Development of Si-Composite Anode for Large-Format Li-ion Batteries

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Hydro-Quebec

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Project ID : ES222

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Overview

Timeline

- Start date: October 2012
- End date: September 2016
- 81% 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 (V. Battaglia)
- PNNL (J. Zhang)
- 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 nano-Si*.

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

Milestones

- **Accomplishments**
  - Production of *nano*-Si powder : Milling process vs. Plasma process.
  - Study the effect of precursor composition : Si, SiO_x.
  - Synthesis of *nano*-Si/Carbon composite using spray-dry process.
  - Characterize the gas generated in slurry and cell.
  - Characterization : SEM, *dual-beam* Microscope.

- Deliverables to Collaborators
  - *nano-Si powder* : ANL, 900g (B. Polzin, July-2015).
  - *nano-Si anode electrode* : LBNL, 10m of *nano*-Si electrode (V. Battaglia, Jun-2015).
  - *nano-Si/NCM cells* : LBNL, 2 dry cells of 49,5 Ah (V. Battaglia, Sep-2015).

Milestones

- **On going:**
  - Optimize nano-Si/C composite using spray-dry process.
  - Continue to study the effect of precursors in Plasma process : Si, SiO_x, Si-SiO_x.
  - Continue to study SEI passivation, fracture of electrode and particles by *in-situ* SEM, dual-beam microscope.
  - Increase the loading of Si electrode : development of binder and electrode architecture.

Contents

- **Material Development**
  - ✓ ***nano*-Si powder by Milling process**
  - ✓ ***nano*-SiO_x powder by Plasma process**
  - ✓ ***nano*-Si/C composite by Spray dryer process**
- **Process and Cell Development**
  - ✓ **Gas generation in <u>water-based</u> alginate binder**
    - **Mixing, Coating and Formation process**
  - ✓ **Cell performance evaluation of the deliverable Y2015**
- **Post-mortem analysis**

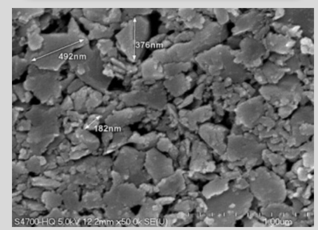
Milling Process → Low $ nano-Si Powder

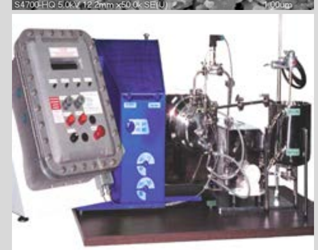
Milling Process in Y2014

Large Si chunk

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

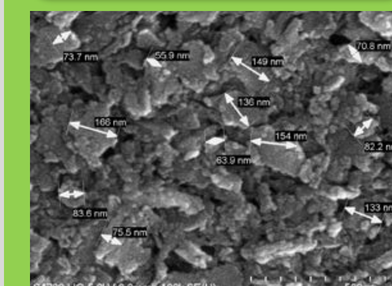
Jaw crusher d_{50} < 13 mm → Roll crusher d_{50} < 1 mm → Jet mill d_{50} < 10 μm → Wet mill Ⅰ d_{50} < 0.2 μm → Wet mill Ⅱ d_{50} ~ 0.1 μm





Milling Process in Y2015

- ❑ ***Parameter control***
- ✓ ***Milling time (Y15)***
- ✓ ***Beads size (Y15)***
- ✓ ***Solid contents (Y16)***
- ✓ ***Power (Y16)***



Milling Process → Bead Size Effect

Bead Size; 2.0 mm (Y14)

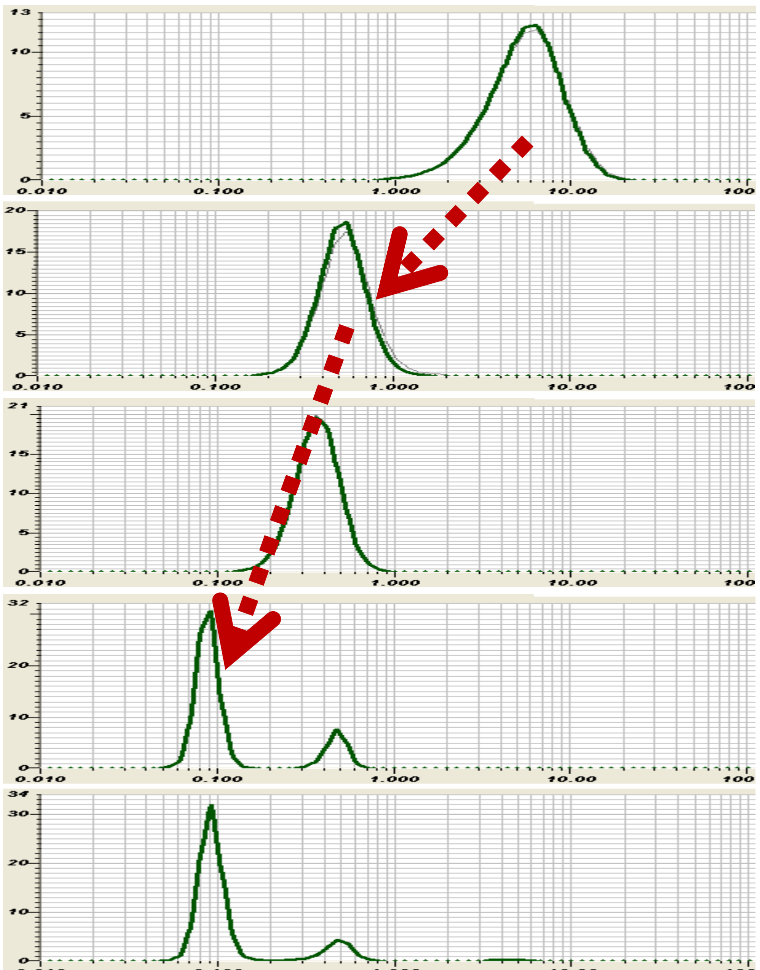
0 hr

1 hr

3 hrs

5 hrs

21 hrs

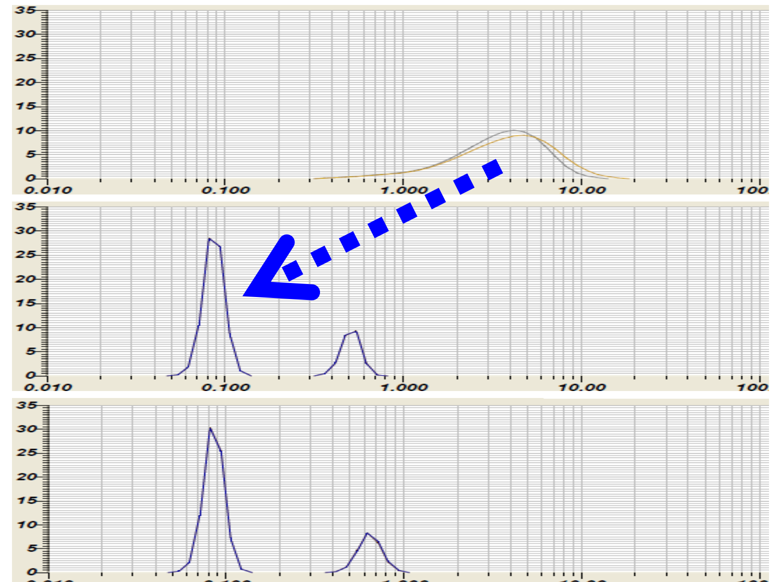


Bead Size; 1.0 mm 4hrs (Y15)

0 hr

0.5 hr

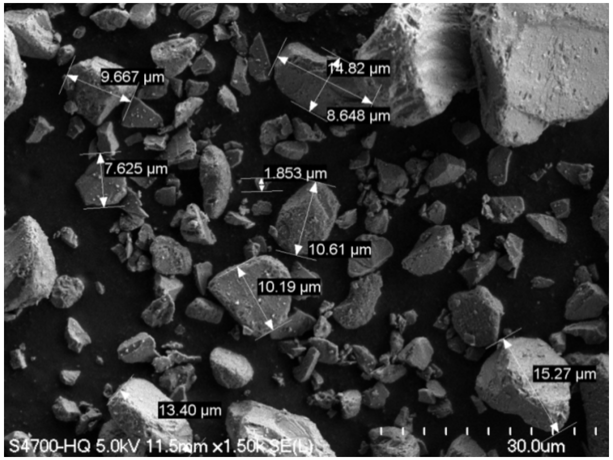
3 hrs

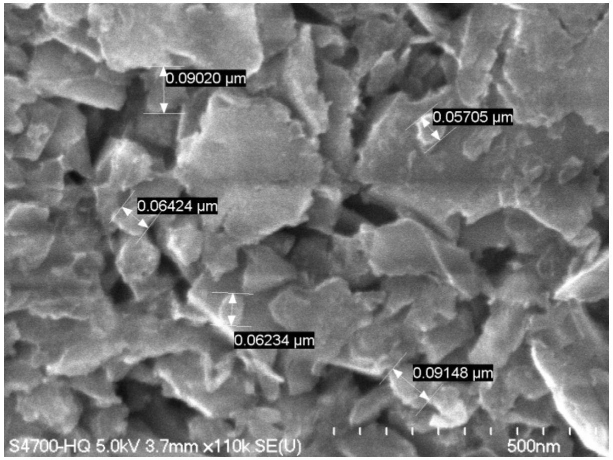


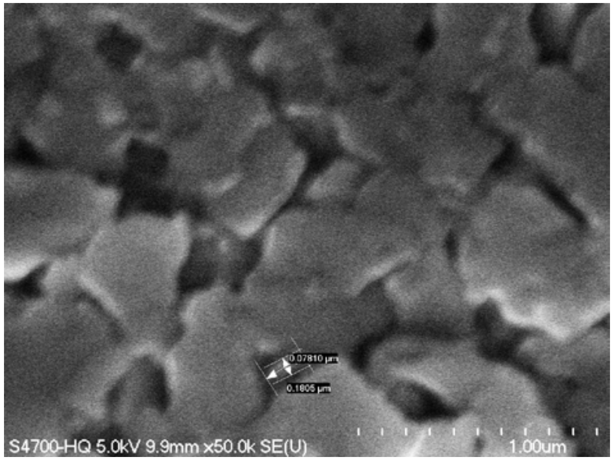
- ***Process time was reduced by bead size control; from 5hrs to 30 min to reach the sub-micron size.***

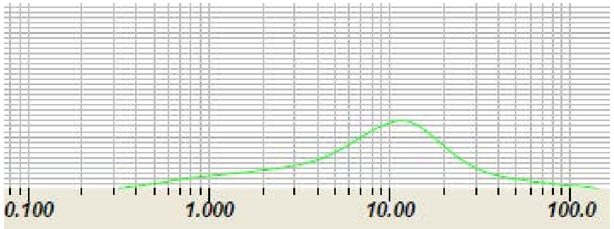
Milling Process → ⌀1.0 mm Beads

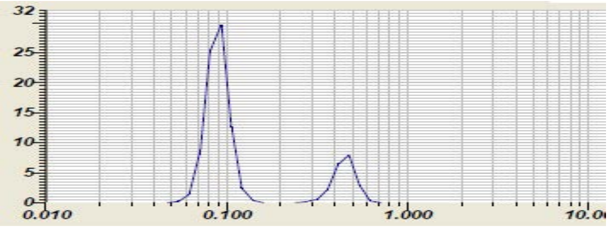
Jet-mill	Wet-mill : 1,0 mm (10 hrs)	Wet-mill : 1.0 mm (24 hrs)

