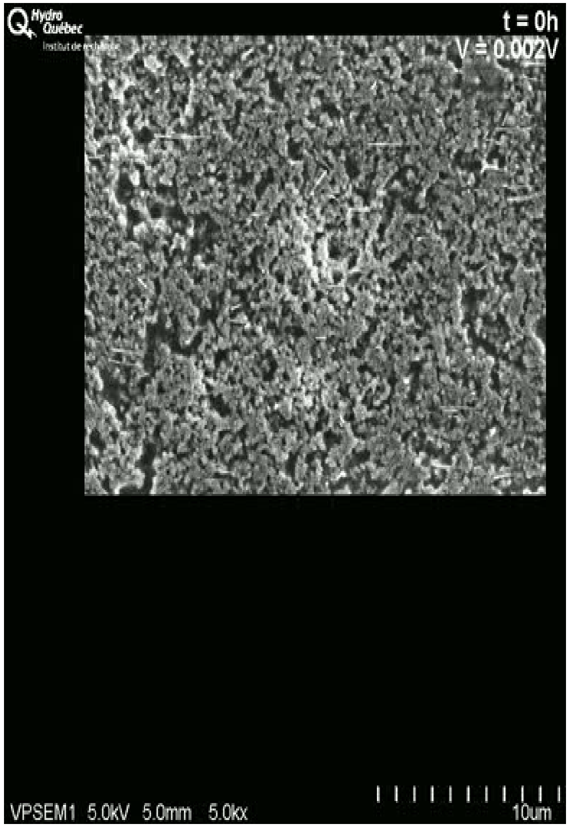


- ✓ ***In-situ*** **evolution of micron-sized Si particles on real time cycling**
- ✓ **Cracking of particles leading to the loss of electrode integrity**

Nano-Si (electrode)

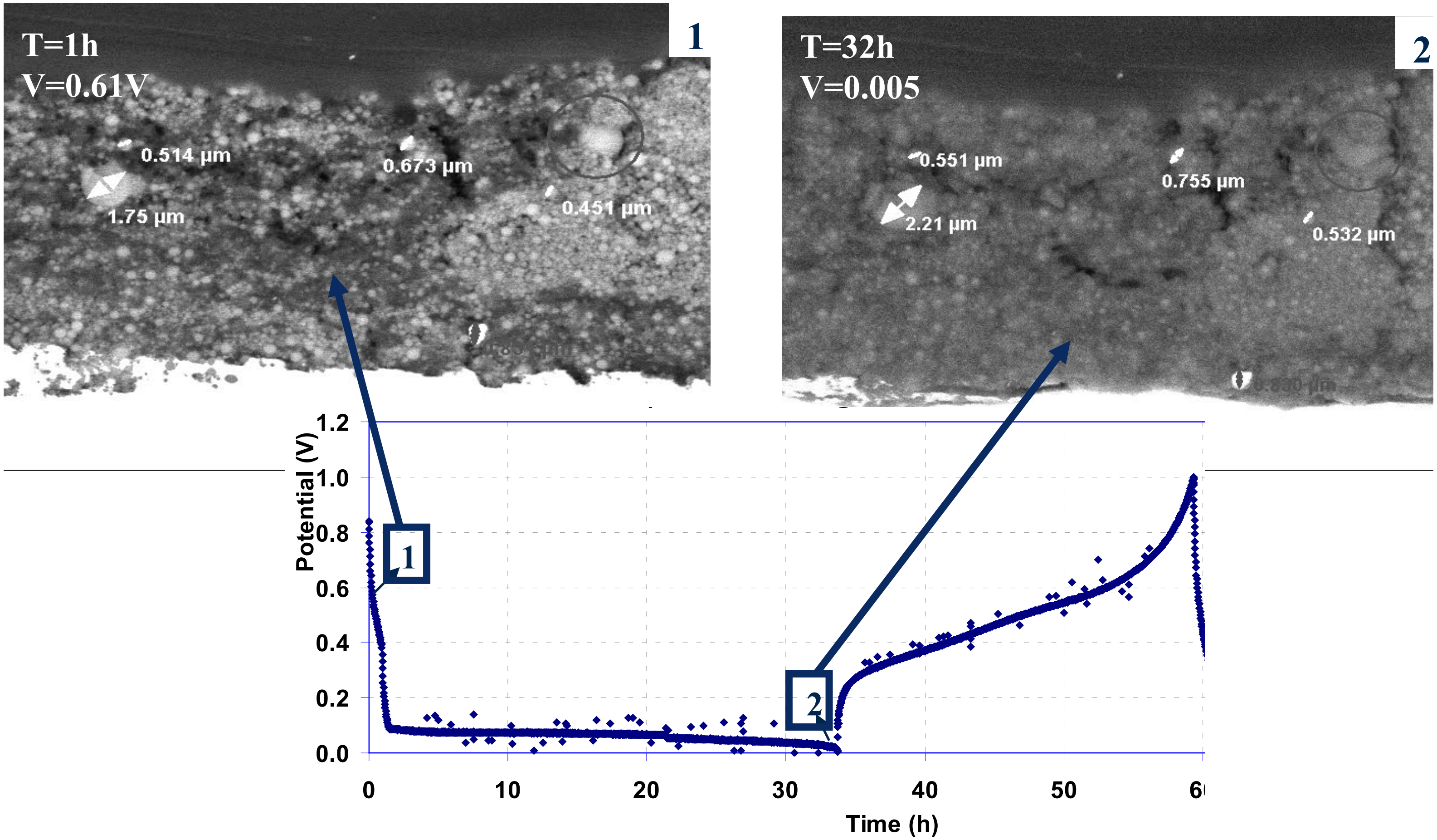






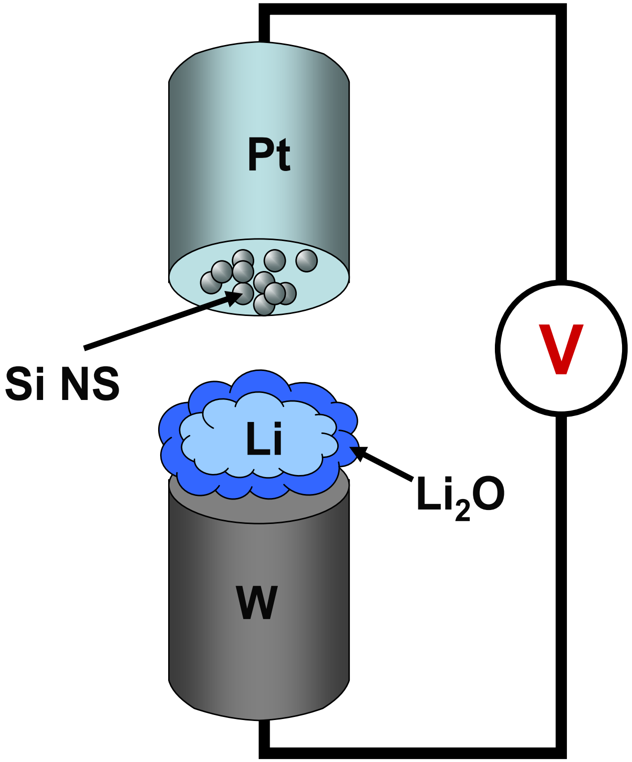
- ✓ **No cracking for nano-sized particles.**
- ✓ **Even the biggest particles (200 nm) did not crack.**
- ✓ **Advanced electrode architecture with nano Si is needed for commercialization**

Nano-Si (electrode)



- ✓ ***In-situ* evolution of nano-sized Si particles on real time cycling**
- ✓ **Electrode densification after lithiation**

