High Energy Lithium Batteries for Electric Vehicles

Deepak Karthikeyan, Charan Masarapu, Bing Li, Iris Li, Swapnil Dalavi, Subramanian Venkatachalam, Sujeet Kumar, Michael Sinkula, Herman Lopez (PI)

Envia Systems

DOE Vehicle Technologies Program Annual Merit Review
Washington D.C.
June 8–12, 2015

Project ID: ES247

Program Overview

TIMELINE

- Project start date: Jun 2014
- Project end date: Jun 2017
- Percent complete: 25%

BARRIERS

- Meet USABC EV energy and power cell specs
- Meet cycle life and calendar life
- Enable a cell cost target of 100$/kWh

BUDGET

- Total project funding:
  - ✓ DOE share: $3,859,246
  - ✓ Envia & partners share: $3,859,246
- Funding received in FY2014:
  - ✓ $563,813
- Funding for FY2015:
  - ✓ $1,748,629

PARTNERS

3M
DU PONT
DAIKIN
AsahiKASEI
Nanoscale Components
A123 SYSTEMS

envia SYSTEMS

Project Relevance

- **Goals:**

  Develop high capacity cathode and anode materials, screen commercial electrolytes and separators, optimize pre-lithiation process and integrate to build high capacity pouch cells that meet the USABC electric vehicle (EV) battery goals for CY 2020

- **Project Timeline:**

Year 1				Year 2				Year 3			
Q1	*Q2*	*Q3*	*Q4*	*Q5*	*Q6*	*Q7*	*Q8*	*Q9*	*Q10*	*Q11*	*Q12*

Project start date: June 26, 2014

- **Barriers and Tasks:**

✓ Develop high capacity cathode and anode materials and electrodes
✓ Mitigate cycle life challenges associated with Si anodes and Li-rich cathodes
✓ Develop an economical and manufacturable pre-lithiation process
✓ Cell development to ensure meeting the cell metrics, safety and cost targets

- **Deliverables:**

  Demonstrate & deliver cells that meet the USABC EV cell targets with independent validation from the National Labs (INL, SNL, & NREL)

- **USABC EV Cell Targets for 2020:**

End of Life Characteristics at 30°C	Units	Cell Level
Peak Discharge Power Density, 30 s Pulse	W/L	1500
Peak Specific Discharge Power , 30 s Pulse	W/kg	700
Peak Specific Regen Power , 10 s Pulse	W/kg	300
Useable Energy Density @ C/3 Discharge Rate	Wh/L	750
Useable Specific Energy @ C/3 Discharge Rate	Wh/kg	350
Useable Energy @ C/3 Discharge Rate	kWh	N/A
Calendar Life	Years	15
DST Cycle Life	Cycles	1000
Selling Price @ 100K units	\$/kWh	100
Operating Environment	°C	-30 to +52
Normal Recharge Time	Hours	< 7 Hours, J1772
High Rate Charge	Minutes	80% ΔSOC in 15 min
Maximum Operating Voltage	V	N/A
Minimum Operating Voltage	V	N/A
Peak Current, 30 s	A	400
Unassisted Operating at Low Temperature	%	> 70% Useable Energy @ C/3 Discharge rate at -20 °C
Survival Temperature Range, 24 Hr	°C	-40 to+ 66
Maximum Self-discharge	%/month	< 1