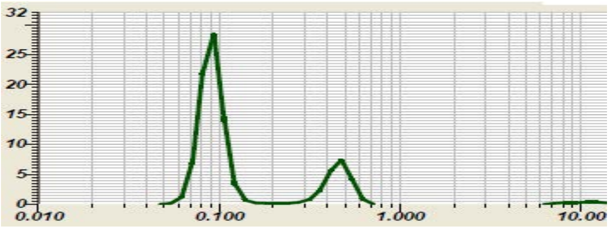








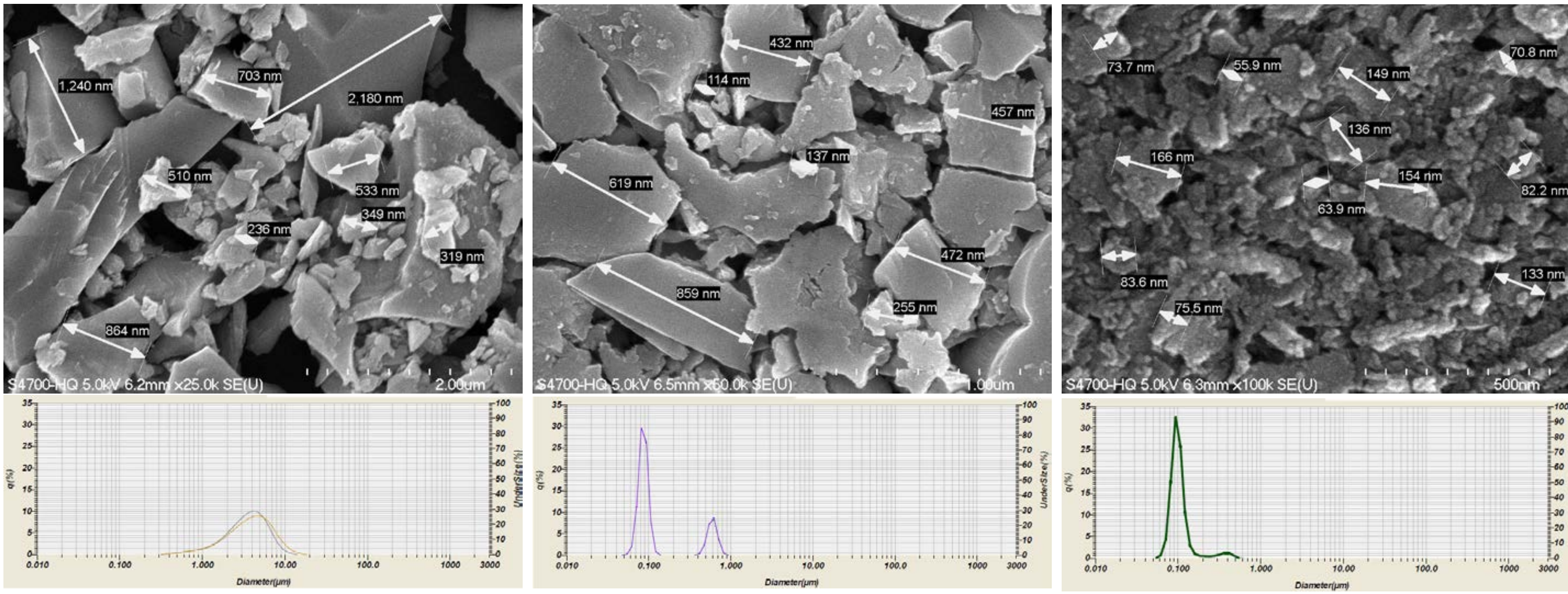




➢ ***Mean particle size is limited to ~100 nm : Bead size ⌀1.0 → ⌀0.3 mm.***

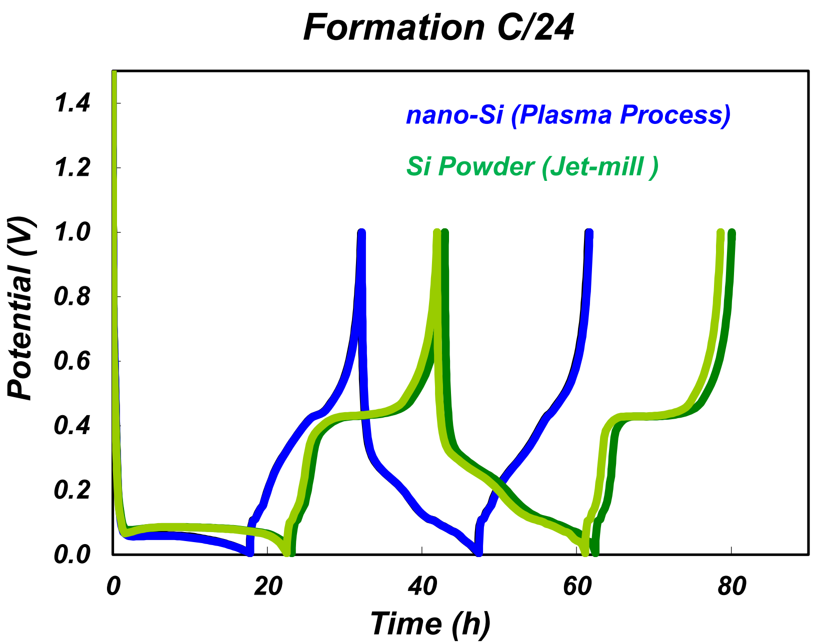
Milling Process → ⌀0.3 mm Beads

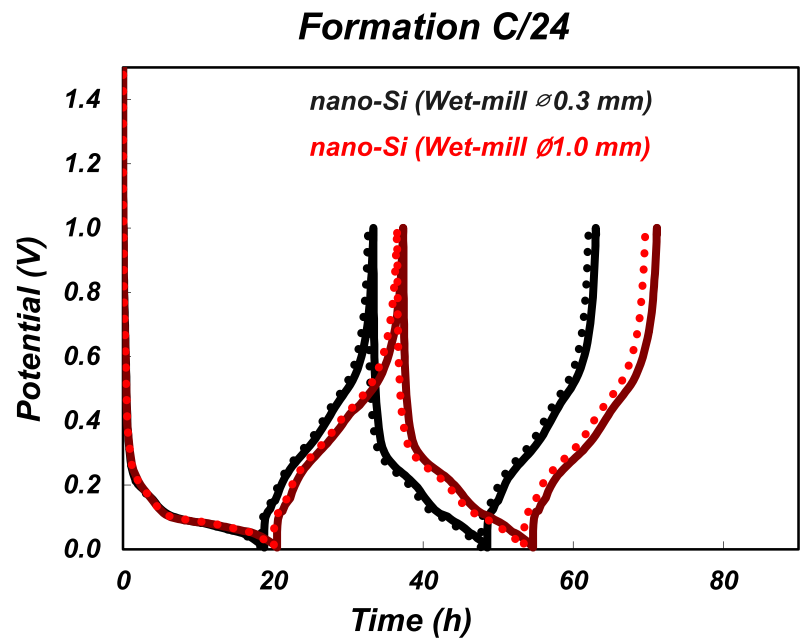
Jet-mill	1^{st} wet-mill : ⌀ 1,0 mm (4hrs)	2^{nd} wet-mill : ⌀ 0.3 mm (24hrs)



- *Mean particle size measured by PSA remains at ~100 nm.*
- *The 2^{nd} wet-milling using ⌀0.3 mm generates the nanometric primary particles of < 50 nm with the blunt edges.*

Milling Process → Electrochemical Test





	Charge 1 (mAh/g)	Discharge 1 (mAh/g)	Charge 2 (mAh/g)	Discharge 2 (mAh/g)	Efficiency 1 (%)	Efficiency 2 (%)
Plasma	3108	2527	2651	2501	81.3	94.2
Jet-mill	3937	3401	3351	3065	86.4	91.5
Wet-mill (Ø1.0 mm)	3513	2879	2954	2835	81.9	96.0
Wet-mill (Ø0.3 mm)	3220	2495	2625	2512	77.5	95.7

- ***The columbic efficiency and capacity are lowered with more grinding.***

Jet-mill > Wet-mill Ø1.0 mm > Wet-mil Ø0.3 mm

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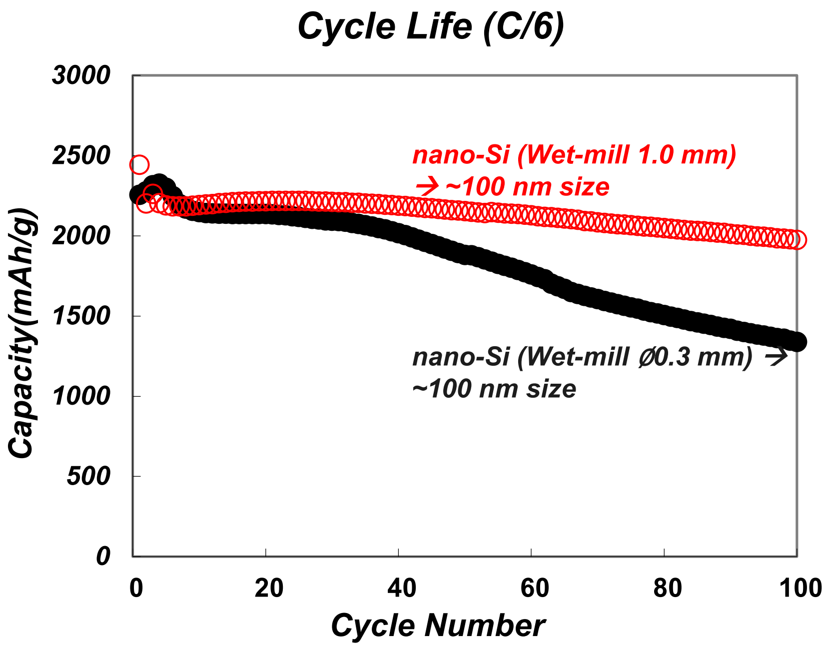
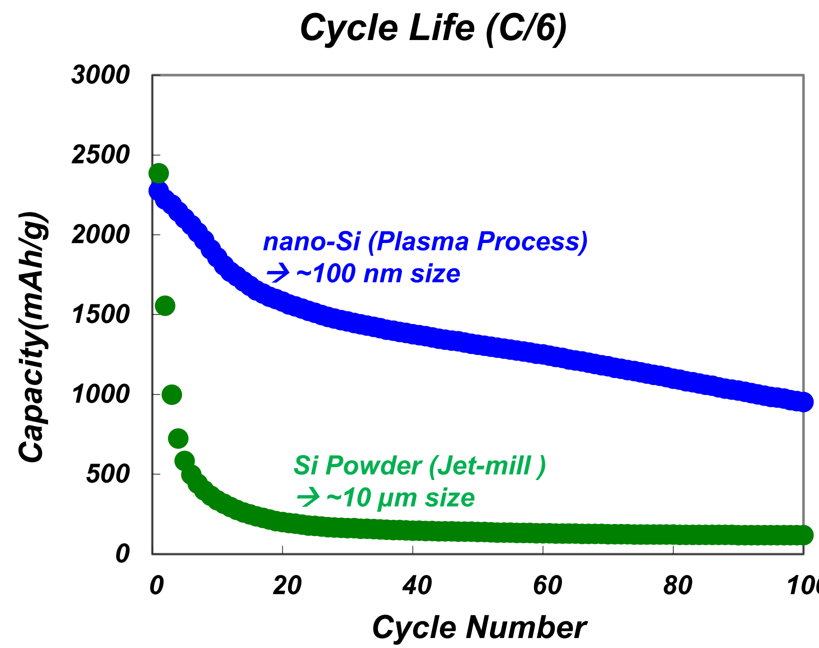
Milling Process → Electrochemical Test



Electrode	Nano-Si (Ø1.0mm)	Nano-Si (Ø0.3mm)
TOTAL Loading (mg/cm²)	2.75	2.1

½ cell (Lithium 200µm) at RT
Electrolyte: 1M $LiPF_6$ EC DEC + 10% FEC
Voltage cut-off : 0.005 ~ 1.0 V

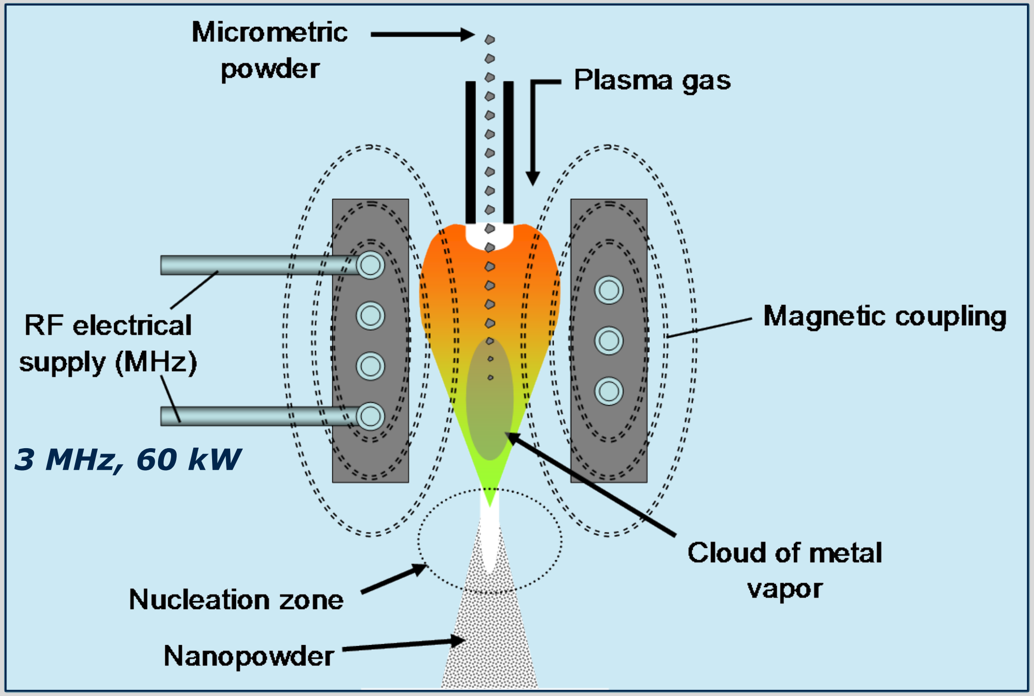


Electrode	Nano-Si (Plasma Process)	Si Powder (Jet-mill)
TOTAL Loading (mg/cm²)	2.28	2.27

- ***Nano-Si made by milling process shows better cycle performance than that of nano-Si obtained by Plasma process.***

Plasma Process → *nano*-SiO_x Powder

Plasma Process in Y2014



Silicone powder (µm size, 99.999wt%) $\xrightarrow{\text{Heat}}$ ***Metal vapor*** $\xrightarrow{\text{Quenching}}$ ***nano-Si Powder***

- ❑ ***High process cost > $50/kg***

Plasma Process in Y2015

- ❑ ***New precursor***
- ✓ ***SiO_x***
- ❑ ***Operation parameter***
- ✓ ***Quench condition (Y15)***
- ✓ ***Feeding rate (Y15)***