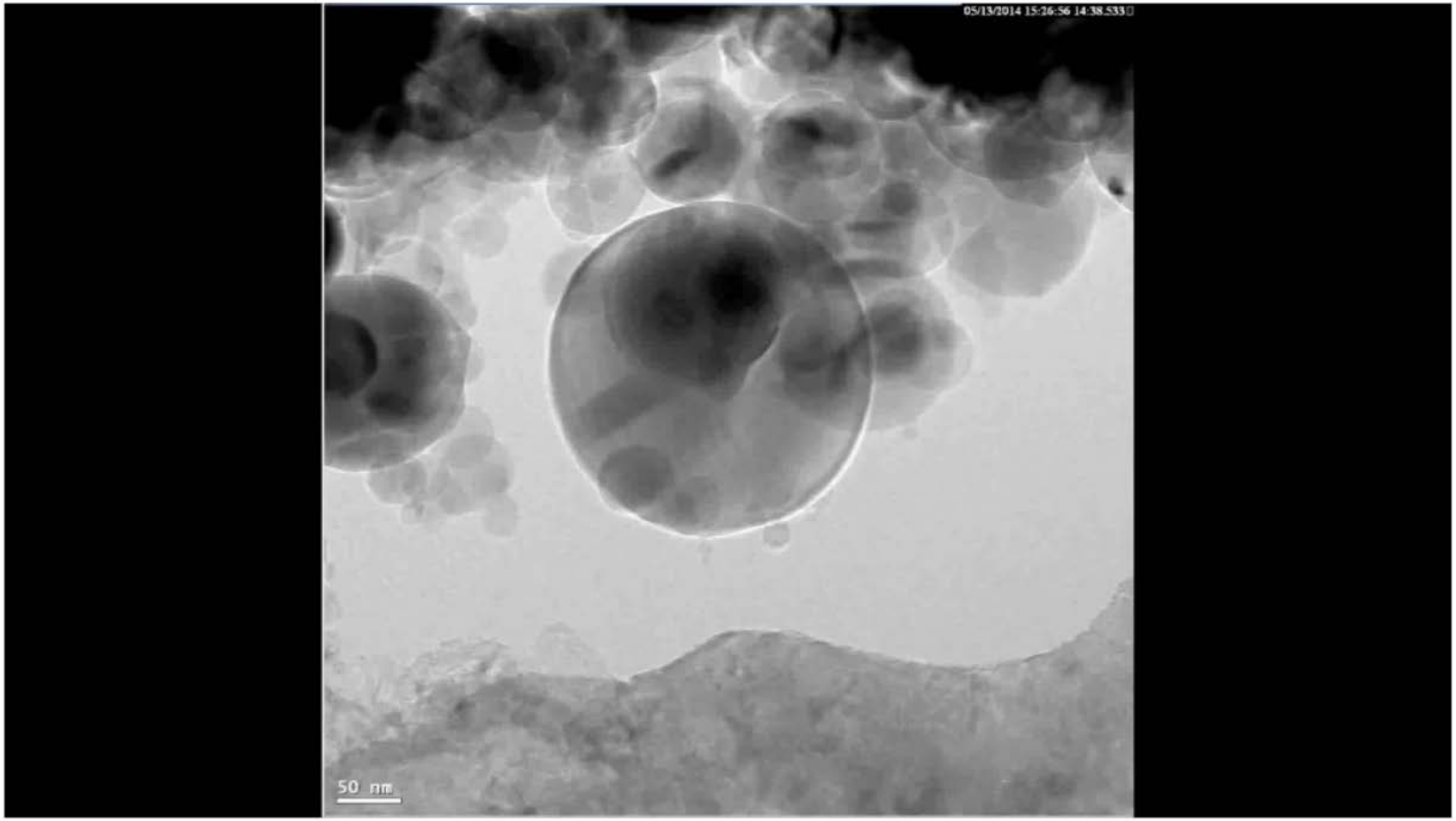
In situ TEM; Collaboration with PNNL



- Silicon nanoparticles were loaded on a platinum electrode.
- Lithium metal was loaded on a tungsten tip, which was fixed to a piezosystme, with lithium oxide surface layer serving a solid electrolyte.
- Insertion of lithium into Si particles was controlled by application of bias voltage of -2 ~-5 V.
- Titan 80-300 with a probe corrector was operated at 300 kV for imaging.

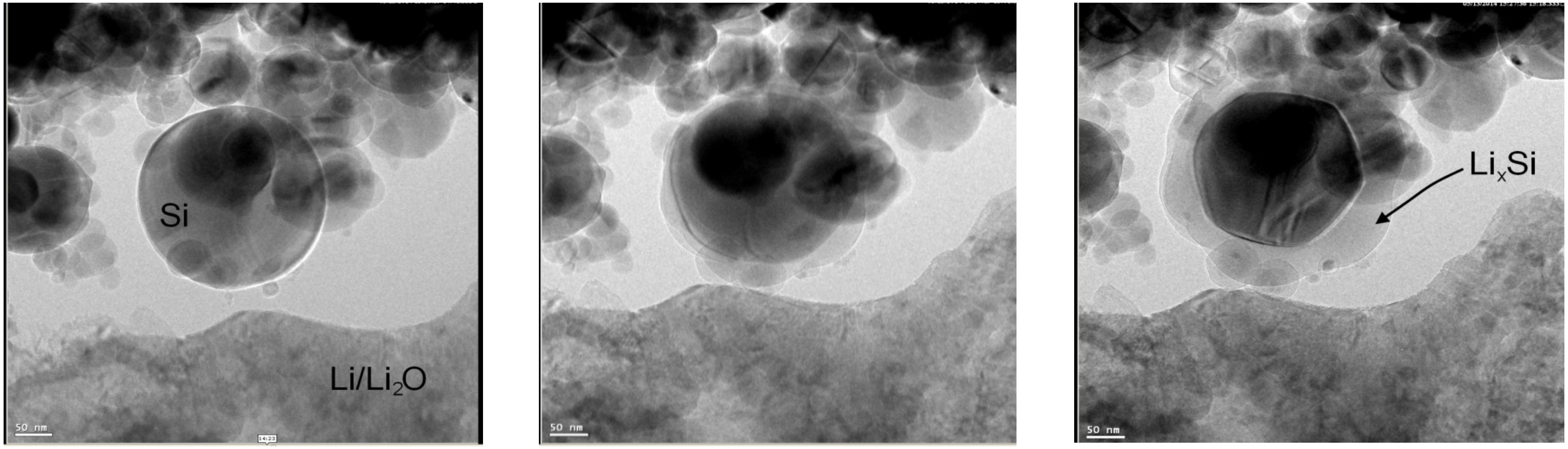
In situ transmission electron microscopy observations of lithiation of silicon nanopowder produced by induced plasma atomization, Journal of Power Sources, Volume 279 (2015) 522-527
Dominic Leblanc, Chongmin Wang, Yang He, Daniel Bélanger, Karim Zaghib

In situ TEM : Si/Li_2O/Lithium



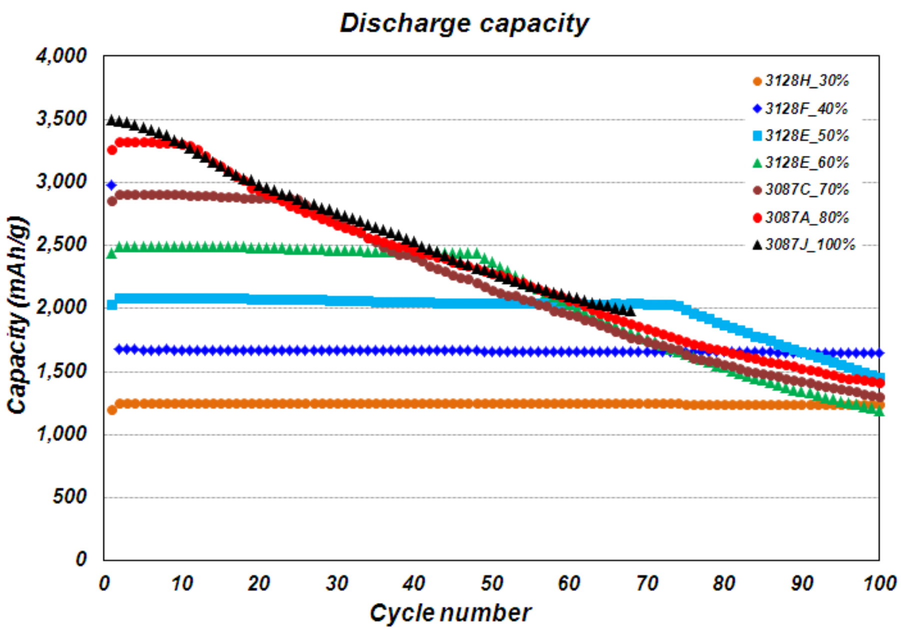
In situ TEM : $Si/Li_2O/Lithium$

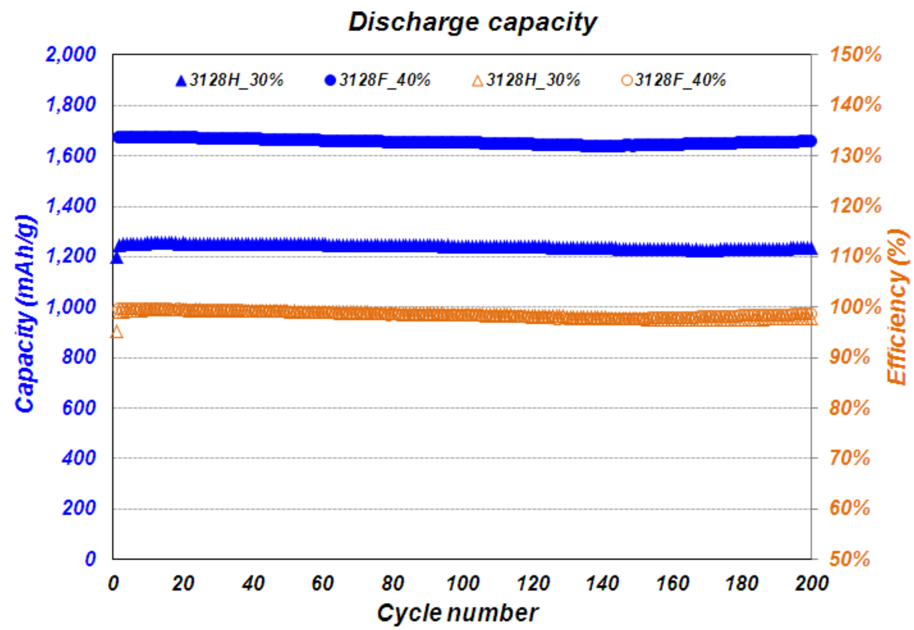
(a) (b) (c)