envia SYSTEMS

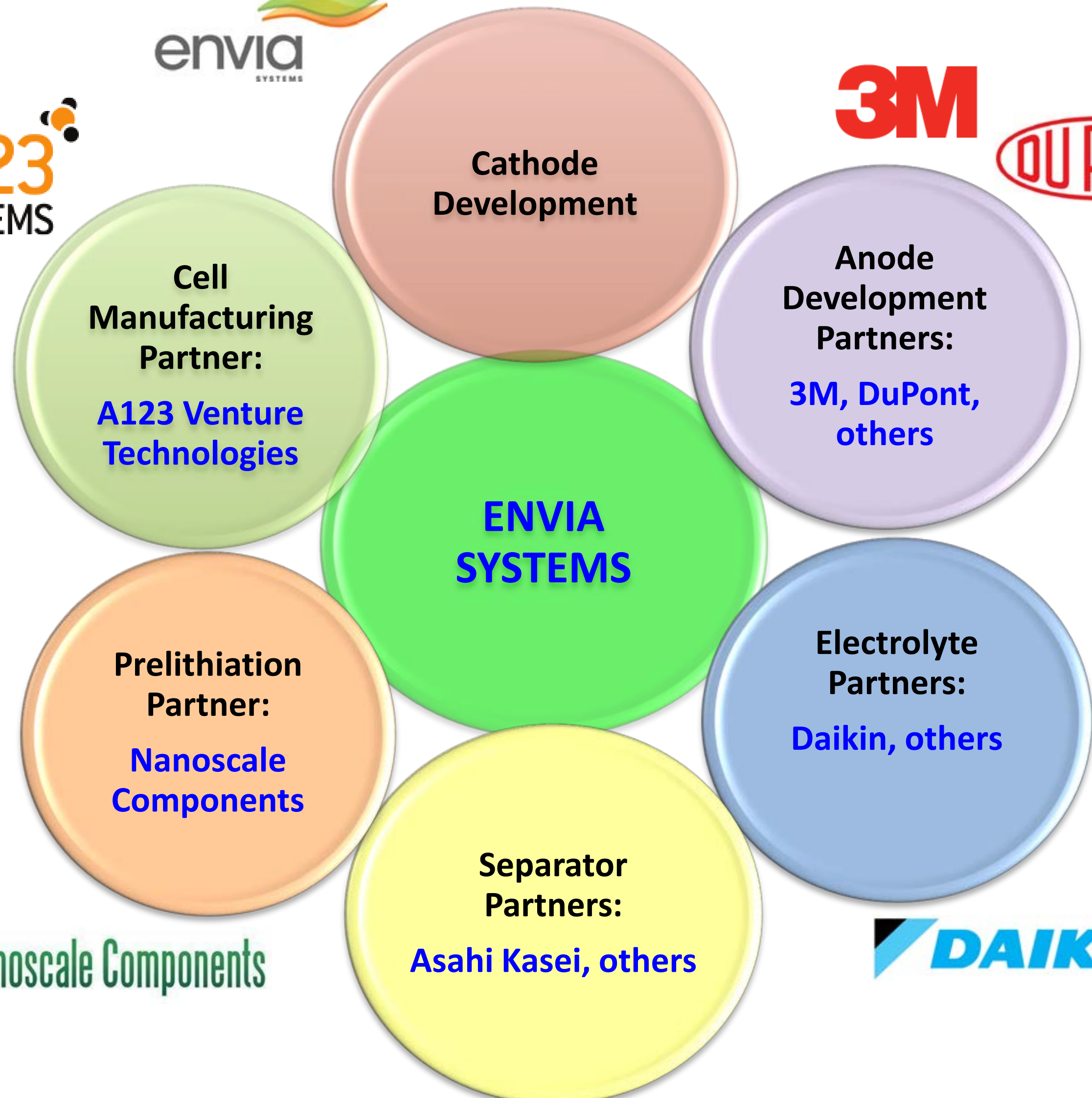
Project Milestones & Gates

Task Number	Major Project Tasks	PROJECT TIME											
		YEAR 1				YEAR 2				YEAR 3			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
8	**MAJOR PROJECT DELIVERABLE SUMMARY**												
6.1.5	Ship 12 (twelve) 20Ah baseline cells fabricated by Envia to selected National Labs for independent testing		◆										
6.2.14	Build and test 1Ah cells from cell build #1 as an internal build and report and use learning for future cell builds					◆							
6.3.14	Ship 27 (twenty-seven) 20Ah capacity cells fabricated by A123 from cell build #2 to the National Labs for independent testing							◆					
6.4.9	Build and test 20Ah cells from cell build #3 as an internal build and report and use learning for final cell build									◆			
6.5.14	Ship 27 (twenty-seven) 50Ah capacity cells fabricated by A123 from cell build #4 to the National Labs for independent testing											◆	
7.1.3	Deliver final USABC project cell cost model												◆
8.1	Final USABC project report												◆
9	**REVIEW AND DECISION GATES**												
9.1	Down-select best cathode composition (Li, Ni, Co, Mn & amount of Li^2MnO^3), conducting coating (polymer, carbon or metallic) and dopant to be integrated in 1Ah cells from cell build #1				◆								
9.2	Down-select best prelithiation process conditions (lithiation loading, time, speed, drying, handling, etc.) to build 1Ah cells from cell build #1				◆								
9.3	Down-select and focus material development efforts on the most promising Si-based anode approach from development on Si-alloys and Si-C and SiO_x-C composites					◆							
9.4	Freeze best separator material to be used in remaining cell builds					◆							
9.5	Down-select best prelithiation process conditions (lithiation loading, time, speed, drying, handling, etc.) to build 20Ah cells from cell build #3							◆					
9.6	Freeze best cathode composition, conducting coating, dopant and process conditions to build 20Ah cells from cell build #3								◆				
9.7	Freeze best Si-based anode material composition, coating and process conditions to build 20Ah cells from cell build #3								◆				
9.8	Freeze best electrolyte formulation to be used in remaining cell builds								◆				