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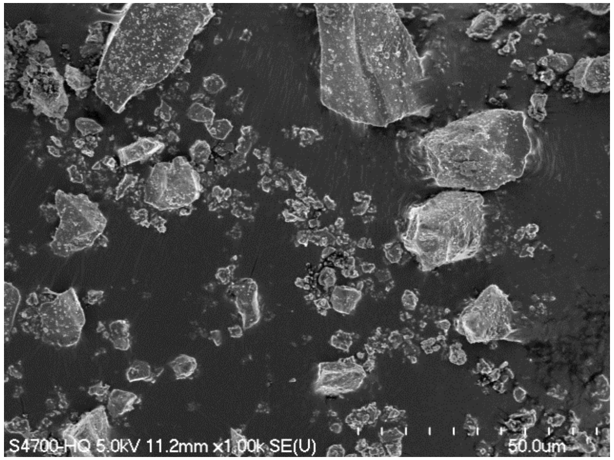
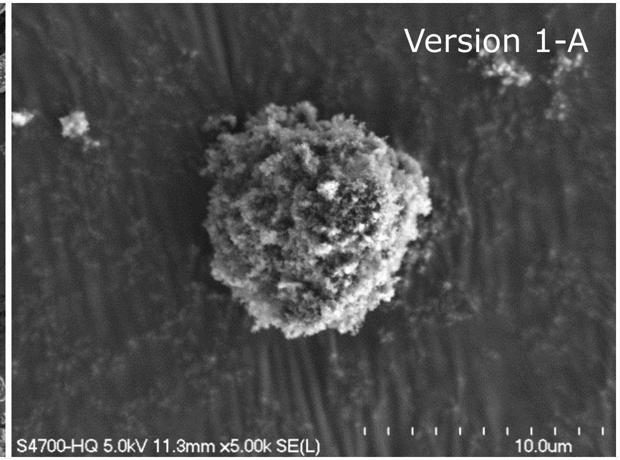
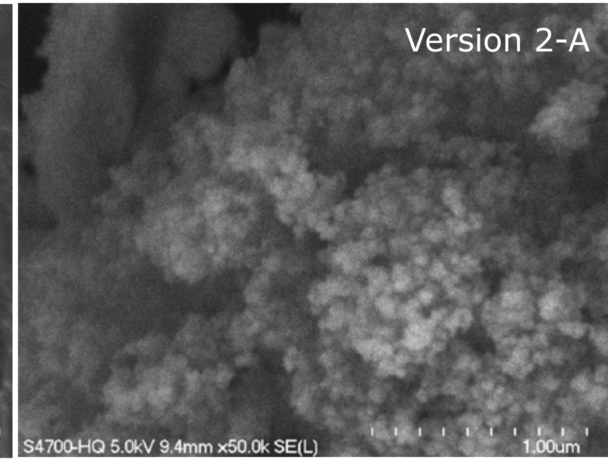
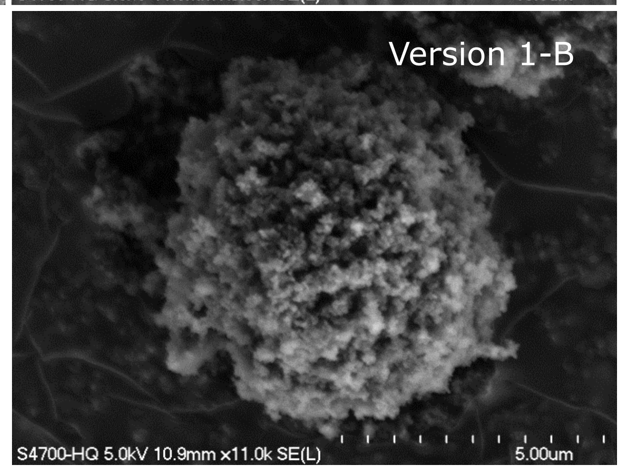
Plasma Process → Process Control

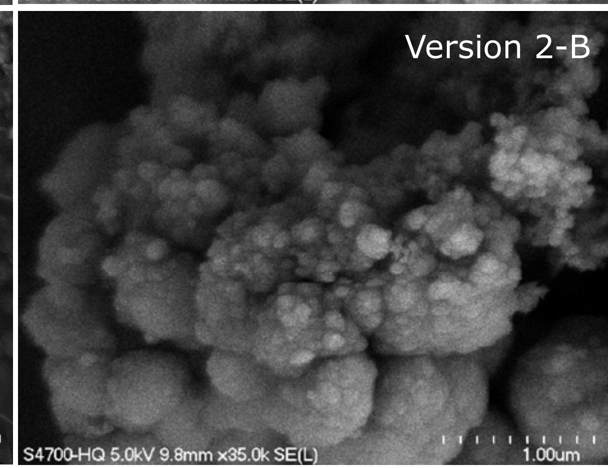
Raw Material	SiO_x Ver.1	SiO_x Ver.2; Quenching Speed ↓





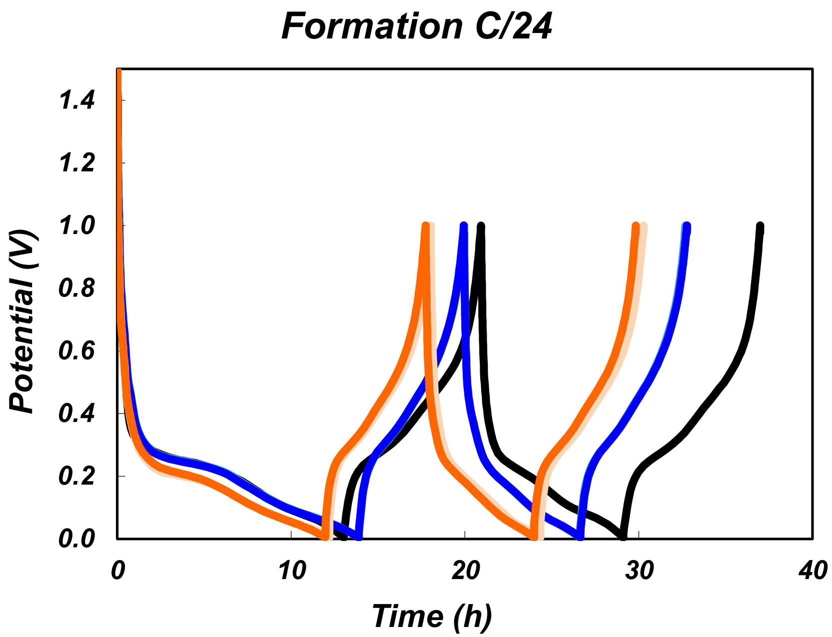


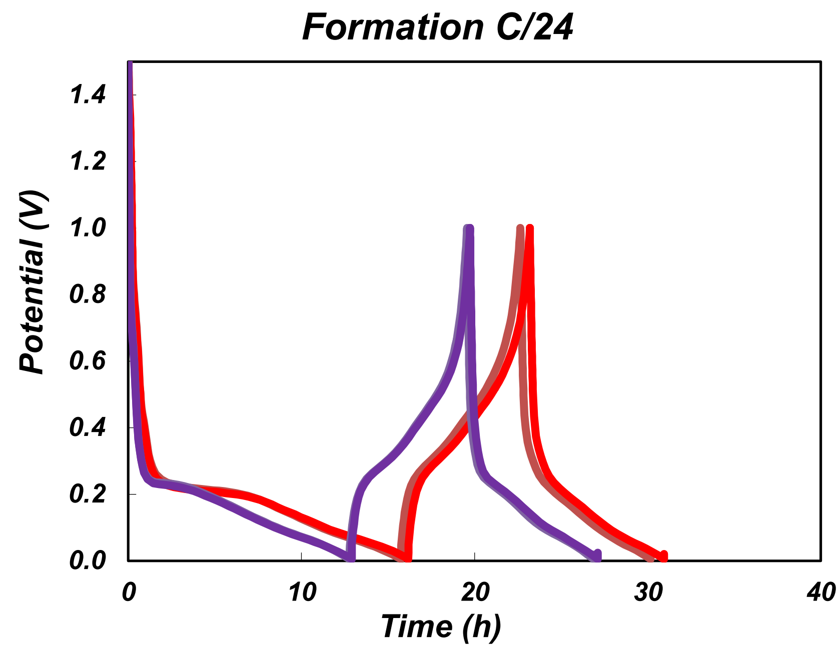




- ***SiO_x with primary particle size <100 nm was obtained by plasma process***

Plasma Process → Electrochemical Test

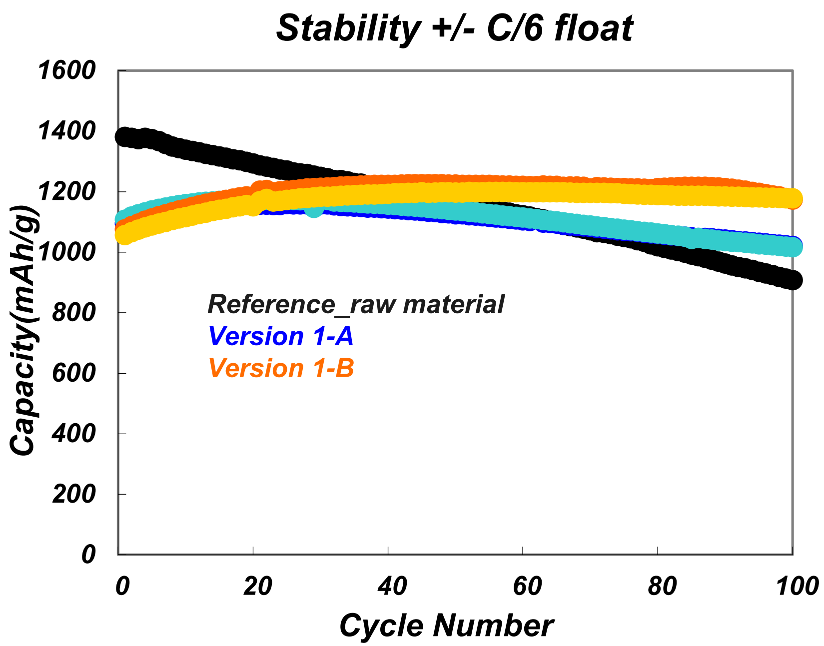


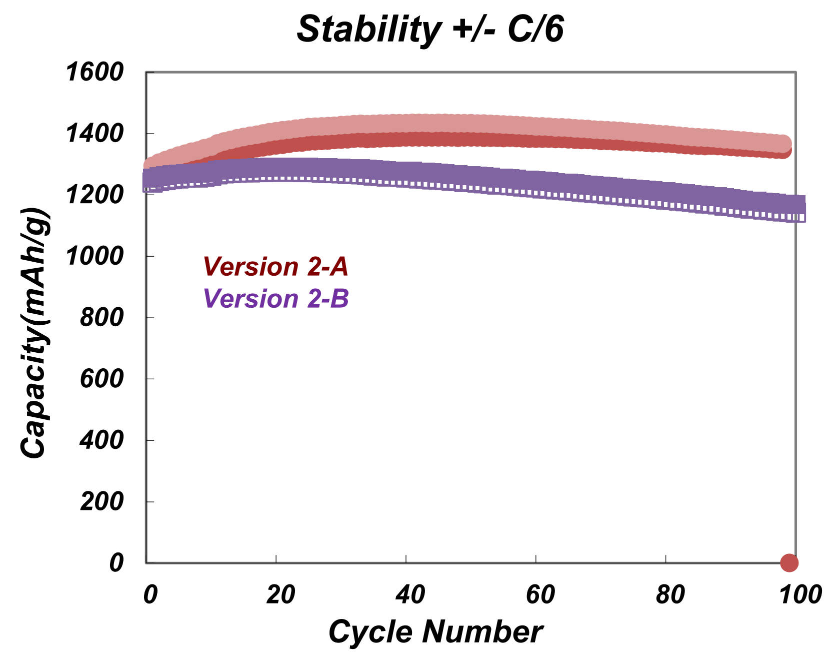


	Charge 1 (mAh/g)	Discharge 1 (mAh/g)	Charge 2 (mAh/g)	Discharge 2 (mAh/g)	Efficiency 1 (%)	Efficiency 2 (%)
Reference	2280	1383	1430	1379	60.6	96.5
Version 1-A	2432	1057	1164	1067	43.5	91.7
Version 1-B	2095	1008	1091	1024	48.1	93.8
Version 2-A	2757	1205	1316	-	43,7	-
Version 2-B	2237	1187	1277	-	53,0	-

- ***Lower quenching speed in the plasma process leads to better capacity.***

Plasma Process → Electrochemical Test



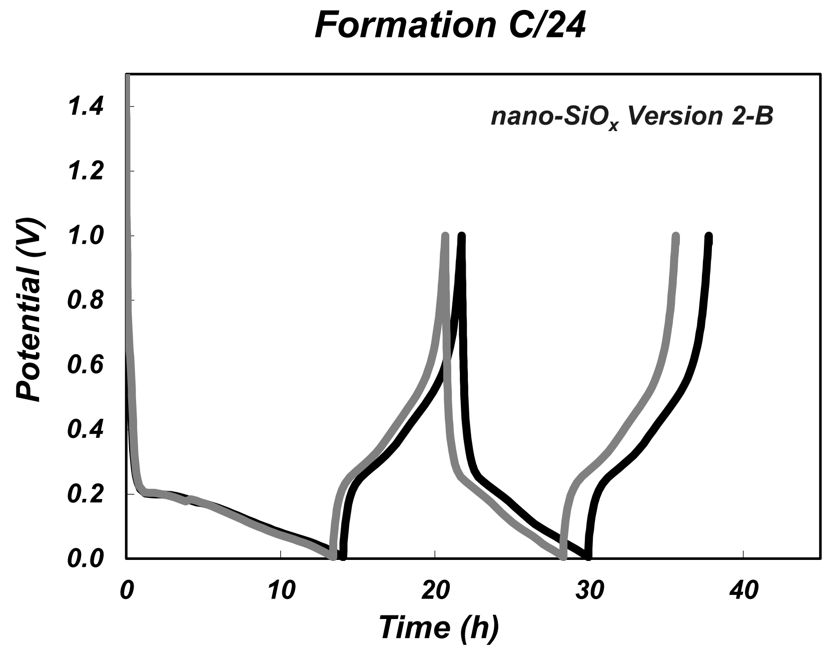


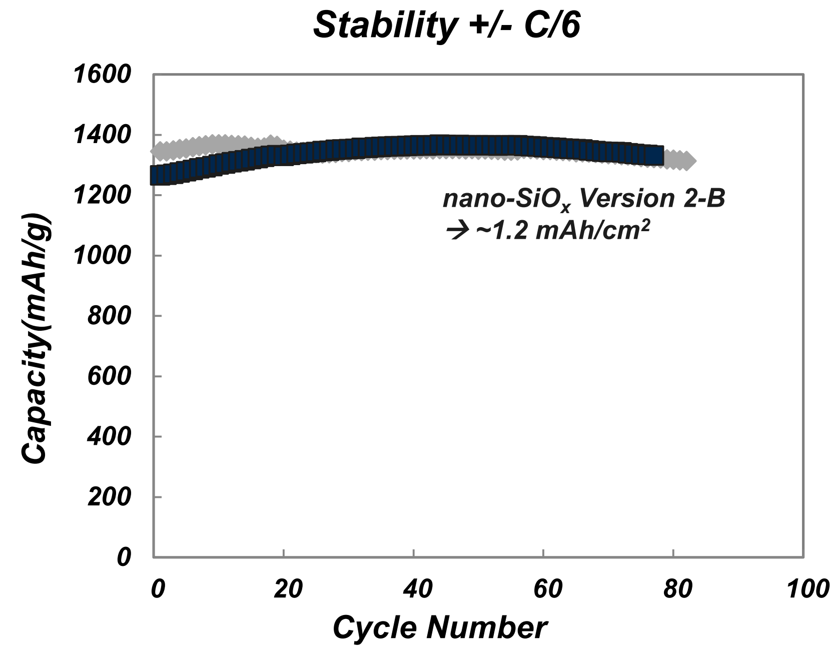
Electrode	Raw Material	Version 1-A	Version 1-B
Thickness (µm)	16	17	16
Vol. Density (g/cm^3)	1.05	0.95	1.11
Loading Total (mg/cm^2)	~0.55	~0.63	~0.65