- a) *Particles in discharged state : 50 – 200 nm spheres*
- b) *Initiation of lithium insertion : rapid reaction from the surface forms a core-shell structure.*
- c) *Growth of amorphous LixSi alloy : particle expansion without collapsing*

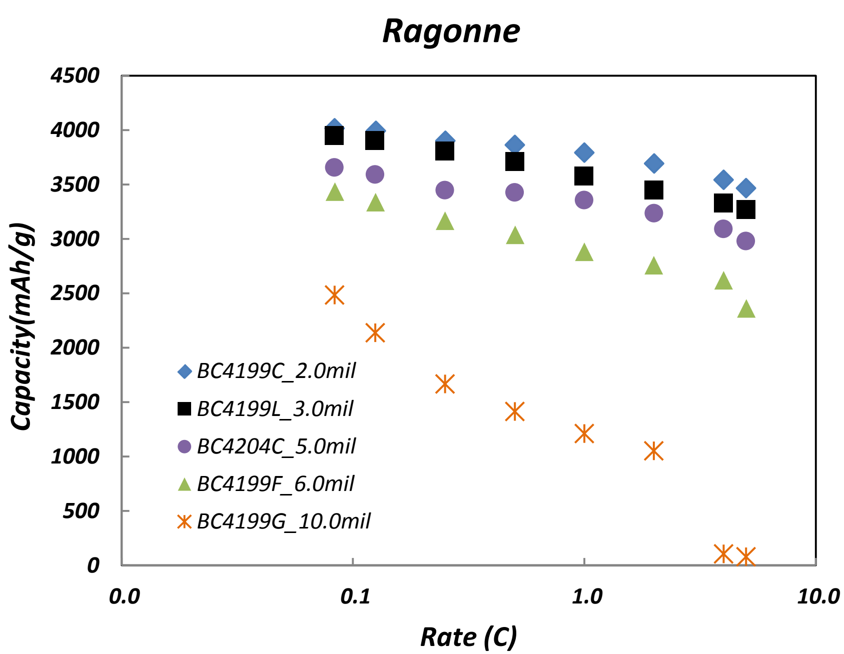
Effect of SOC Control

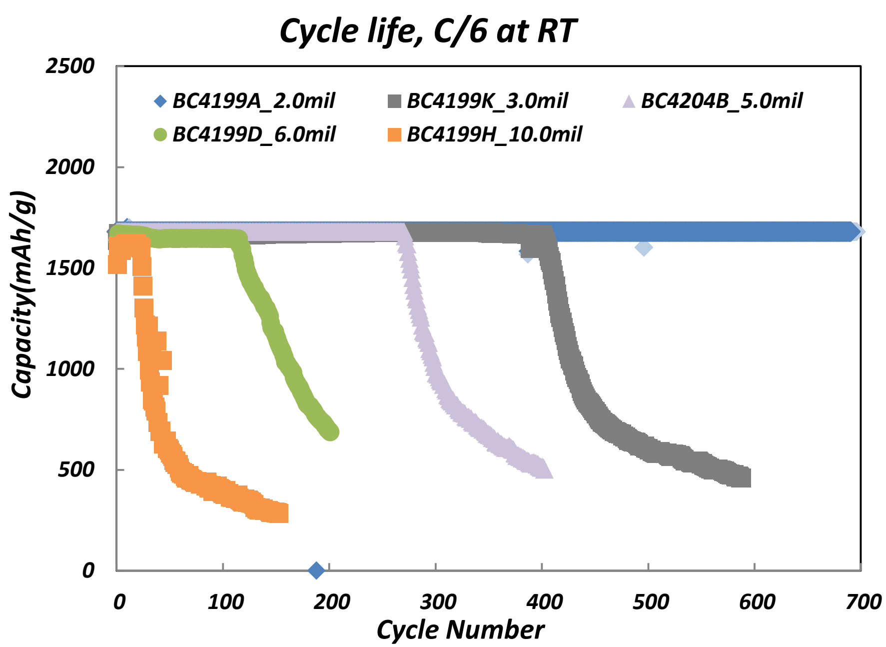




- ✓ ***Discharge capacity of 3500 mAh/g was achieved at 100% SOC/DOD.***
- ✓ ***SOC should be limited to < 40% in order to reach the cycle life >100 cycles***
- ✓ ***Useable capacity at 40% SOC : ~1670 mAh/g.***
- ✓ ***Cycle life > 200 cycles***

Effect of Electrode Loading





Coating Gap	Loading Level	C-rate	Cycle
(mil)	(mg/cm^2)	-	-
2	0.45	OO	>700
3	0.75	O	>400
5	0.99	Δ	>250
6	1.26	X	>100
10	1.96	XX	<50

- ✓ *Electrode chemical performance of Si electrode is highly dependent on the electrode loading.*
- ✓ *Cycle life > 700 cycles at the low loading of 0.45 mg/cm^2 .*

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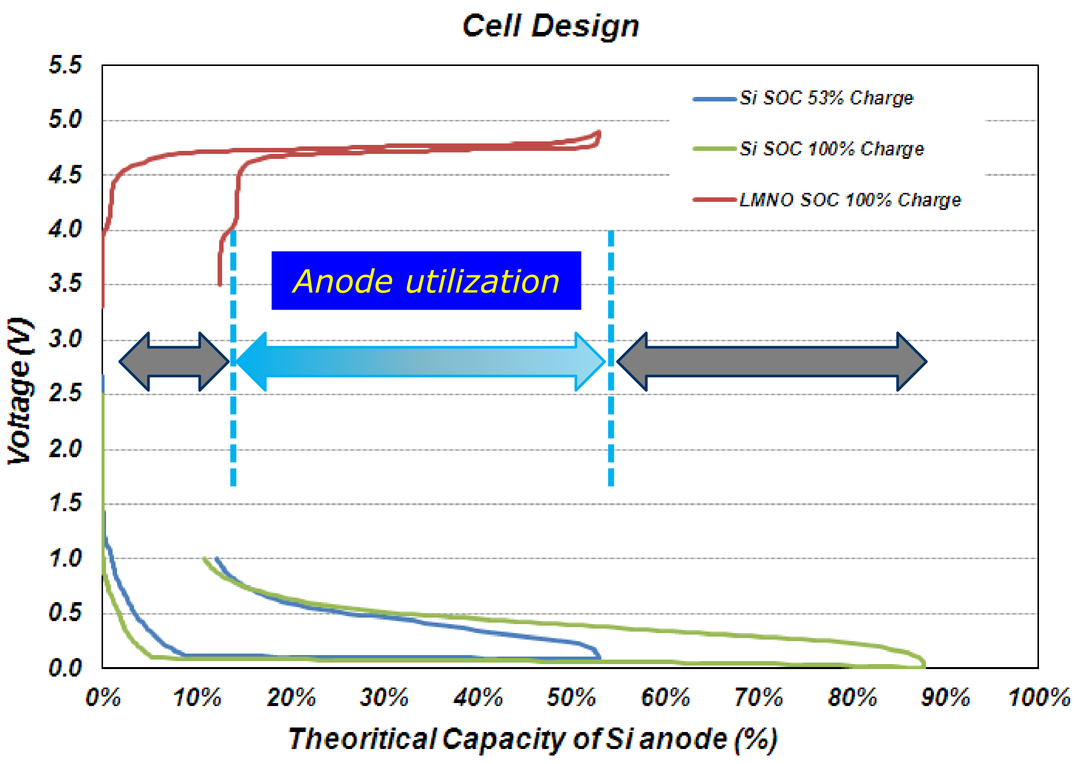
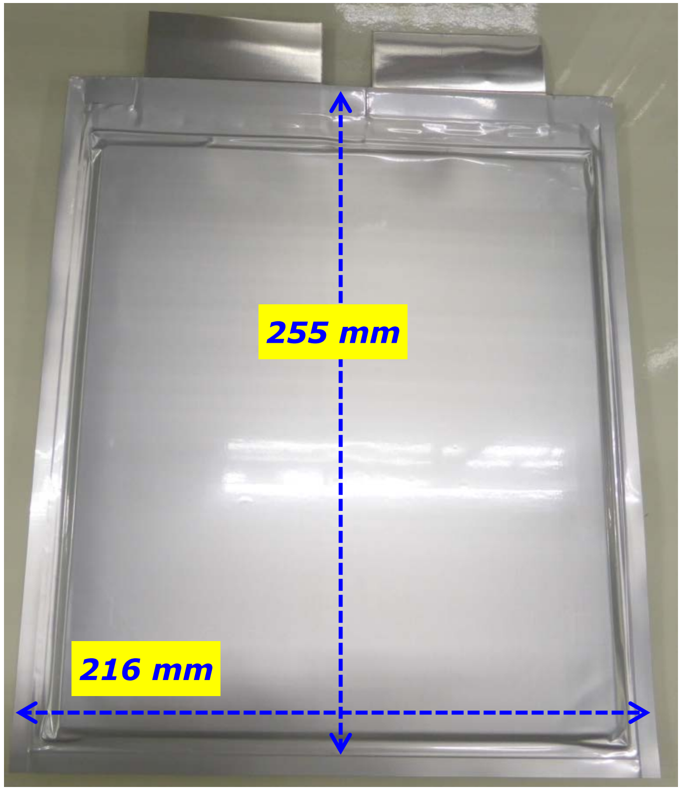
Design of Large Format Cell (ver.1)