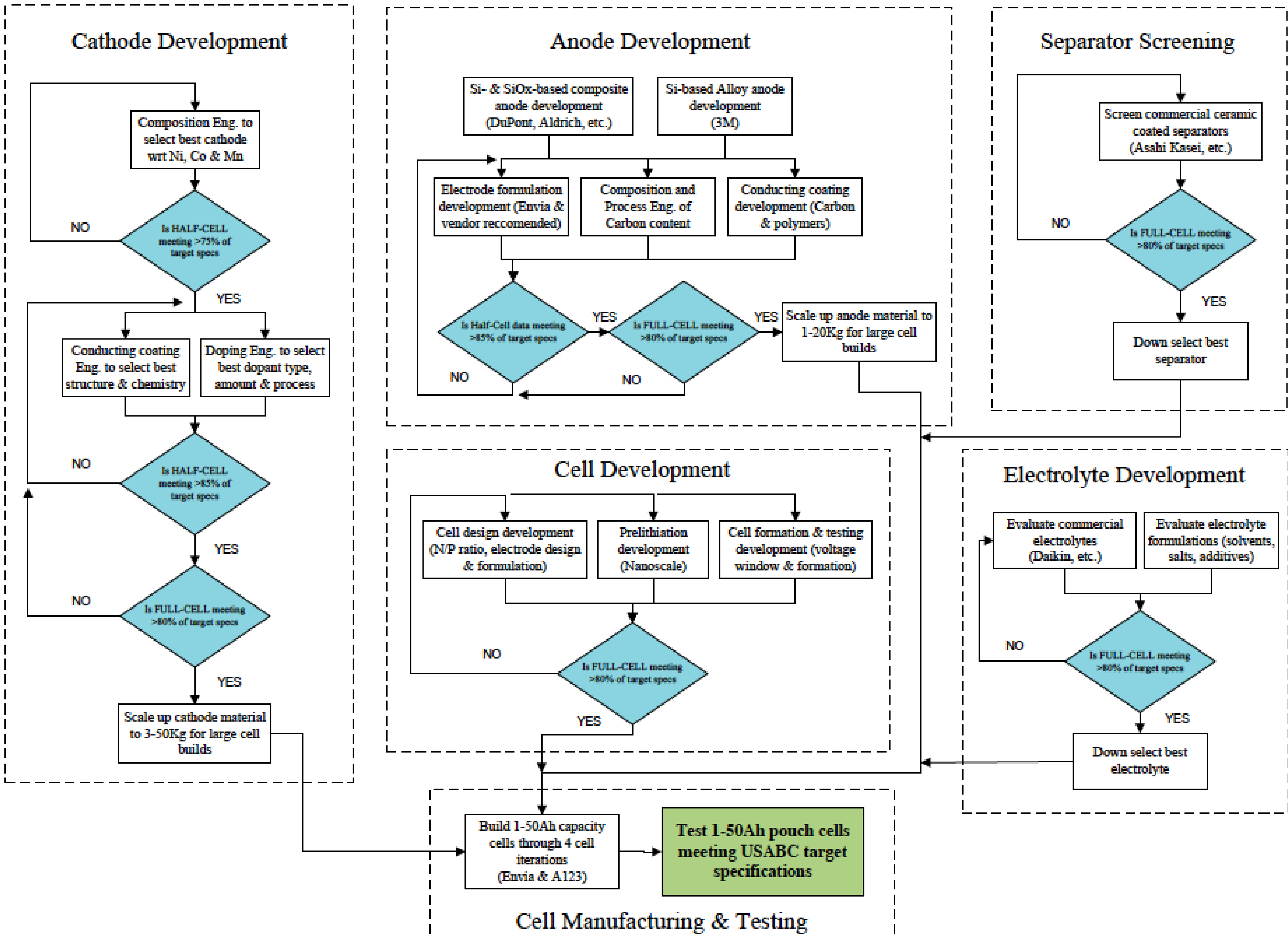
Project start date: June 26, 2014

Development Areas & Partners

Envia has partnered with leaders in their respective fields to develop materials, processes and cells which will meet the USABC EV cell goals