Electrode	Version 2-A	Version 2-B
Thickness (µm)	22	27
Vol. Density (g/cm^3)	0.63	0.47
Loading Total (mg/cm^2)	~0,65	~0,85

- ***Nano-SiO_x shows improved cycle life compared to the pristine SiO_x.***
- ***Lower quenching speed leads to better cycle life.***

Plasma Process → Electrochemical Test





	Discharge 1 (mAh/g)	Charge 1 (mAh/g)	Discharge 2 (mAh/g)	Charge 2 (mAh/g)	Efficiency 1 (%)	Efficiency 2 (%)
Version 2-B	2464	1340	1439	1362	54.4	94.7

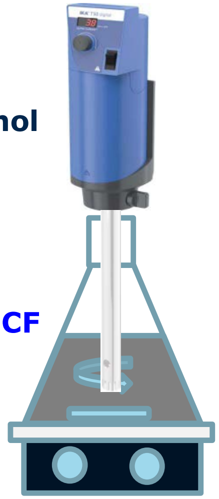
Electrode	Version 2-B
Thickness (µm)	39
Vol. Density (g/cm^3)	0.68
Loading Total (mg/cm^2)	~1.82

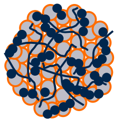
➢ ***Nano-SiO_x shows very stable cycle life even with high electrode loading.***

Spray Dryer → nano-Si/C composite

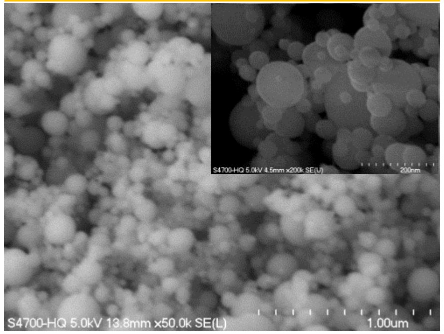
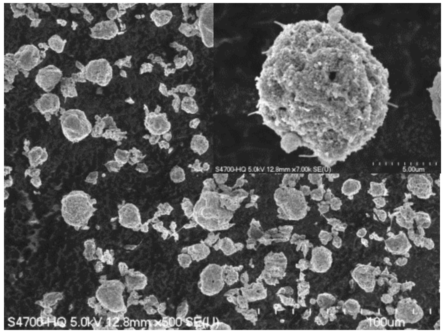
Mixing → Spray-drying → Heat-treatment → Nano-Si/C composite

Methanol
+
PAA
+
Si
+
DK/VGCF



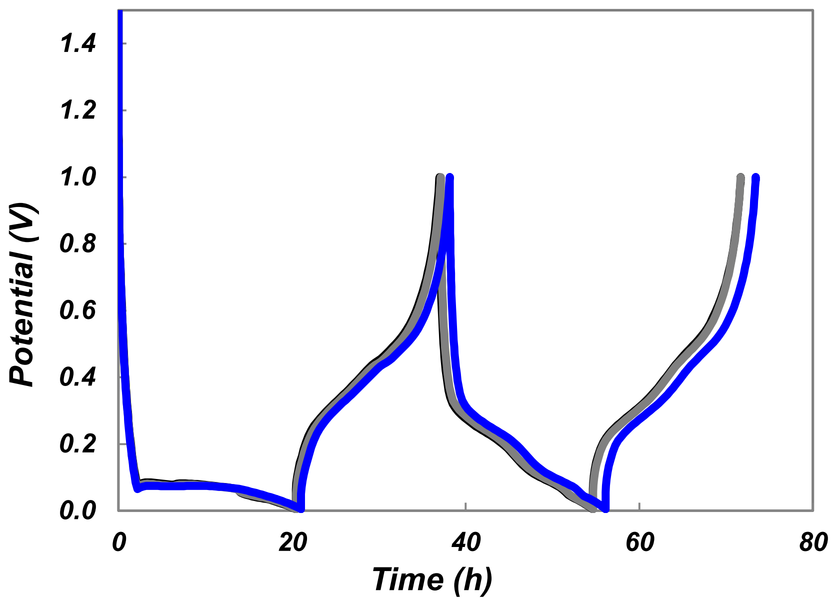


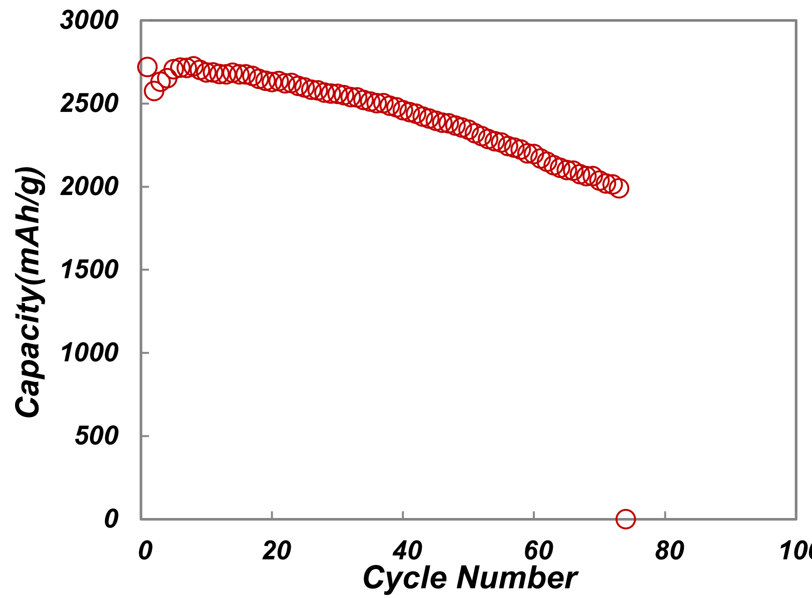
Si/PAA/DK/VGCF

Before Spray Drying	After Spray Drying
	

- Micro-sized Si/C composite was prepared by Spray-drying process, using the nano-Si primary particles.

Spray Dryer → Electrochemical Test





Charge 1 (mAh/g)	Discharge 1 (mAh/g)	Charge 2 (mAh/g)	Discharge 2 (mAh/g)	Efficiency 1 (%)	Efficiency 2 (%)
3577	2895	3091	2981	80.9	96.4

Electrode	PT-1936
Thickness (μm)	47
Vol. Density (g/cm^3)	0.57
Loading Total (mg/cm^2)	1.24

➢ ***Nano-Si/C composite shows comparable cycle performance to that of original nano-Si (plasma).***

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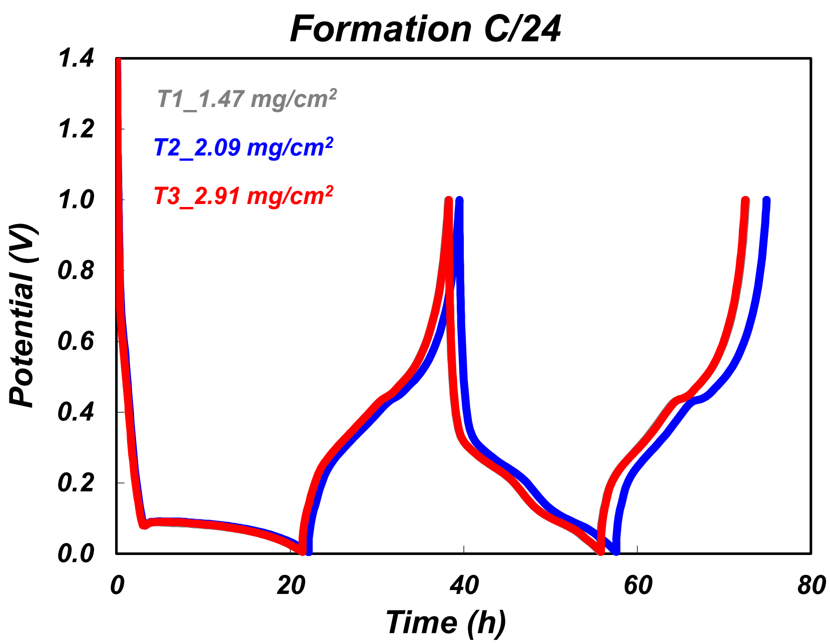
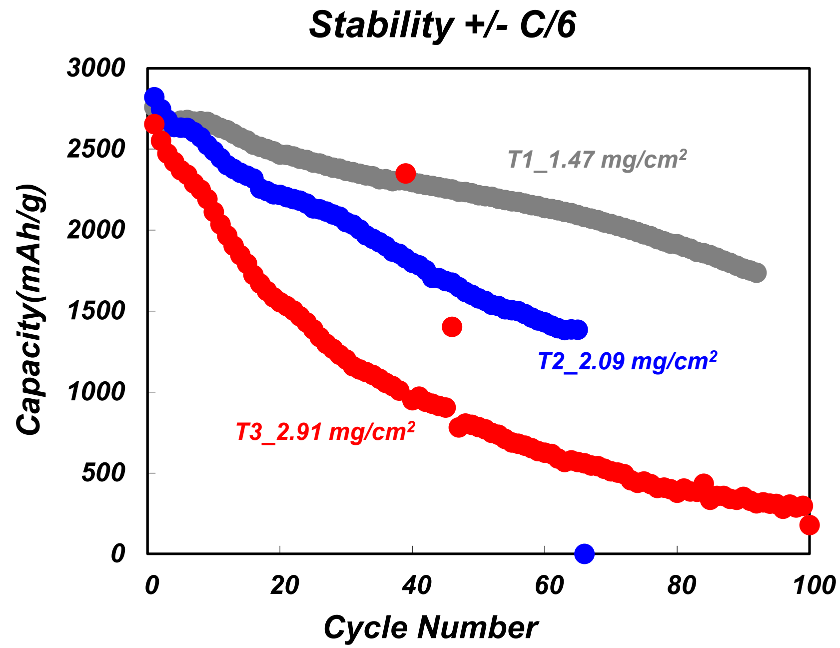
Spray Dryer → Electrochemical Test





	Charge 1 (mAh/g)	Discharge 1 (mAh/g)	Charge 2 (mAh/g)	Discharge 2 (mAh/g)	Efficiency 1 (%)	Efficiency 2 (%)
T1	3743	2940	3056	2944	78.5	96.4
T2	3868	3041	3159	3033	78.6	96.0
T3	3743	2951	3064	2906	78.8	94.8

Electrode	T1	T2	T3
Thickness (µm)	30	36	43
Vol. Density (g/cm^3)	1.30	1.24	1.36
Loading Total (mg/cm^2)	1.47	2.09	2.91

- ***With polyimide binder, adhesion strength of electrode was improved, which permits higher loading : 2.9 mg/cm^2.***

Gas generation → In Mixing Process

 # Possible cause; Hydrolysis

$2Si + 2H_2O \rightarrow 2SiOH + H_2(g)$

 # Approaches

(1) Surface coating of nano-Si powder; Spray dryer

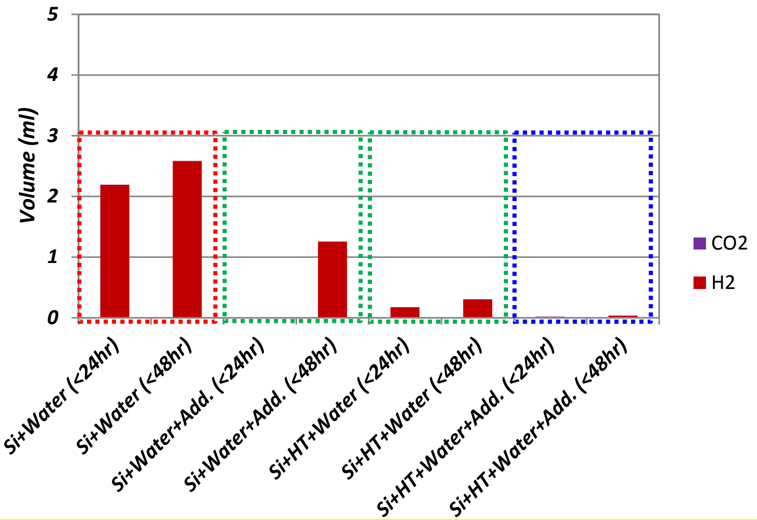
(2) pH control with additives

(3) Surface oxidation by low temperature heat-treatment; 24hrs, 80~150℃

(4) Aging the slurry more than 24hrs

Aging	Mixing Condition @ He filled Glove-box	Vials	Slurry	Sample Volume
24 hrs	Si+Water	20 ml	5 ml	5 ml
	Si+Water+Add.	20 ml	5 ml	5 ml
	Si+Water+HT	20 ml	5 ml	5 ml
	Si+Water+HT+Add.	20 ml	5 ml	5 ml
48 hrs	Si+Water	20 ml	5 ml	5 ml
	Si+Water+Add.	20 ml	5 ml	5 ml
	Si+Water+HT	20 ml	5 ml	5 ml
	Si+Water+HT+Add.	20 ml	5 ml	5 ml

(Add. ; Additive for pH control, HT ; Heat-treatment)



- ➢ **H_2 is the main component in the generated gas from the water-based slurry.**
- ➢ **Gas generation can be supressed by pH control of slurry and heat-treatment of Si.**

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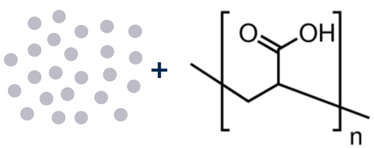
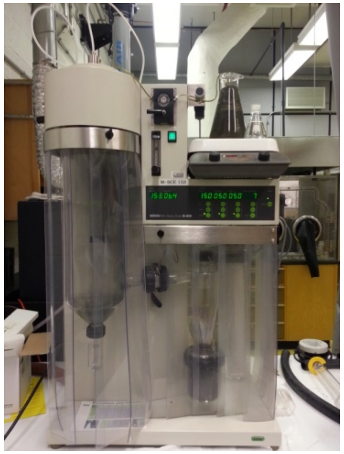
Gas generation → PAA Coating on nano-Si