- ***Cathode : HV LMNO***
- ***Anode : nano Si***
- ***Cathode determining design with limited utilization (40%) of anode***

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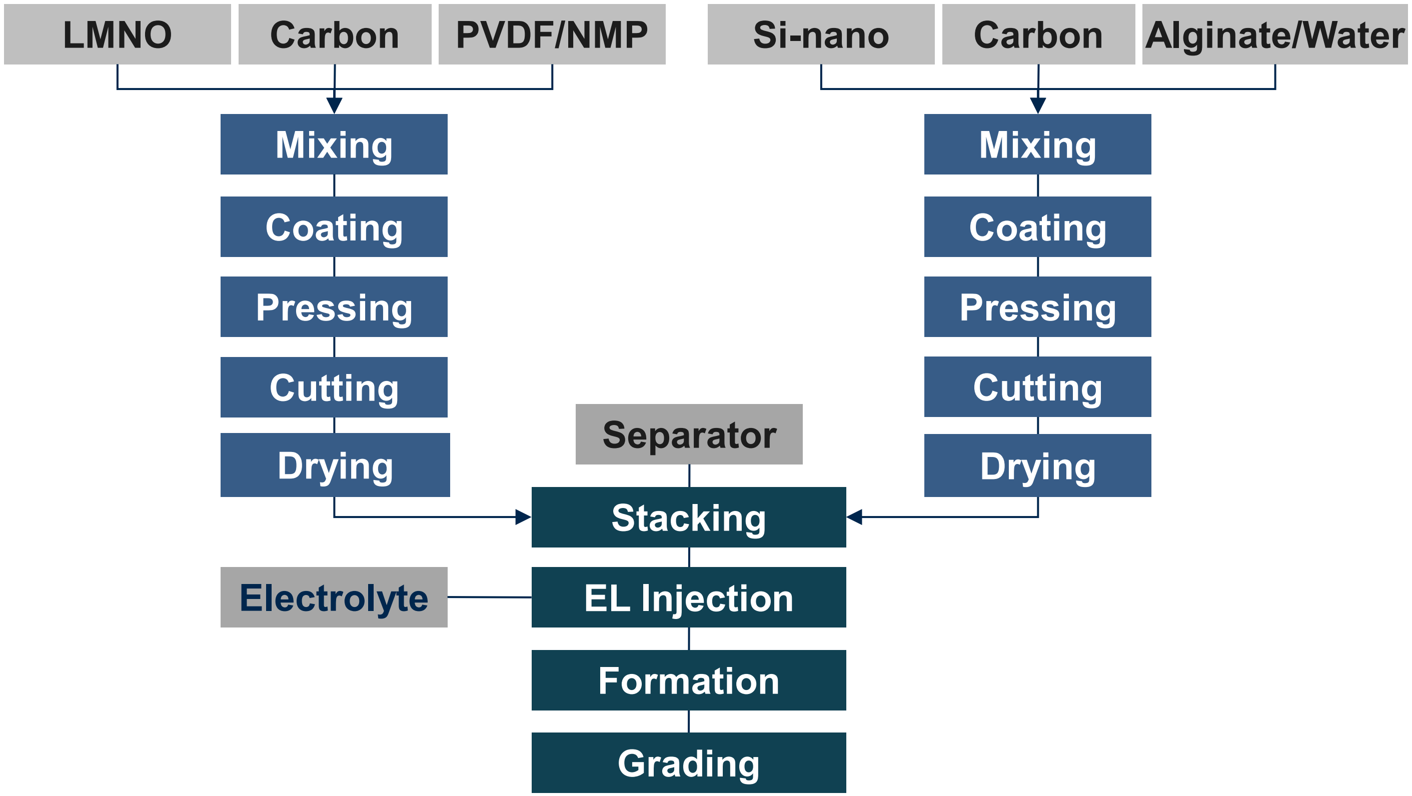
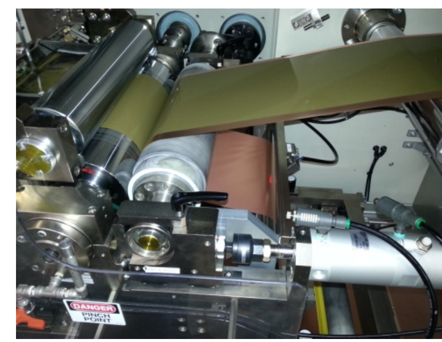
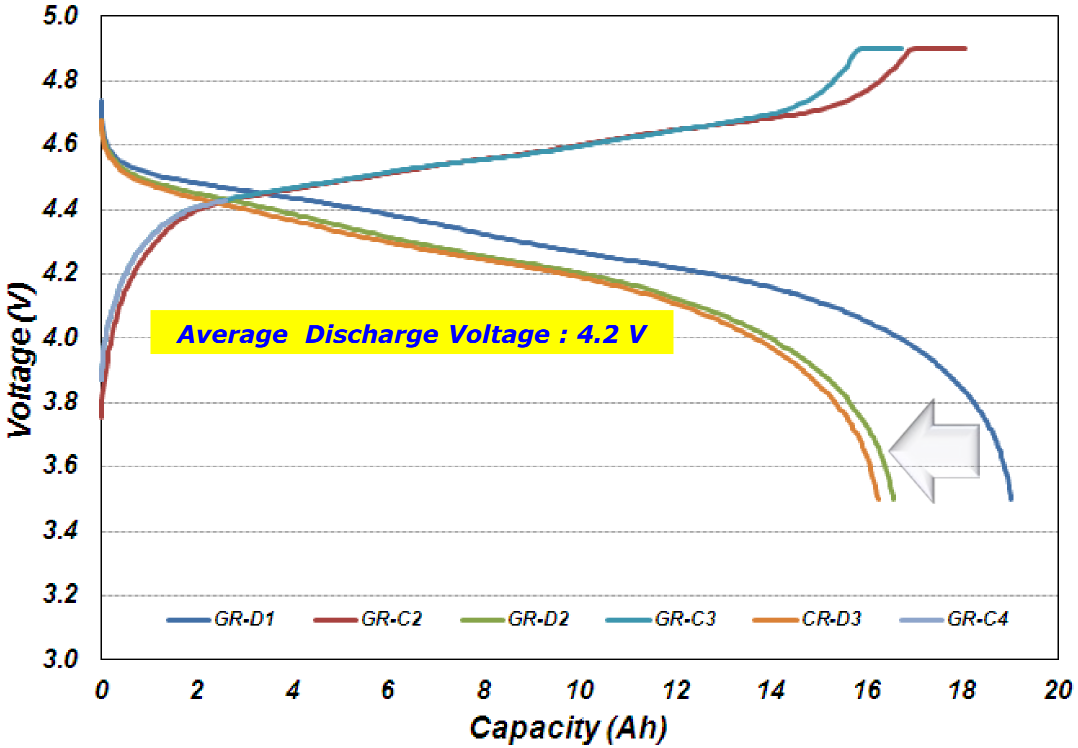
Process Flow (Automatic Pilot Line)





Voltage Profile (ver.1)