Approach Strategy



HCMR™ Cathode Development & Challenges

HEV, PHEV & EVs have different battery requirements ranging from power characteristics to cycle life. Envia solves the problem at the materials level by tailoring the cathode for each application

Morphology:

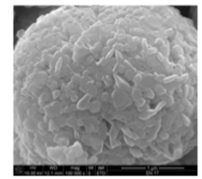
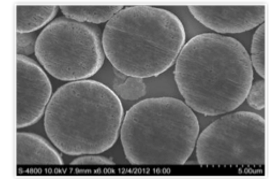
- Particle size, shape, distribution, tap density & porosity

Composition:

- Ni, Co, Mn ratio, & Li_2MnO_3 content
- Dopants & concentration

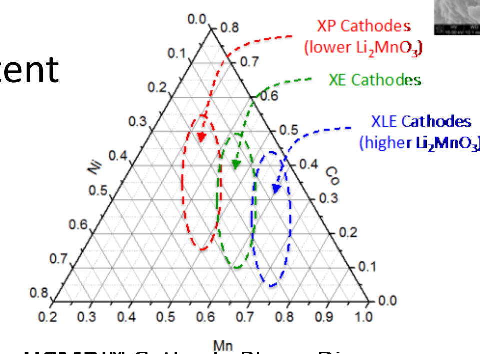
Nanocoating:

- Chemistry: fluorine, oxide, etc.
- Thickness & uniformity

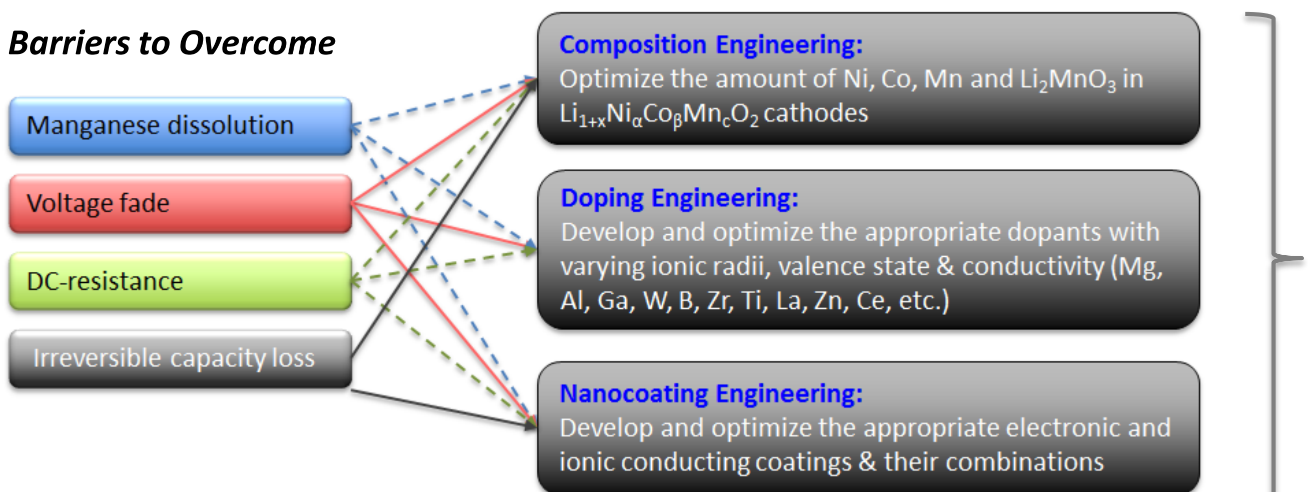
morphology

Nanocoating



HCMR™ Cathode Phase Diagram

HCMR™ Type	C/10 Capacity Range at 4.6V-2.0V (mAh/g)	Status
XP	200 ~ 220	Commercialization
XE	225 ~ 240	R&D
XLE	240 ~ 280	R&D