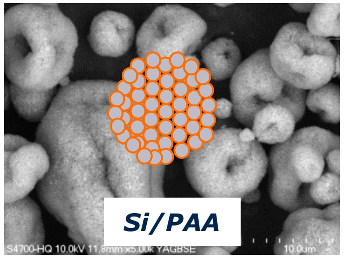
Surface Coating of nano-Si Powder

Methanol
+
PAA
+
Si



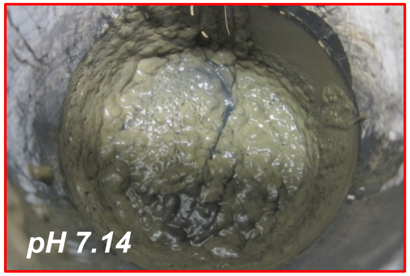
Si ***Poly(acrylic acid)***



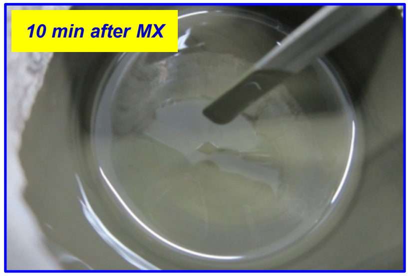


nano-Si in H_2O

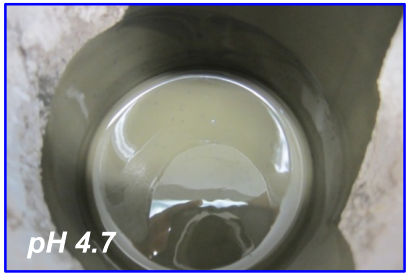
24 hrs



Surface coated nano-Si in H_2O



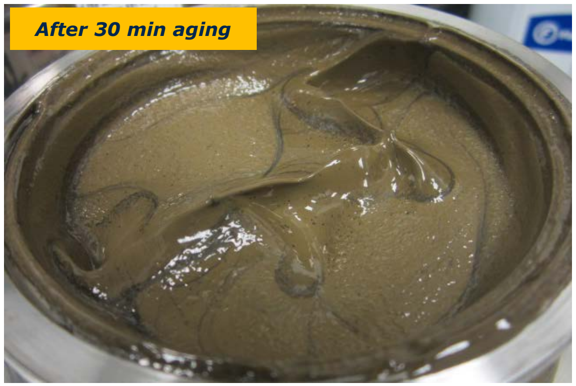
24 hrs

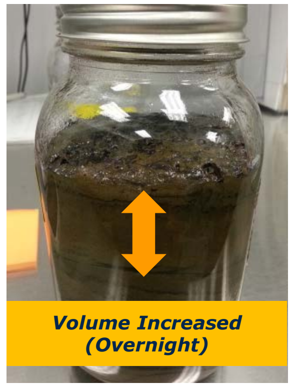


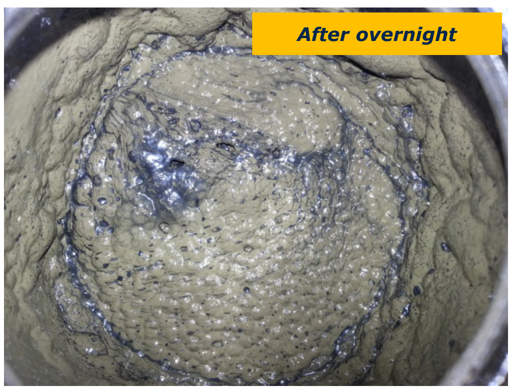
- ***Gas generation in water-based slurry is greatly suppressed by PAA coating on Si surface.***

Gas generation → Polyimide Binder

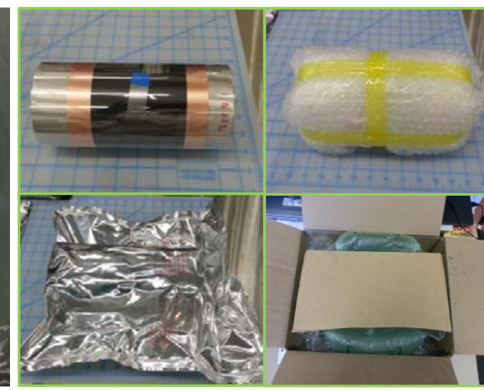
Water-based Alginate binder







NMP-based Polyimide binder



- ***Due to the processing issues related with the gas generation, polyimide binder system was selected for the deliverable in Y2015.***

Gas generation → In Coating Process

 # Possible cause

Air entrainment during the coating process; Fluid mechanics

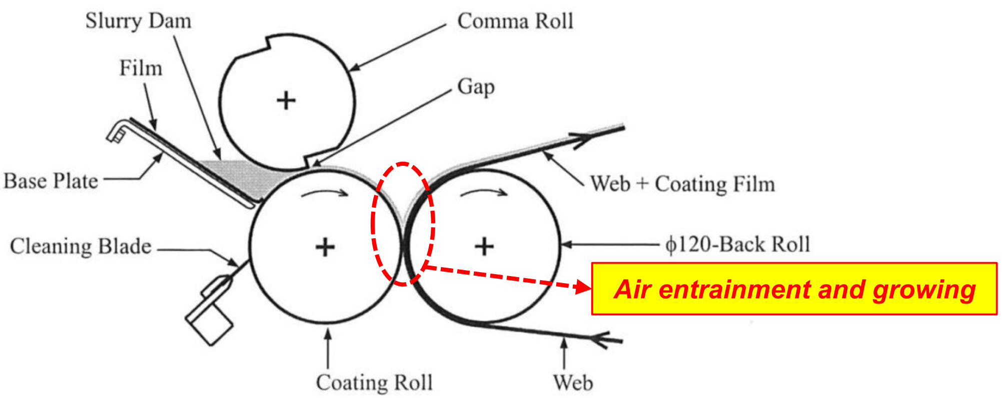
→ Approaches

(1) Coating method; Direct-comma, die-coating, gravure coating etc.

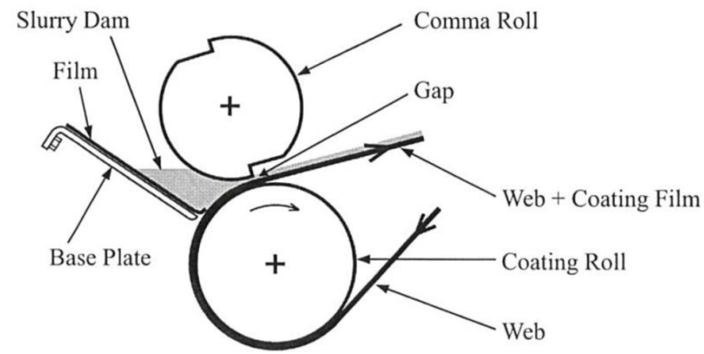
(2) Use additives; defoamer, air release additive

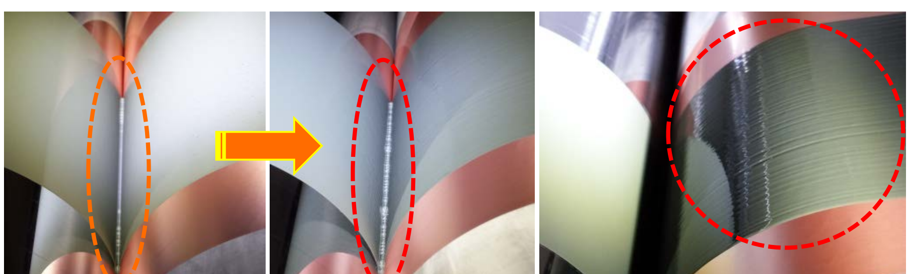
(3) Control process parameters; viscosity, speed, loading level etc.

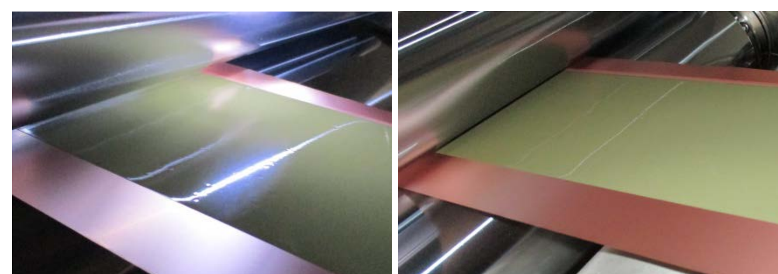
Reverse-comma roll method



Direct-comma roll method







Gas generation → In Formation cycle

\# Possible cause; Electrolyte decomposition at high voltage of LMNO (>4.9V)

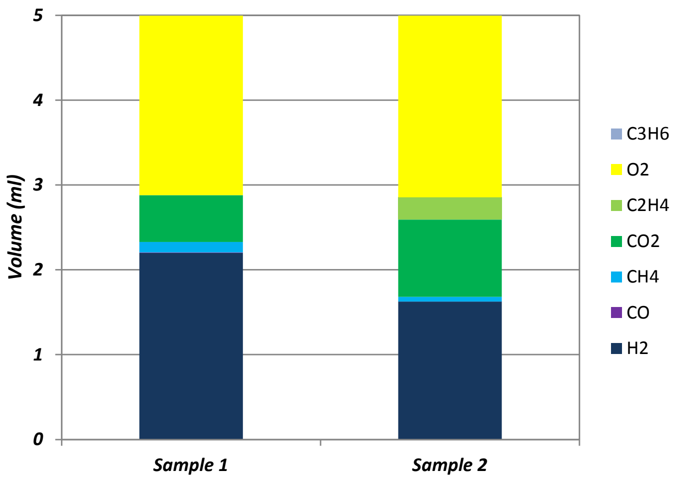
1.0M $LiPF_6$ in EC/DEC 3/7 + 10wt% FEC

→ Approaches

(1) Change the cathode; LMNO(~5.0V) → NCM (~4.5V)

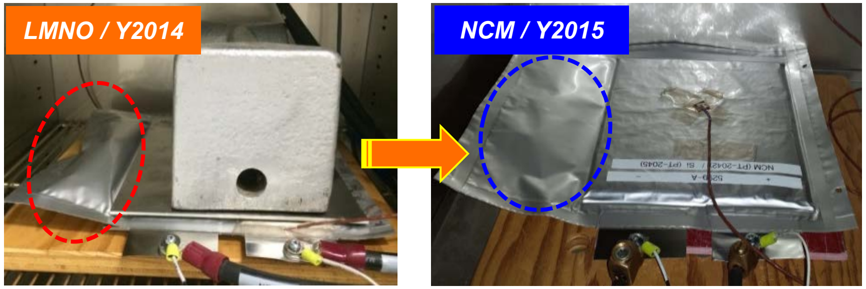
(2) Develop new electrolytes/additives for high voltage application

(3) Surface treatment of LMNO powder to stabilize SEI



- H_2, O_2 and CO_2 are main components.
- CH_4 and C_2H_4 are also detected.

Deliverable_Y2015



✓ No gas generation during the formation step from the cell using NCM cathode.

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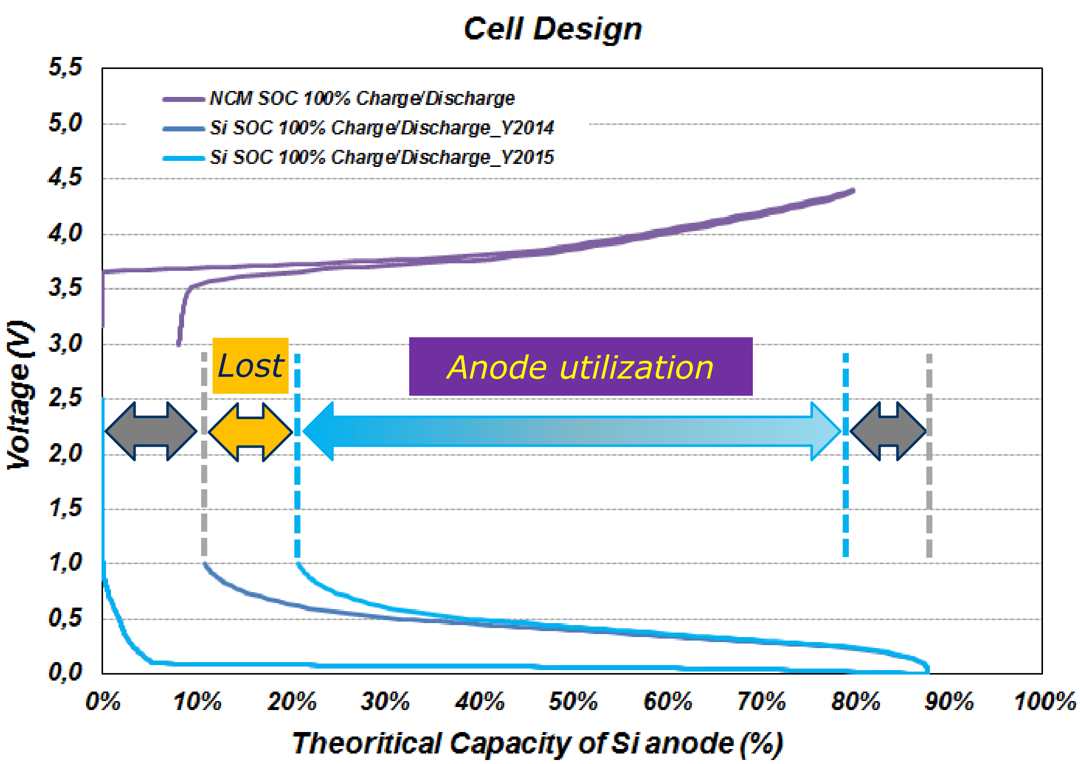
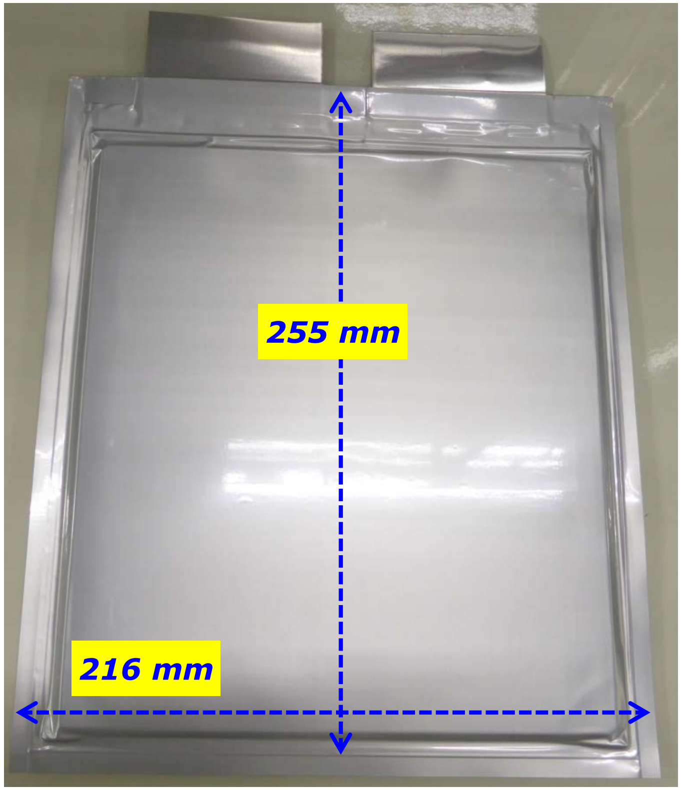
Design of Large Format Cell (Y2015)