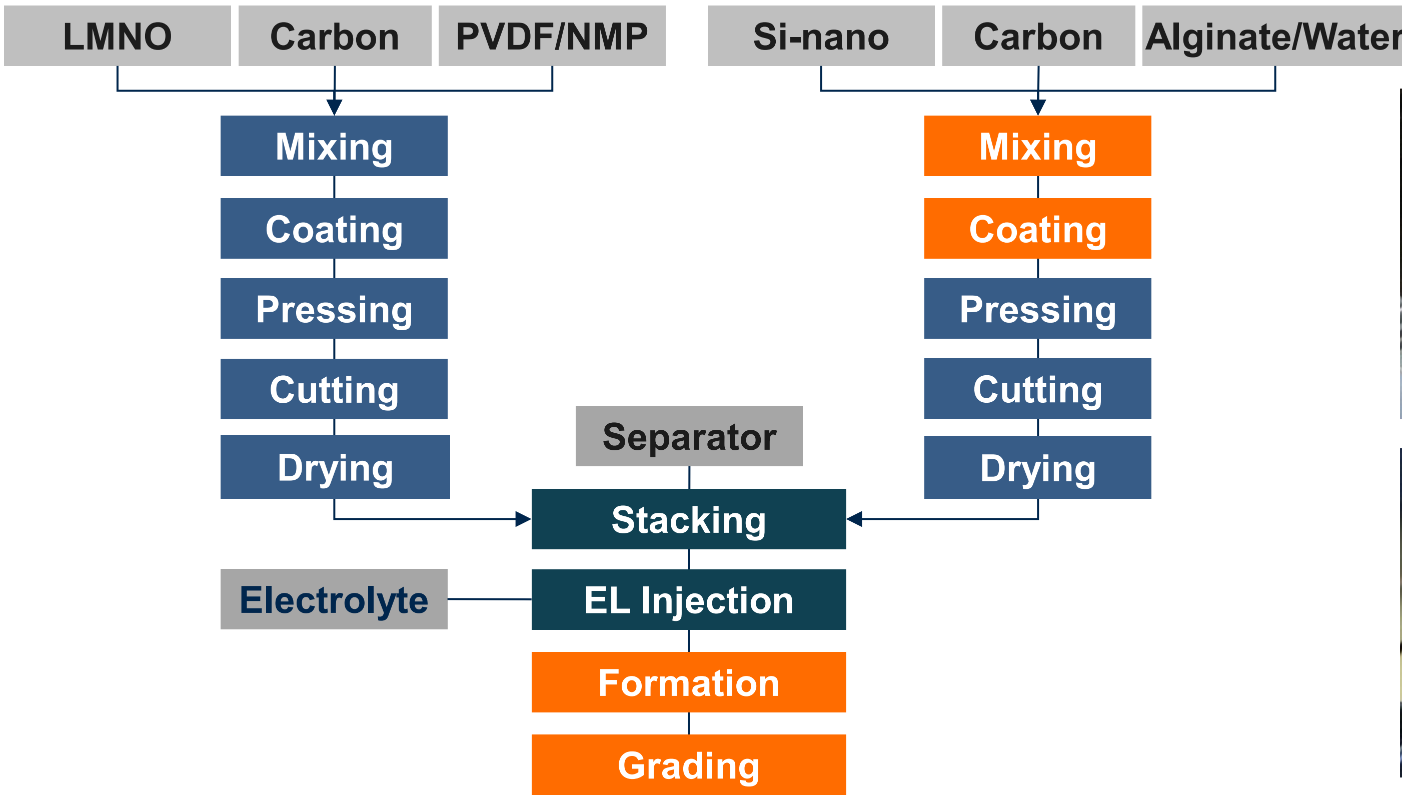


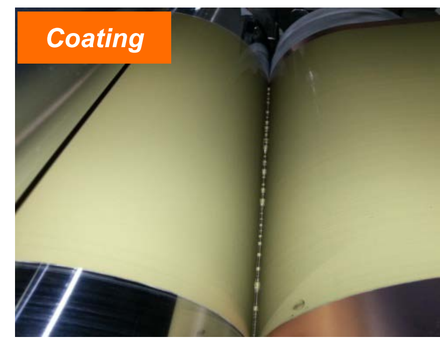
Test Condition

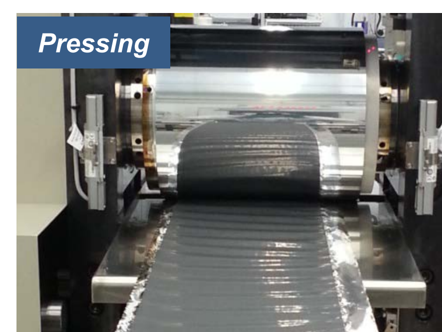
- Charge : CC(6.7A)/CV(4.9V to 1A) at RT

- Discharge : CC(6.7A) to 3.5V at RT

Issues in Manufacturing Process (ver.1)

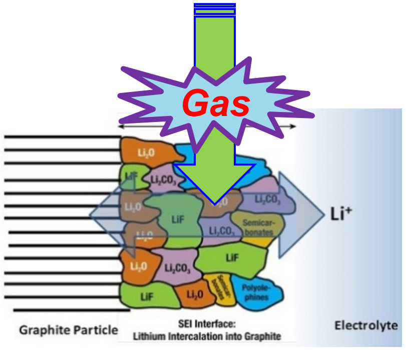






Severe Gas Generation (ver.1)

NCM vs. Graphite



https://www.liv.ac.uk/chemistry/research/hardwick-group/research/

LMNO vs. Si-nano

	Step	SOC	LMNO vs. Si-nano
	EL Injection		
	Pre-formation	30%	Gas
	Degassing		
	Main formation	100%	Gas
	2nd-degassing		
3 cycles	Grading	30%	Gas
	3rd-degassing		
3 cycles	2nd-grading	30%	Gas
	4th-degassing		
3 cycles	3rd-grading	30%	Gas
	5th-degassing		
1 step	Discharge	0%	Gas
	6th-degassing		
1 step	Charge	100%	No Gas
1 step	Discharge	40%	Gas

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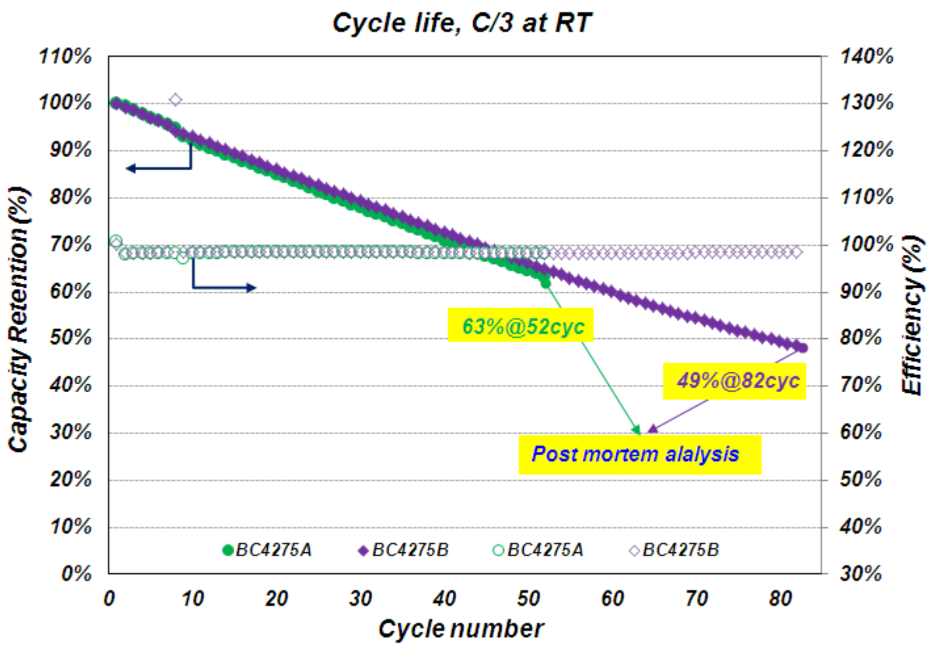
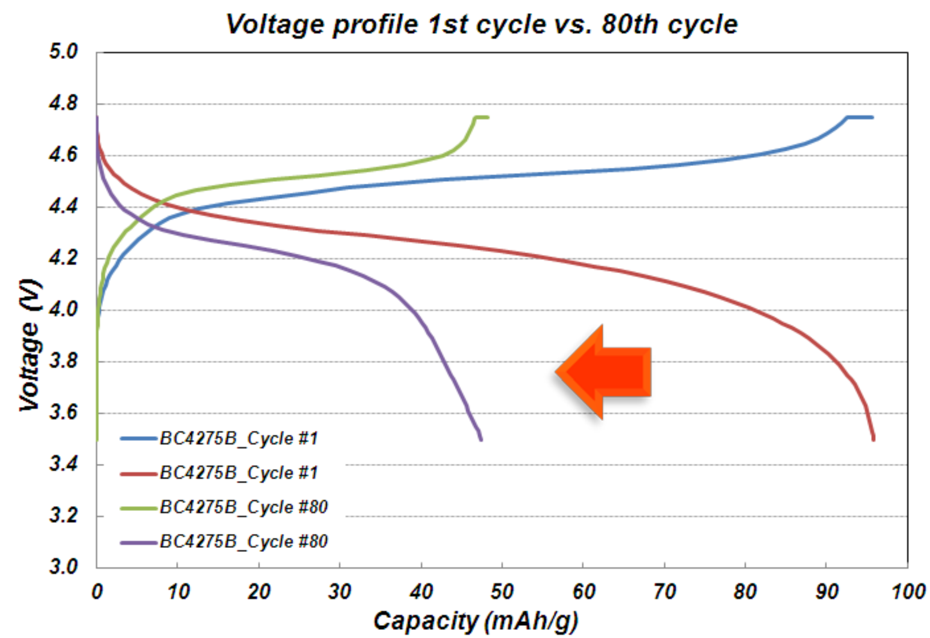
Cycle Test : Coin-type Full Cell (ver.1)