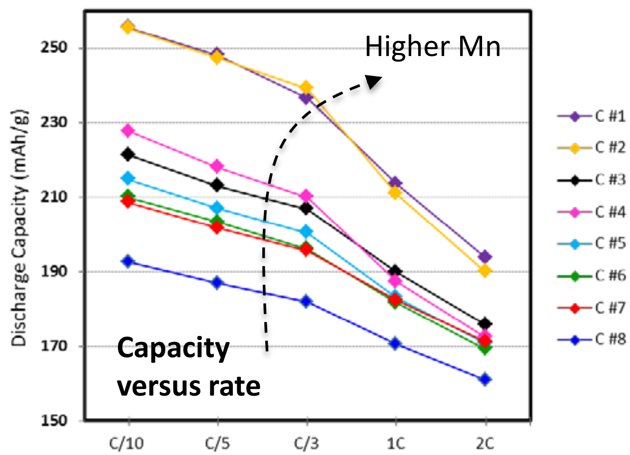


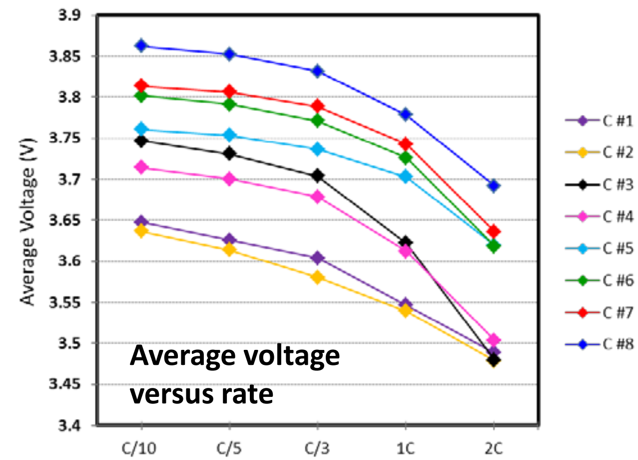
envia SYSTEMS

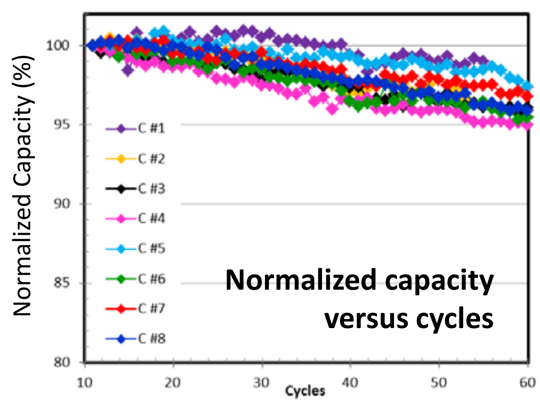
Cathode Composition Engineering

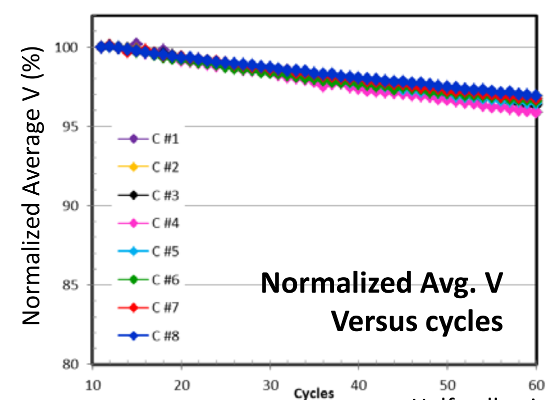
- Various Li-rich NMC cathode compositions (C#1-C#8) with different Li_2MnO_3, Ni, Co, and Mn were synthesized in an R&D reactor and were screened based on high specific capacity, stable average voltage, cycling stability and low DC-resistance
- Composition screening did not optimize the morphology, surface coating or dopants and only focused on material composition

Cathode ID	C/10 DC (mAh/g)	C/3 DC (mAh/g)	Total Energy at C/3 (Wh/kg)
C #1	256	237	853
C #2	255	239	856
C #3	221	207	766
C #4	228	210	773
C #5	215	200	749
C #6	210	196	740
C #7	209	196	741
C #8	193	182	697