45Ah Full Cell

- *Cathode- limited design : HE NCM (Ni 70%)*
- *Anode utilization : 90% of usable capacity*
- *Lowered anode efficiency : 76% vs. 88%*

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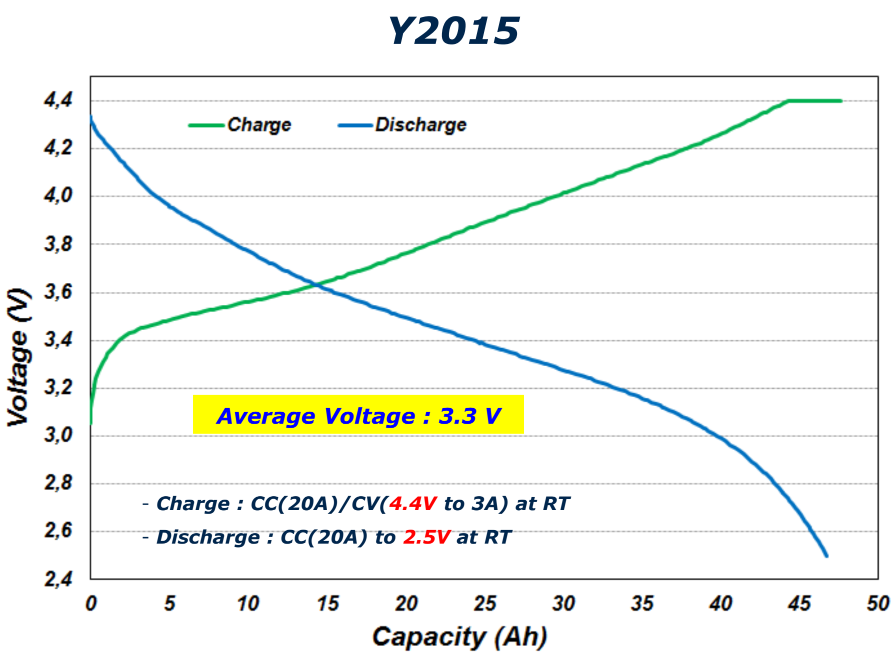
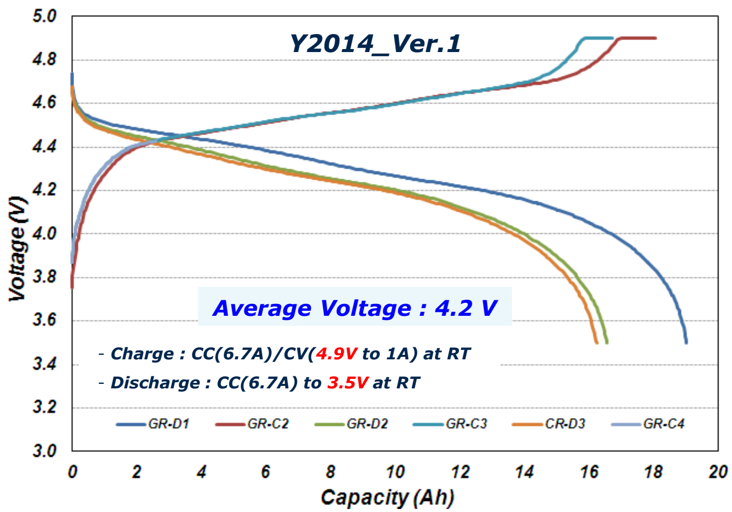
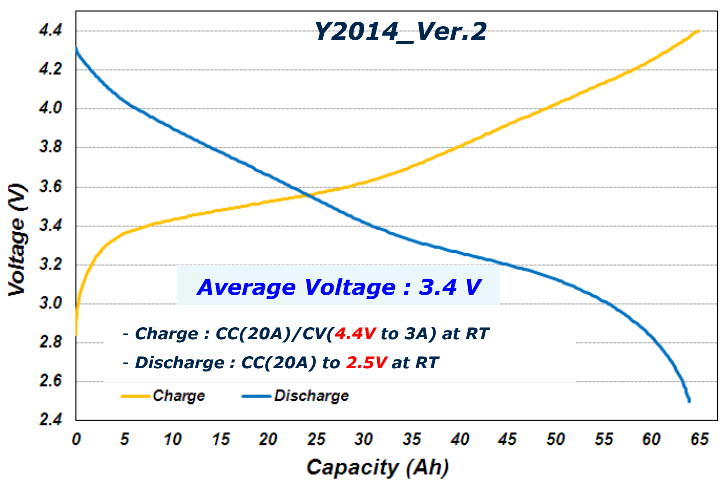
Voltage Profile (Y2015 vs. Y2014)

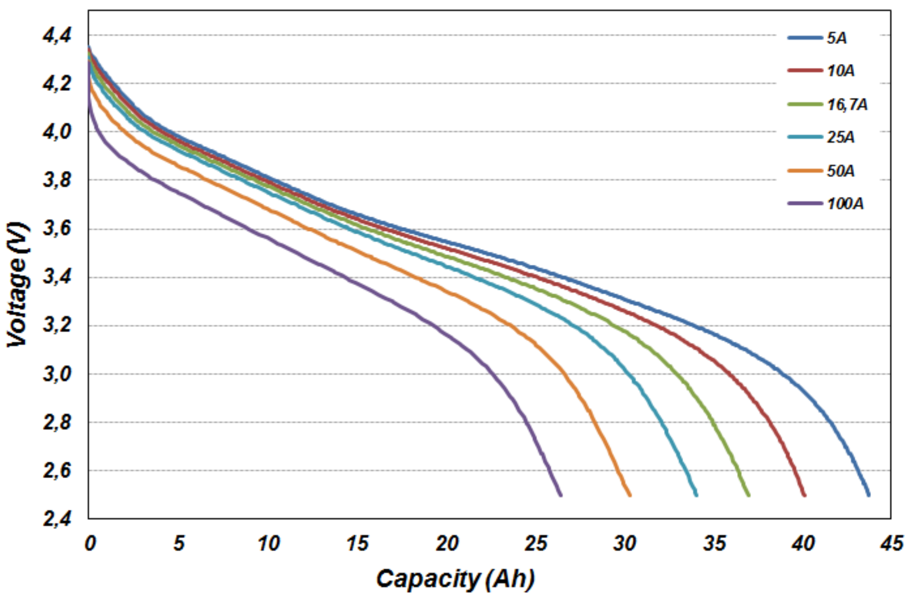






- ➢ No gas generation during cycle
- ➢ Rated capacity : 45Ah
- ➢ Energy density : 193 Wh/kg

Rate Capability (Y2015)



High power capability enables 100A discharge

Test Condition

- ***Charge : CC(C/3)/CV(4.4V to 2,5A) at RT***
- ***Discharge : CC to 2.5V at RT***

Current (A)	Capacity (Ah)	Retention (%)	Average. V (V)	Max. Temp. (°C)
C/10_5A	43,8	100%	3,489	24
C/5_10A	40,1	92%	3,505	27
C/3_16,7A	37,0	85%	3,508	30
C/2_25A	34,1	78%	3,507	32
1C_50A	30,3	69%	3,477	39
2C_100A	26,5	60%	3,409	48

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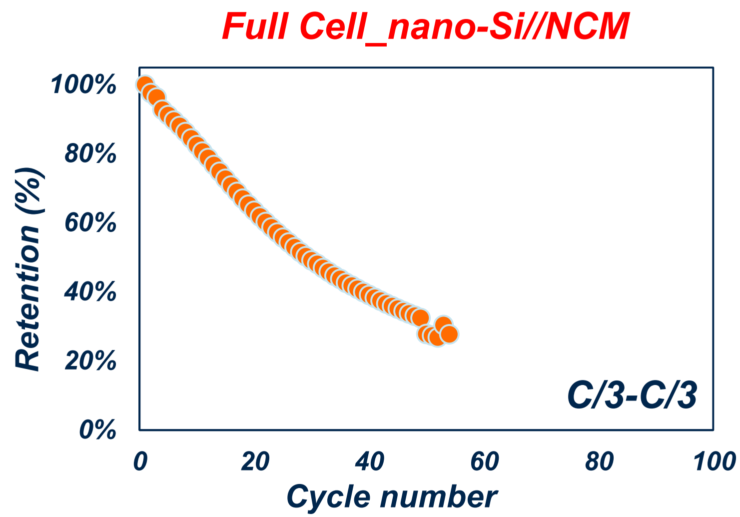
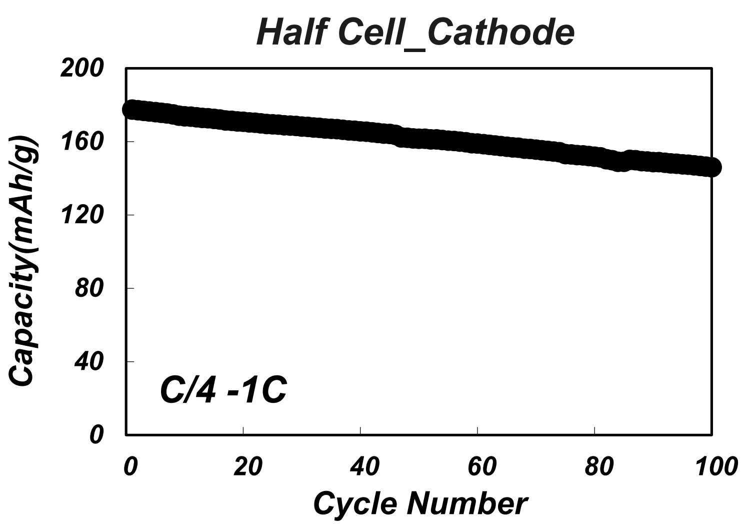
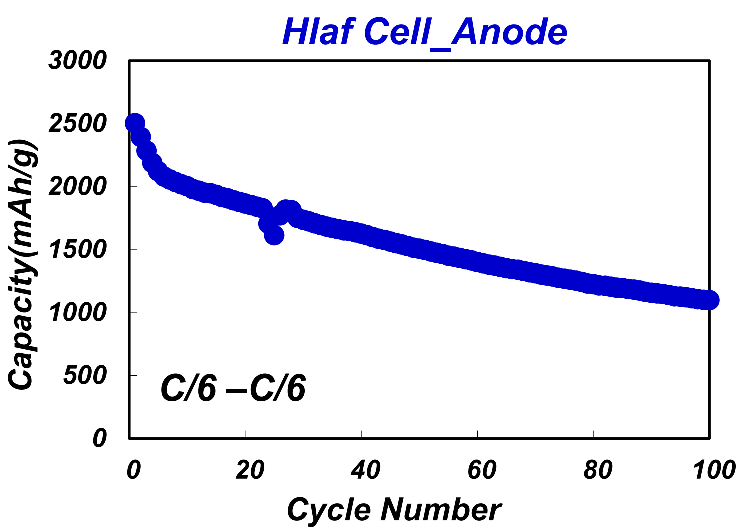
Cycle Life (Y2015)

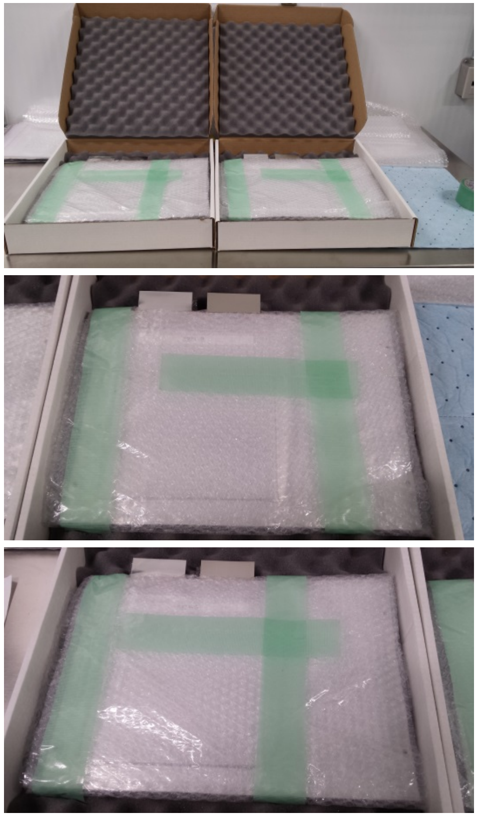


- ***Full cell shows limited cycle life due to the low coulombic efficiency.***
- ***Half cells show much stable cycle life for both cathode and anode.***





Specification (Y2015 vs. Y2014)