- ***Cycle life : <70% at 50th cycle***
- ***Coulombic efficiency : 98.6 ± 0.2 %***

  → Continuous lithium consumption

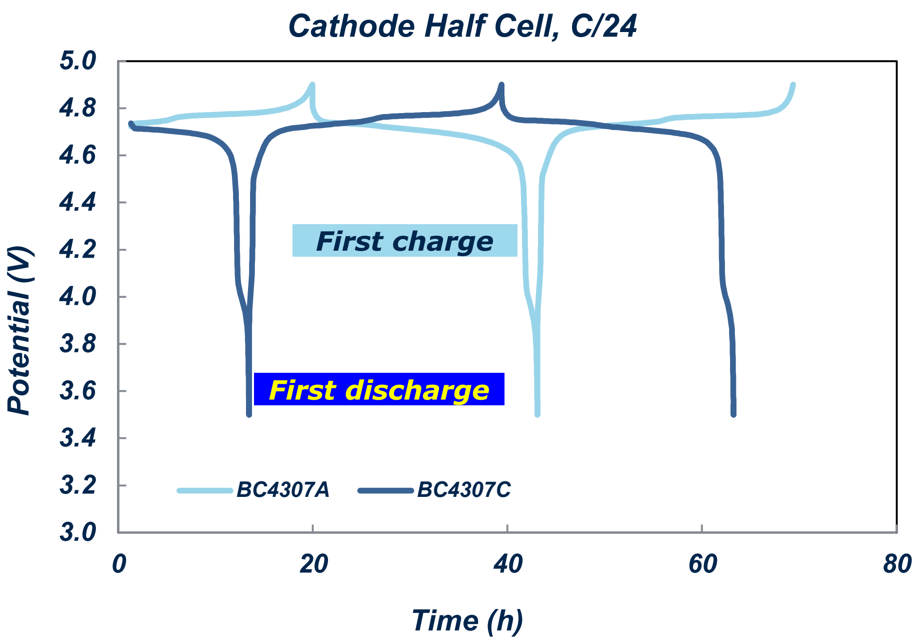
❑ ***Post mortem analysis after 80 cycles***

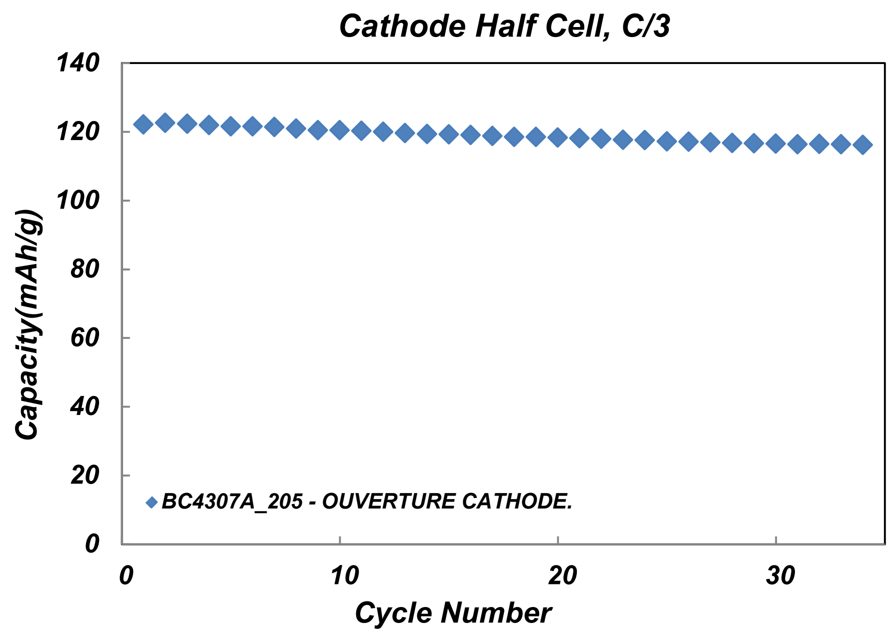
① **Complete discharge to 3.5V with floating for 12hrs**

② **Open the full cell and collect the electrodes**

③ **Re-assemble the half cells using the cathode and anode respectively**

Post Mortem Analysis_Cathode Half Cell





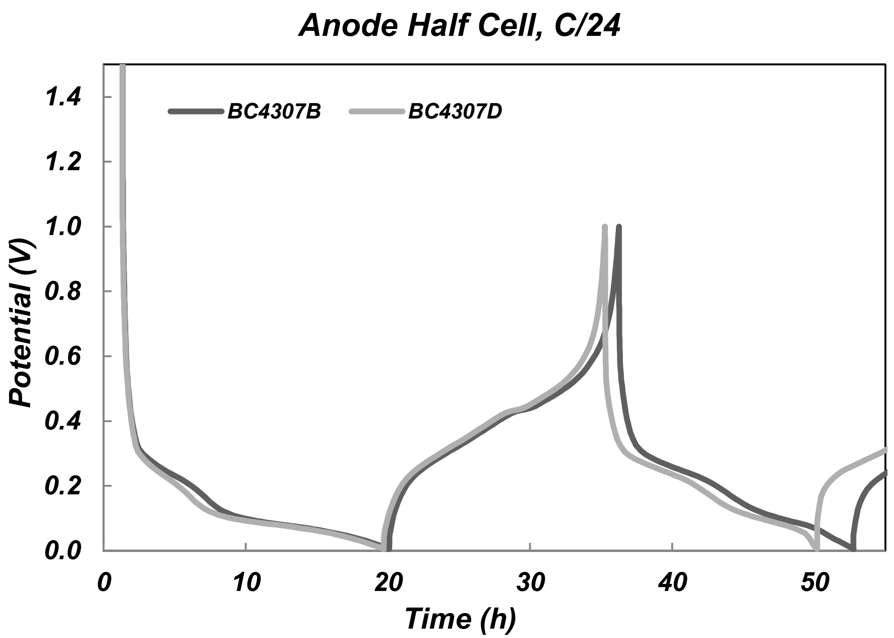
C-rate	Charge (mAh/g)	Discharge (mAh/g)	Charge (mAh/g)	Discharge (mAh/g)	Unused Capacity	Capacity Retention in Full Cell
BC4307A	101	125	142	129	28.9%	63%
BC4307C	-	66	141	129	51.1%	49%

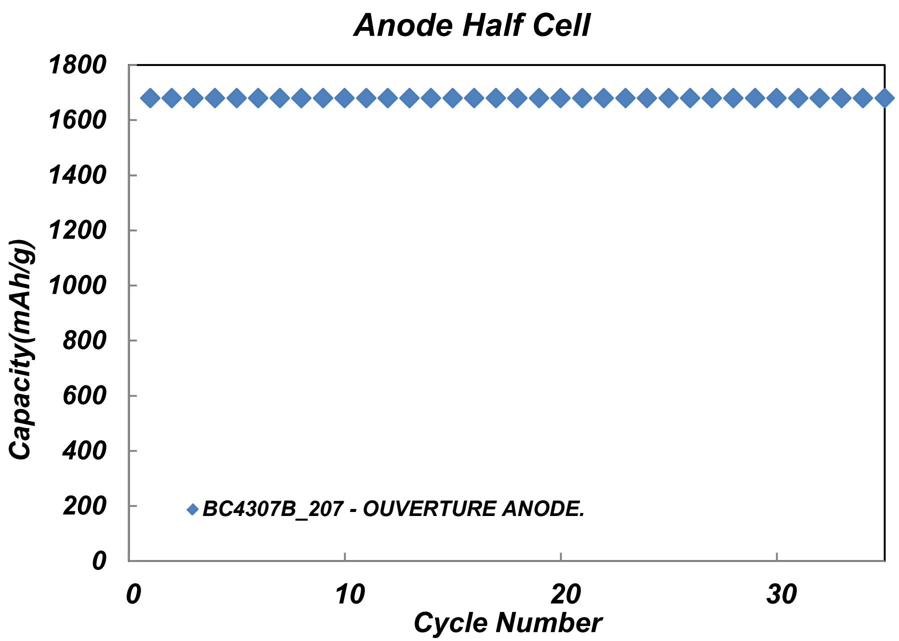
Test Condition

- Charge : CC(C/3)/CV(4.9V for 15 min)
- Discharge : CC(C/3) to 3.5V

- Cathode performance is completely recovered in the half cell.
- Capacity decay in full cell is due to the mismatch of anode-cathode balance, caused by the irreversible loss of lithium.