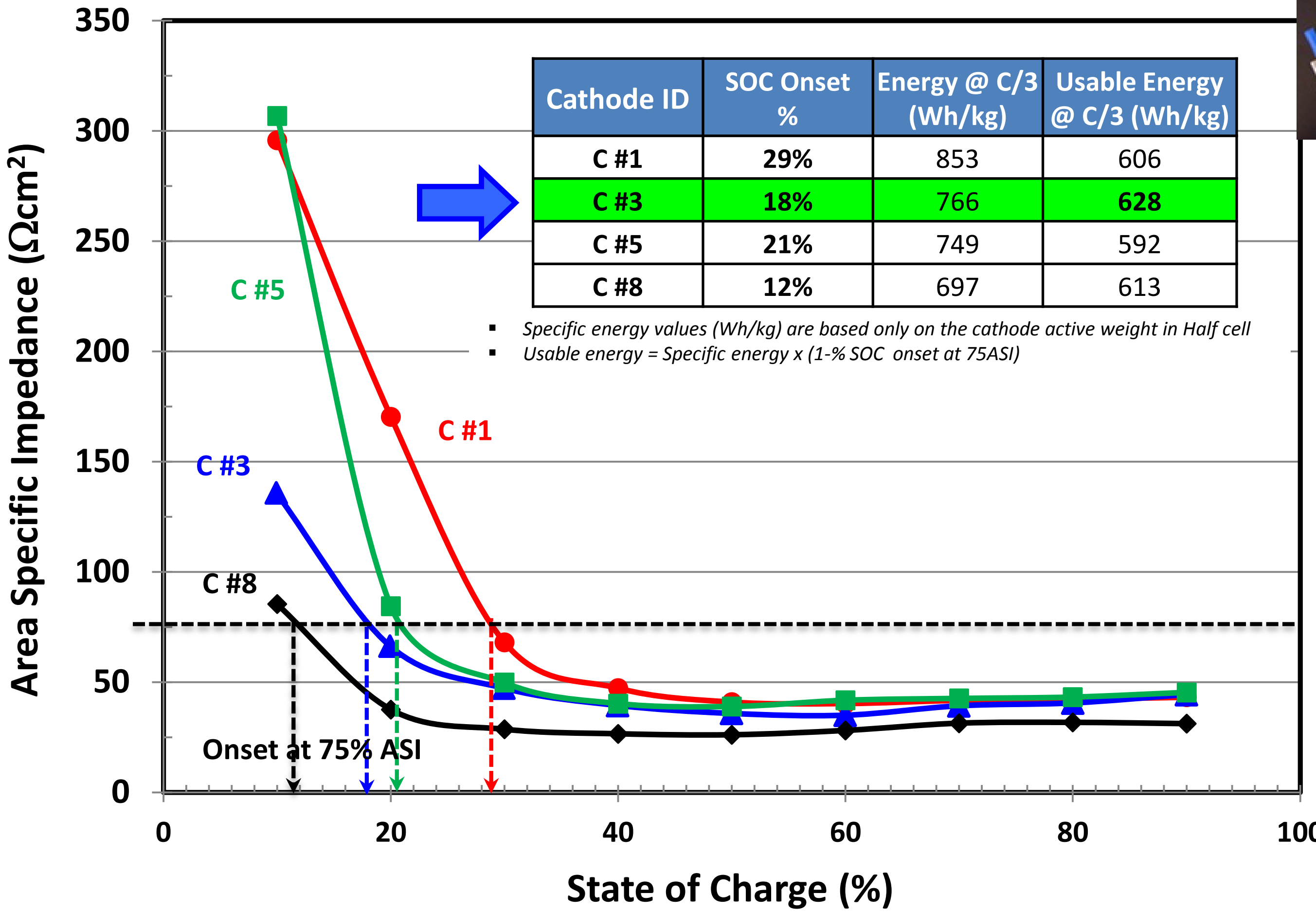






Half-cell coin-cell data tested from 2.0-4.6V and cycled at a C/3 rate

DC-Resistance Data



Cathode ID	SOC Onset %	Energy @ C/3 (Wh/kg)	Usable Energy @ C/3 (Wh/kg)
C #1	**29%**	853	606
C #3	**18%**	766	**628**
C #5	**21%**	749	592
C #8	**12%**	697	613

- *Specific energy values (Wh/kg) are based only on the cathode active weight in Half cell*
- *Usable energy = Specific energy x (1-% SOC onset at 75ASI)*