Item		Unit	2015	2014		Remark
				Version1	Version2	
Material	Cathode	-	HE NCM (Ni 70%)	HV LMN	HE NCM (Ni 60%)	
	Anode	-	Nano Si	Nano Si	Nano Si	
	Anode Binder	-	Polyimide	Alginate	Alginate	
	Separator	-	Ceramic	Ceramic	Ceramic	
	Electrolyte	-	EC/DEC/FEC	EC/DEC/FEC	EC/DEC/FEC	
Cell	Capacity	(Ah)	46.7	19	64	@ C/3
	Average Voltage	(V)	3.427	4.246	3.433	
	Specific Energy	(Wh/kg)	193	124	250	@ C/3
	Energy Density	(Wh/L)	398	204	437	
	Thickness	(mm)	11.5	-	9.13	@ SOC100
	Width	(mm)	216	216	216	
	Length	(mm)	255	255	255	
	Weight	(g)	830	653	880	
			Thickness increase at 1st charge	Gas		

- ***Polyimide binder leads to significant increase of cell thickness with lowered columbic efficiency.***

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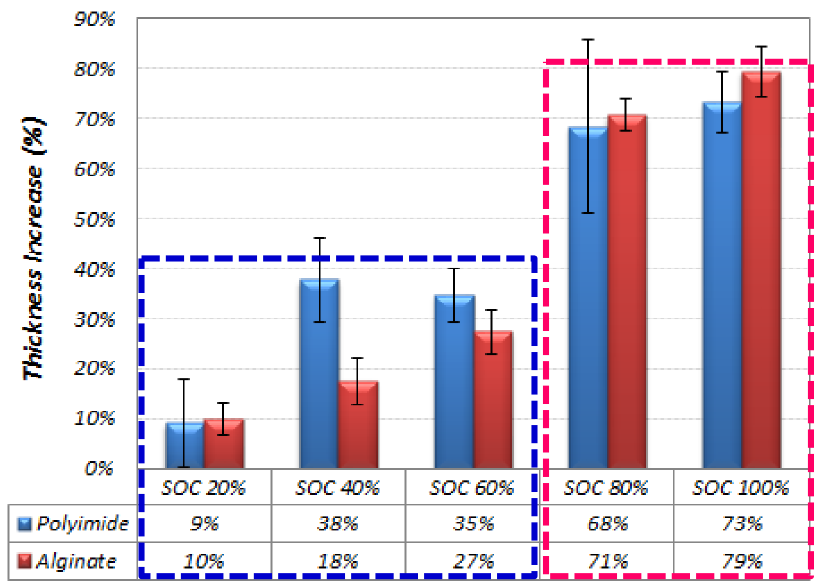
Thickness Increase Issue

Photos after cycle life test (large format)

Thickness evolution with SOC (small format)



- ***Significant deformation during the 1st charge, leading to the thickness increase of the cell; more than 60%. Part of anode electrode is transformed to separator surface.***
- ***Thickness increase is more dominant at high SOC (>80%) → SOC control is required for longer cycle life.***
- ***Alginate binder shows less thickness increase at <SOC60%.***

Post mortem analysis of nano-Si Anode

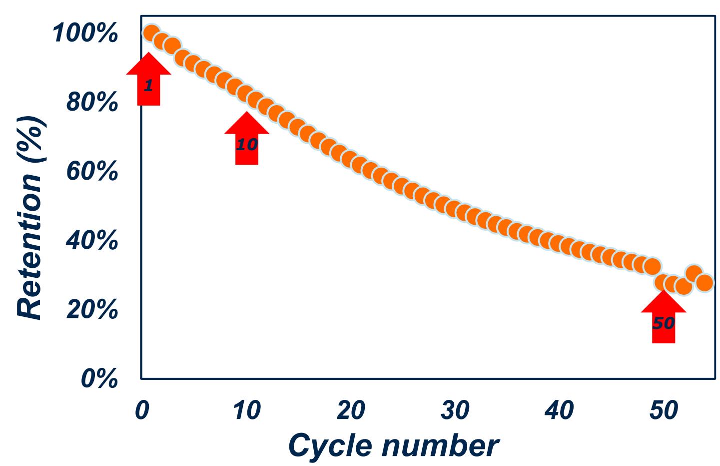
After 1st cycle

After 10th cycles

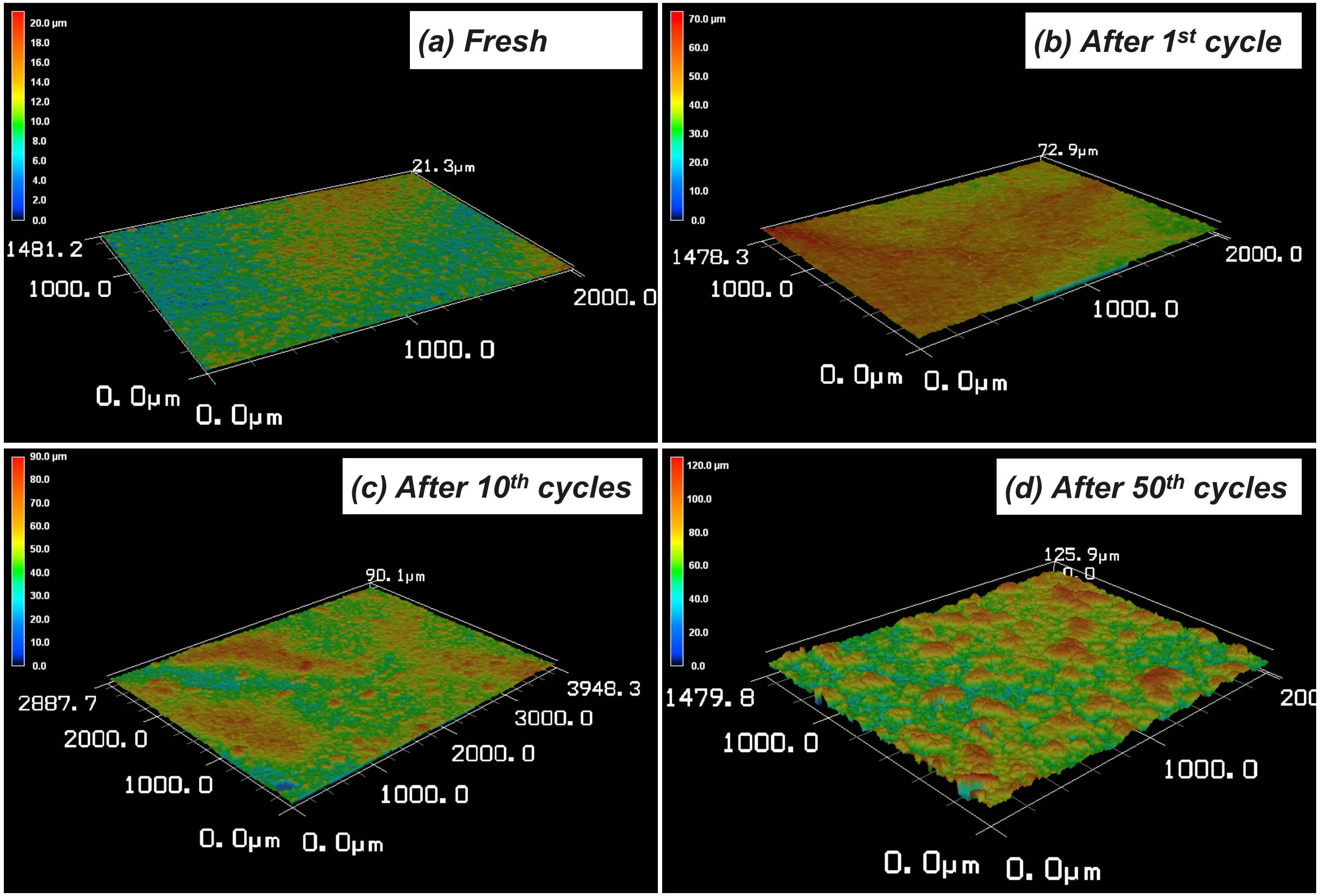
After 50th cycles

- ***Post-mortem analysis was conducted after 1st cycle, 10th cycles and 50th cycles: SEM, 3D optical microscope, TOF-SIMS and Dual Beam Microscope were used.***
- ***The electrode deformation appears even after the 1st cycle.***

Sample Acquisition Points



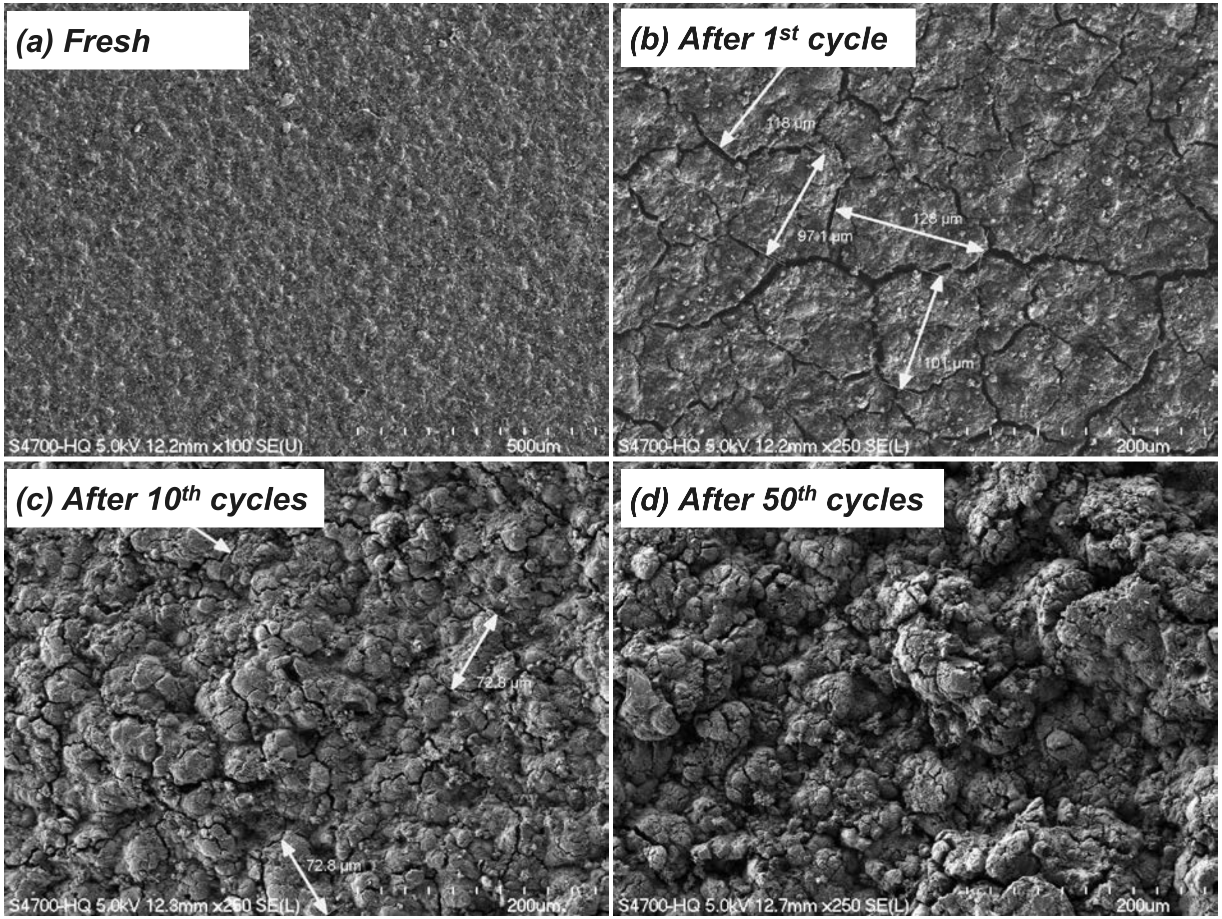
3D Optical Microscope



Sample	Ra (μm)
Fresh	1,3
1st cycled	3,4
10th cycled	5,6
50th cycled	8,4

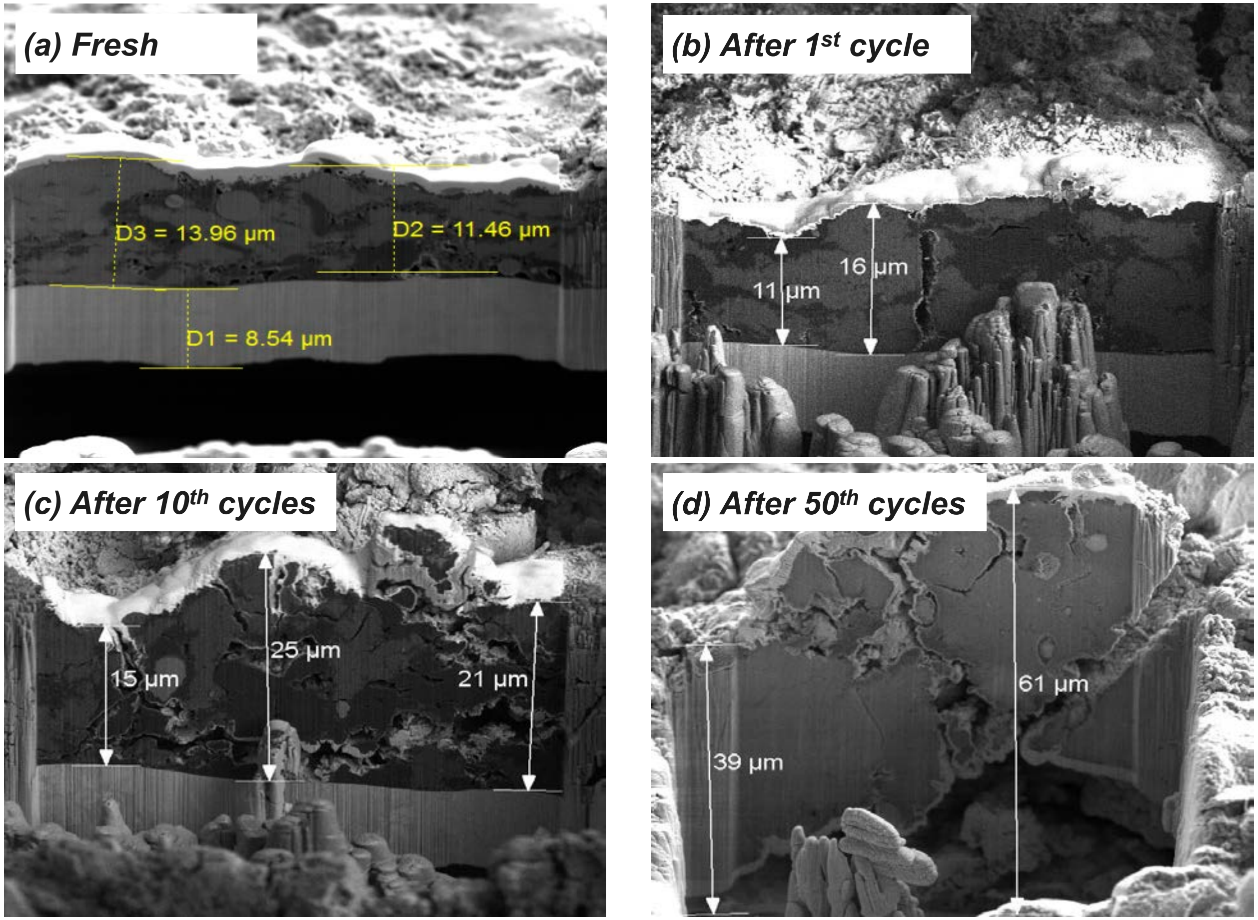
- ***Roughness of nano-Si anode increases more than 600% after 50th cycles.***