Post Mortem Analysis_Anode Half Cell





C-rate	Discharge	Charge	Discharge	Charge	Capacity Loss
	(mAh/g)	(mAh/g)	(mAh/g)	(mAh/g)	
BC4307A	4	3284	2828	2888	-
BC4307C	-	3221	2724	2613	-

Test Condition

- Charge : CC(C/6)/CV(5mV for 15 min, or SOC40% at RT
- Discharge : CC(C/6) to 1.0V at RT

- *Anode performance is completely recovered in the half cell.*
- *Capacity decay in full cell is due to the mismatch of anode-cathode balance, caused by the irreversible loss of lithium.*

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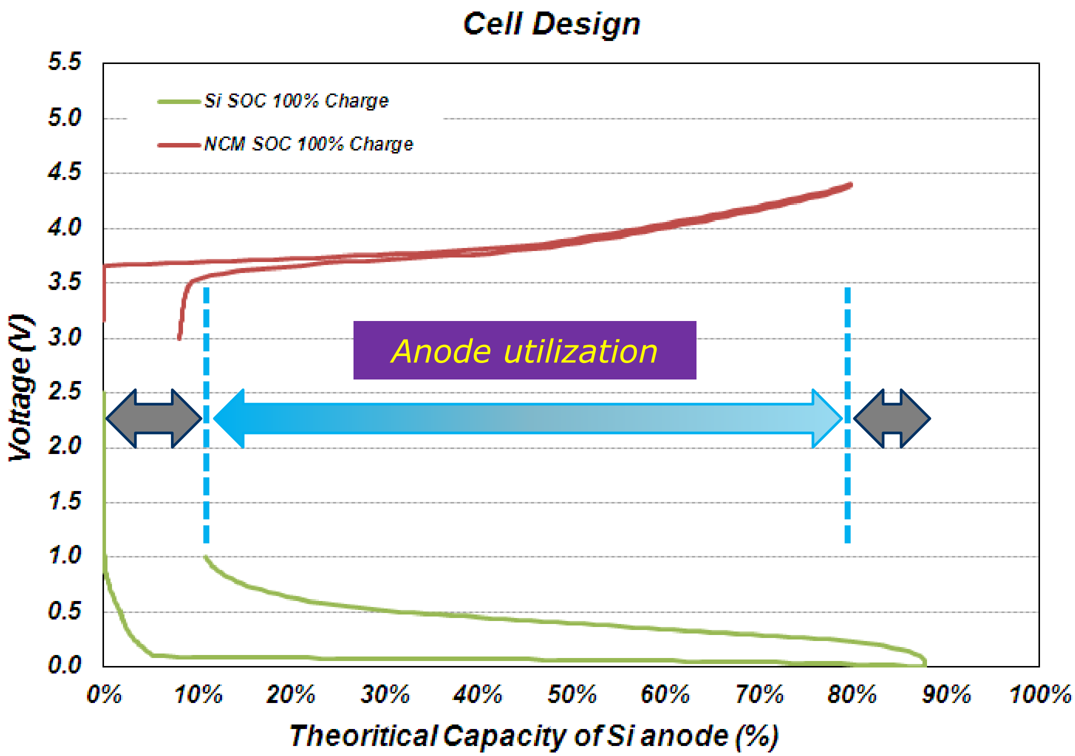
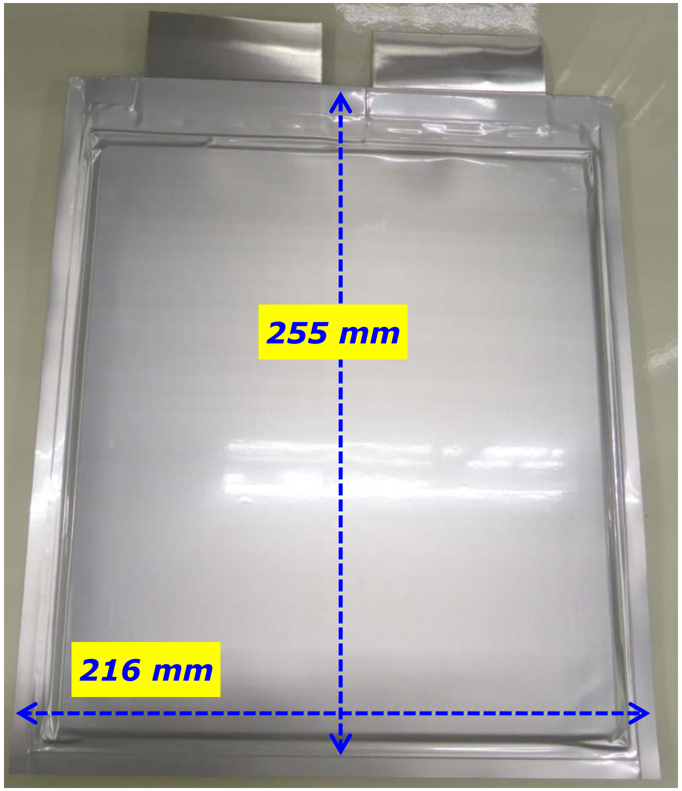
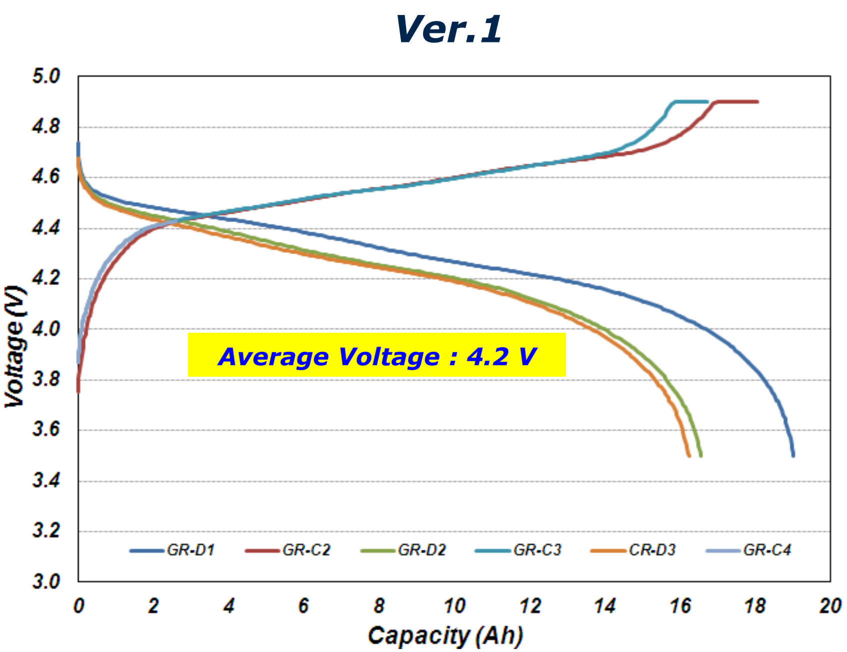
Design of Large Format Cell (ver.2)

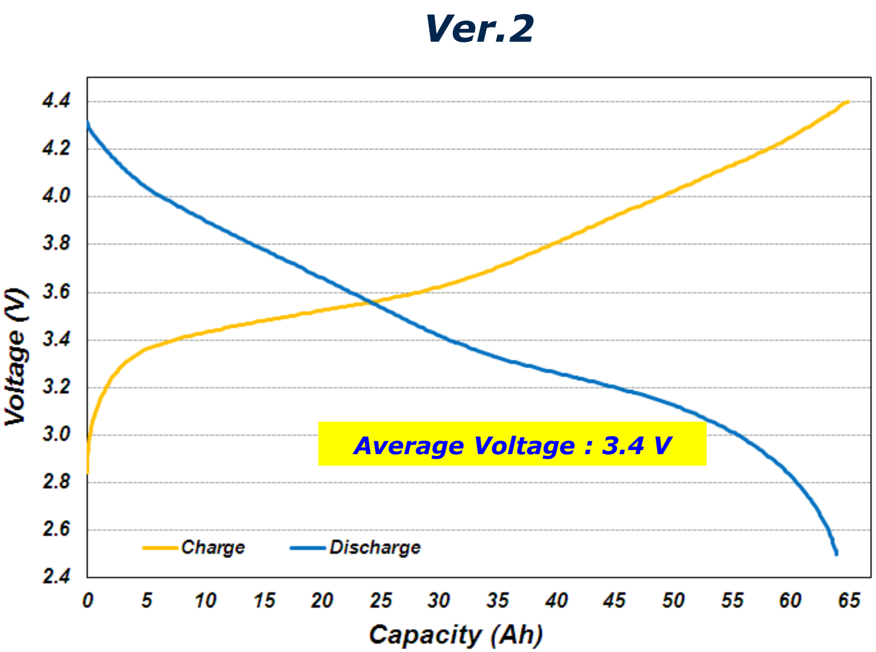




- **Target : specific energy >250 Wh/kg**
- ***Cathode- limited design : HE NCM***
- ***Anode utilization : 90% of usable capacity***

Voltage Profile





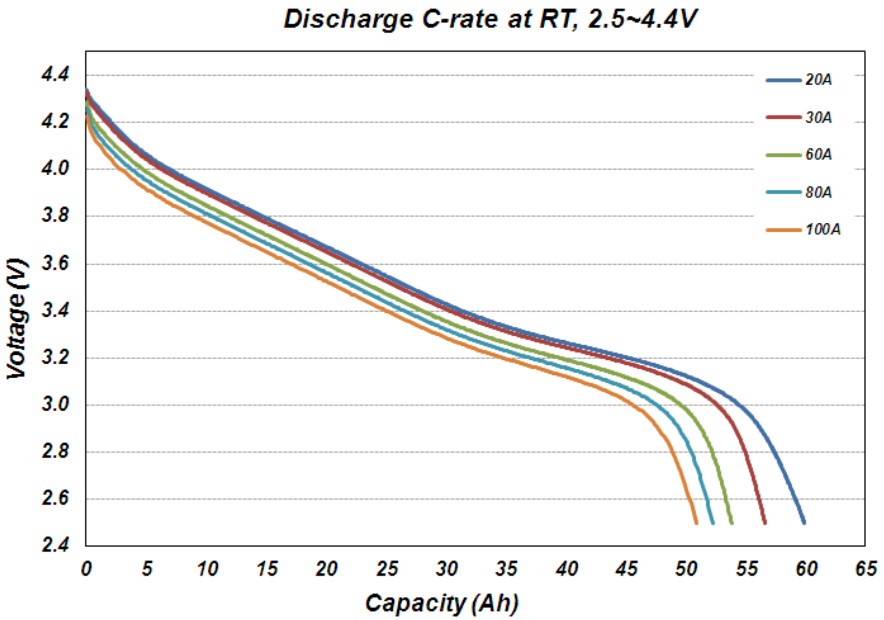
- Charge : CC(6.7A)/CV(4.9V to 1A) at RT
- Discharge : CC(6.7A) to 3.5V at RT

- Charge : CC(20A)/CV(4.4V to 3A) at RT
- Discharge : CC(20A) to 2.5V at RT

❑ No gas generation in ver.2

❑ Cell thickness change : ~7.4% (SOC 100% vs. 0%)

Rate Capability (ver.2)



Test Condition

- ***Charge : CC(C/3)/CV(4.4V to 3A) at RT***
- ***Discharge : CC to 2.5V at RT***

C-rate	Capacity	Retention	Average. V	Energy	Energy Density		Max. Temp.
	(Ah)	(%)	(V)	(Wh)	(Wh/kg)	(Wh/L)	(°C)
C/3_20A	59.9	100%	3.481	209	237	445	27
C/2_30A	56.6	95%	3.494	198	225	423	29
1C_60A	53.8	90%	3.467	187	212	399	33
1.3C_80A	52.3	87%	3.446	180	205	385	38
1.7C_100A	50.9	85%	3.422	174	198	372	42

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Specification : ver.1 vs. ver.2

Item		Unit	Version1	Version2	Remark
Material	Cathode	-	HV LMN	HE NCM	
	Anode	-	Nano Si	Nano Si	
	Binder	-	Alginate	Alginate	
	Separator	-	Ceramic	Ceramic	
	Electrolyte	-	EC/DEC/FEC	EC/DEC/FEC	
Cell	Capacity	(Ah)	19	64	@ C/3
	Average Voltage	(V)	4.246	3.433	
	Specific Energy	(Wh/kg)	124	250	
	Energy Density	(Wh/L)	204	437	
	Thickness	(mm)	-	9.13	@ SOC100
	Width	(mm)	216	216	
	Length	(mm)	255	255	
	Weight	(g)	653	880	
			Gas	No Gas	

Summary

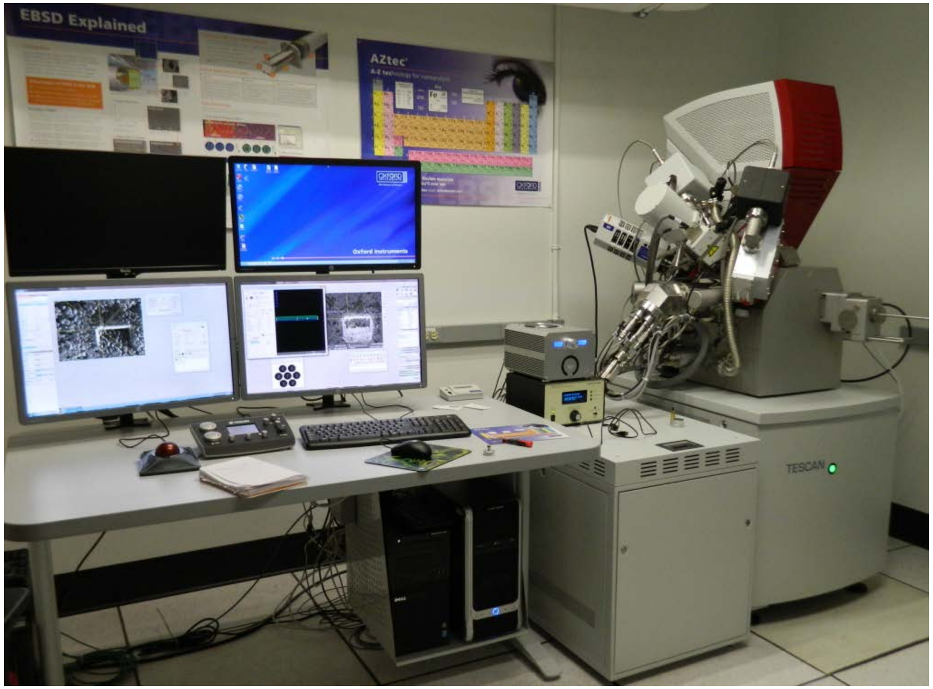
- **Completed:**
  - Production of Si nanopowder : capacity fade less than 20% @100 cycles.
  - In-situ TEM analysis for Si nanopowder
  - Sample delivery
    - **Si powder** to LBNL (1kg), Stanford Univ. (1kg) and Penn State Univ. (0.5kg)
    - **Si anode electrode** to LBNL (Jun-2014, Sep-2014, Dec-2014) with Gr electrode (Dec-2014), to Utah Univ.
    - **Cathode electrode** : HV LMN (Sep-2014), HE NCM (Dec-2014), NCM-LMO (Dec-2014) to LBNL
    - Electrolyte (Sep-2014, Dec-2014) to LBNL
    - **20 Ah large format cell** : ver.1 (Sep-2014) to LBNL
    - **60 Ah large format cell** (250 Wh/kg) : ver.2 (Dec-2014) to LBNL

Future Activities

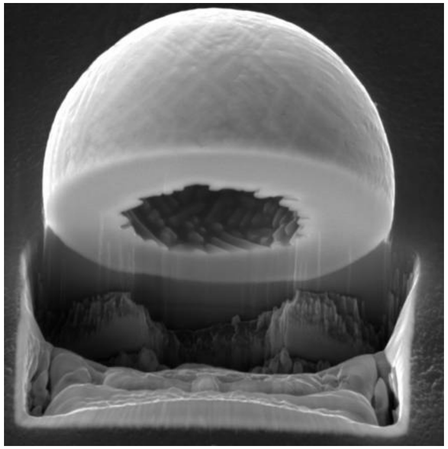
- **On going:**
  - Optimize the particle size (200 ~ 50 nm) and process conditions of nano-Si powder.
  - Study the effect of precursor composition : Si, SiO_x, Si-SiO_x .
  - Synthesis of secondary particles using spray-dry process.
  - Continue to study SEI passivation, fracture of electrode and particles by in-situ SEM, TEM, dual-beam microscope.
  - Increase the energy density to meet the requirement of BMR program
  - Increase the loading Si electrode : further development of binder and electrode architecture.
  - Characterize the gas generation in slurry and cell.
  - Surface treatment of nano-Si powder by using spry dryer.
  - HQ wants to be a provider of baseline nano-Si powder for BMR program and supply it to PI’s without NDA.

Dual-beam(electron+ion) Microscope

- Dual-beam microscope for in-situ specimen preparation and 3D characterization
- '**One of a kind**' instrument
  - TOF-SIMS (H, Li,…)
  - 2 EDS (Li detectable)
  - 1 EBSD
  - 2 BSE detector
  - 5 gas injections
  - 1 micro-manipulator



Tescan Lyra3 FIB-FESEM



New Pouch Cell Assembly Line (1-5Ah)

Coin Half Cell → **1-5 Ah Full Cell** → **10~50 Ah Full Cell**

- ✓ Coin type
- ✓ Cylindrical type (1~3 Ah)
- ✓ **Pouch type (1~5 Ah)**
- ✓ Pouch type (10~50 Ah)

Stamping

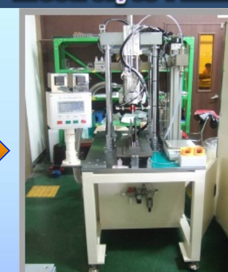
→ **Z-Stacking**

→ **Tab Welding**

→ **Pouch Forming**

→ **Side Sealing**

→ **Electrolyte Filling**



Formation

→ **Degassing**

→ **Pouch Cutting**

→ **Hot Press**

→ **OCV/IR Check**

→ **Pouch Cell**

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