SEM → Top view



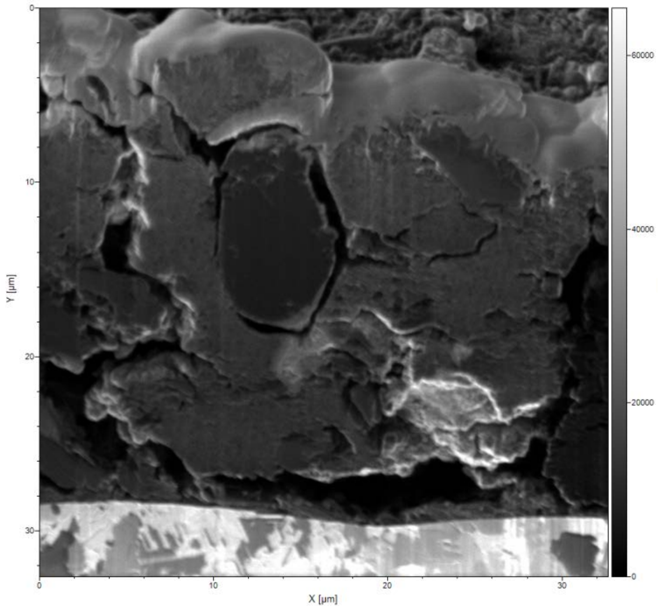
- ***Significant fractures are developed from the 1st cycle and getting worse with cycles.***

SEM → Cross-Section

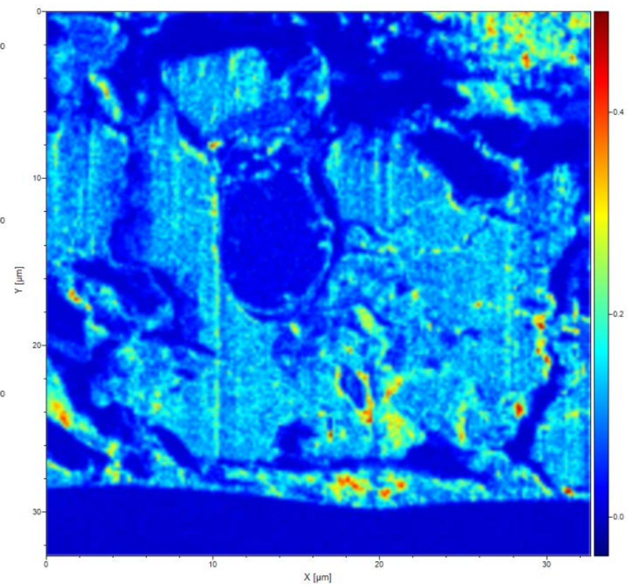


- ***Significant thickness increase and electrode deformation with cycles.***
- ***The electrodes are partly detached from the current collector.***

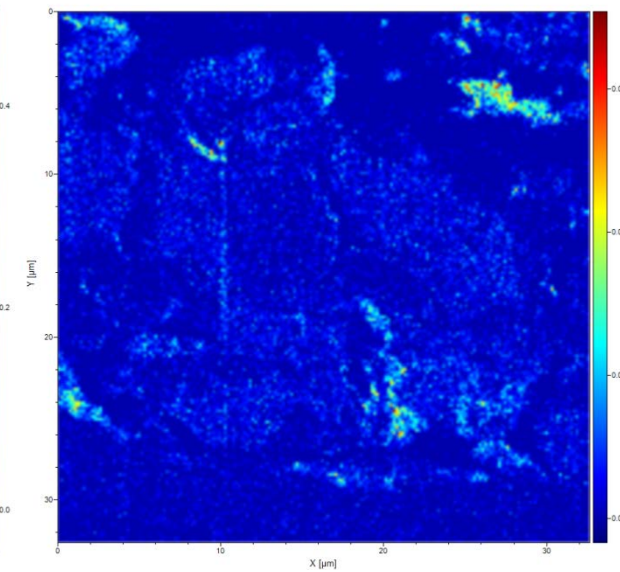
TOF-SIMS Analysis → After 10th cycles



Li (7)



Si (28)

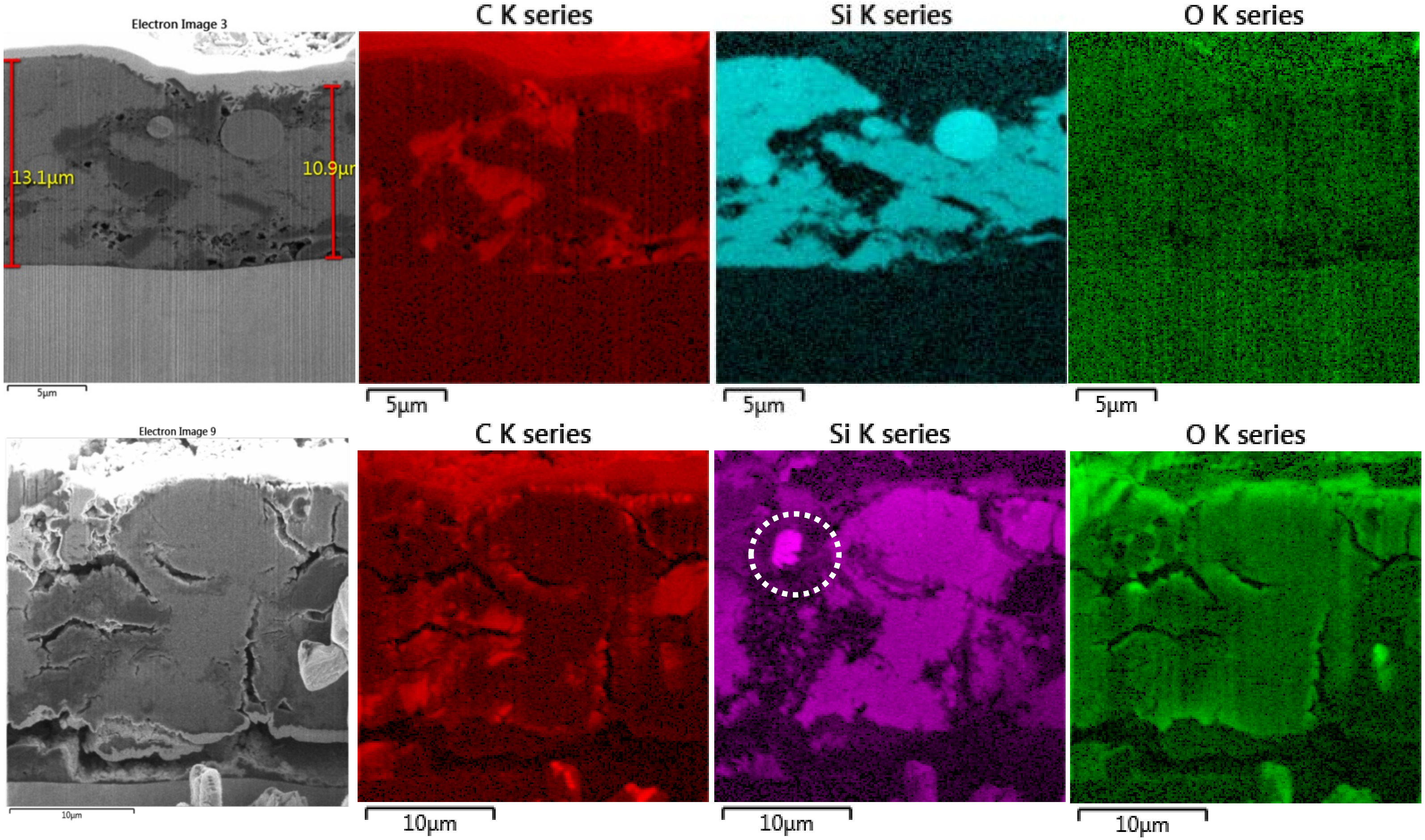


- ***HQ is capable of analyzing the Li distribution using its unique microscopy.***
- ***Li distribution varies with the morphology change.***

Local X-ray Analysis (FIB X-section)

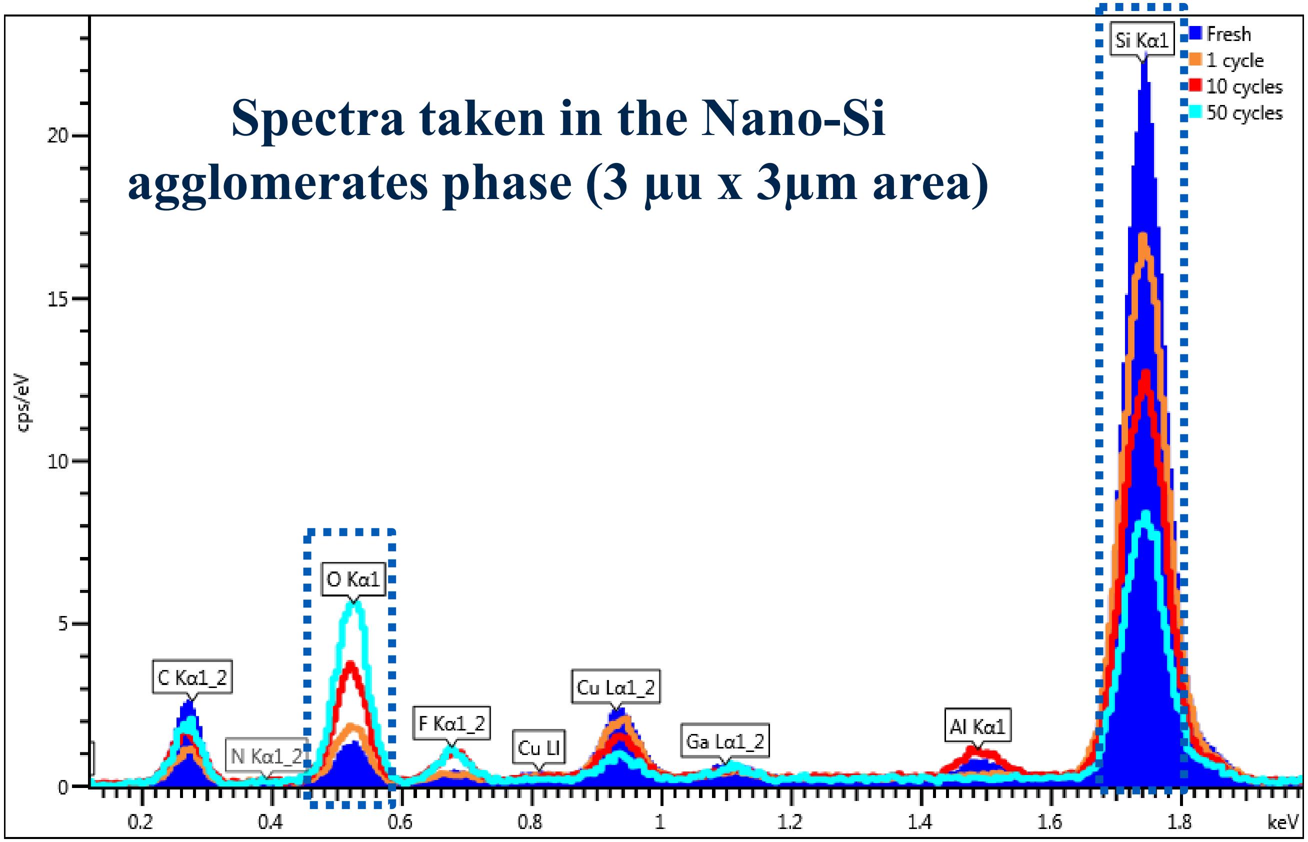
Fresh Electrode

After 10th cycles



➢ ***Increase of oxygen content after cycle, especially at the surface.***

Local Chemical Analysis Comparison



- *Si intensity decreases with enhanced O K intensity over cycles; Si K intensity is only half of the fresh electrode after 10 cycles.*
- *SEI layer is regenerated continuously on cycling.*

Summary

- Cycle life of metallurgical Si was greatly improved by optimizing the milling conditions and the particle size.
- SiO_x obtained by plasma process showed improved capacity retention at cycle life test.
- Nano-Si/C composite was developed using a spray-dry technique to supress the gas generation in the water-based slurry.
- The gas generated during the slurry mixing process was identified as $H_{2,}$ which was effectively suppressed by using a polyimide binder.
- Post-mortem analysis using dual beam SEM and TOF-SIMS revealed significant electrode deformation along with the accumulation of electrolyte decomposition products.
- HQ has delivered the large-format cells (46.5 Ah) using the developed material, as well as Si-powder (0.9kg) and Si-electrode (10m).

Future Activities (Y2016)

- ❑ **Optimize nano-Si/C composite**
  - ✓ **1st Deliverable ; Si/C Powder → End of March, 2016**

- ❑ **Develop high loading electrode using nano-Si/C composite with optimized electrode architecture.**
  - ✓ **2nd Deliverable ; Si Electrode → End of June, 2016**

- ❑ **Verify the performance of developed electrode using 2Ah pouch cells**
  - ✓ **3rd Deliverable ; 2Ah Cells → End of September, 2016**

- ❑ **Study the evolution of SEI passivation and electrode morphology by using in-situ SEM and dual-beam microscope.**

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