Single layer pouch cells

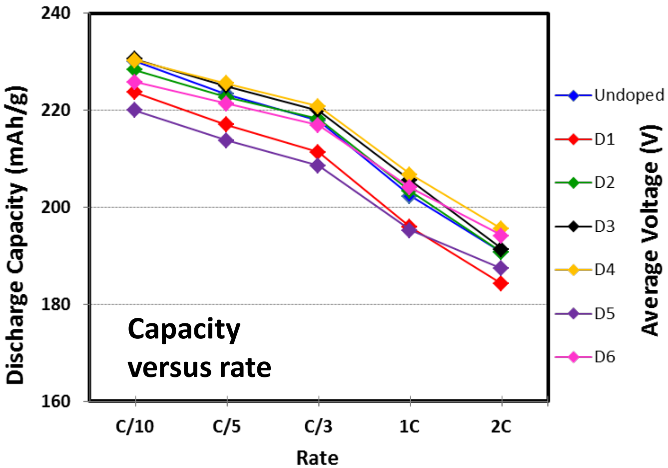
Based on usable energy, cathode **C#3** shows higher USABLE ENERGY compared to other cathodes and was down-selected for dopant development

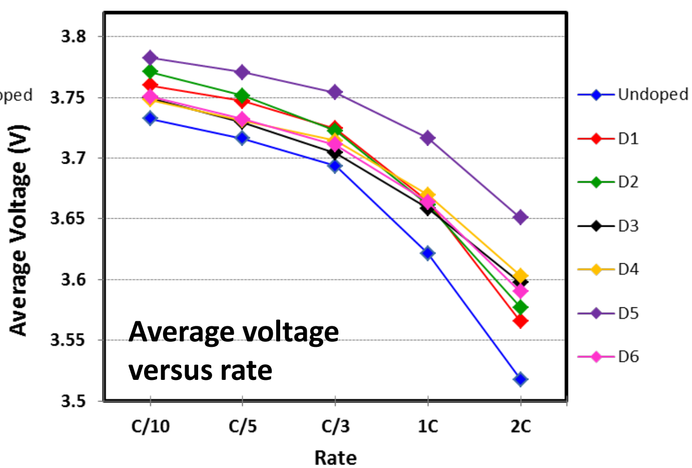
Cathode Dopant Engineering

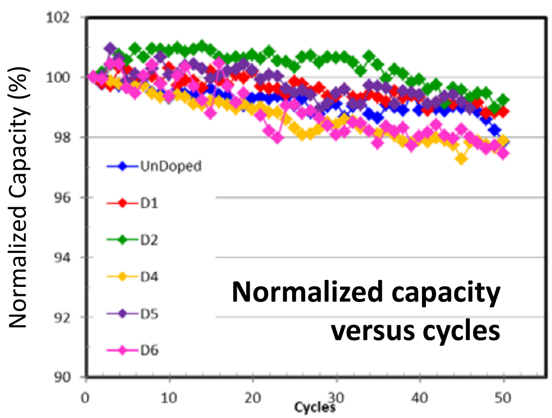
- Various dopants based on ionic radii, valence state & conductivity are introduced into the cathode lattice to stabilize the structure to improve calendar life and cycle life
- Various dopants and dopant concentrations have been incorporated to the down selected **C#3** cathode

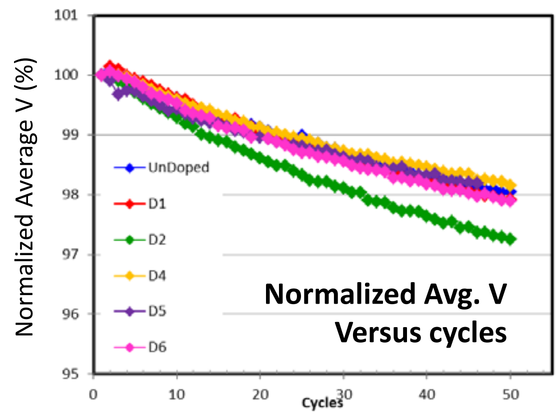
Cathode ID	Dopant	C/10 DC (mAh/g)	C/3 DC (mAh/g)	Total Energy at C/3 (Wh/kg)
C #19	C#3 Undoped	230	218	804
C #20	D #1	224	211	787
C #21	D #2	228	218	812
C #22	D #3	231	220	814
C #23	D #4	230	221	820
C #24	D #5	220	209	783
C #25	D #6	226	217	805

Higher average voltages are observed for doped cathodes



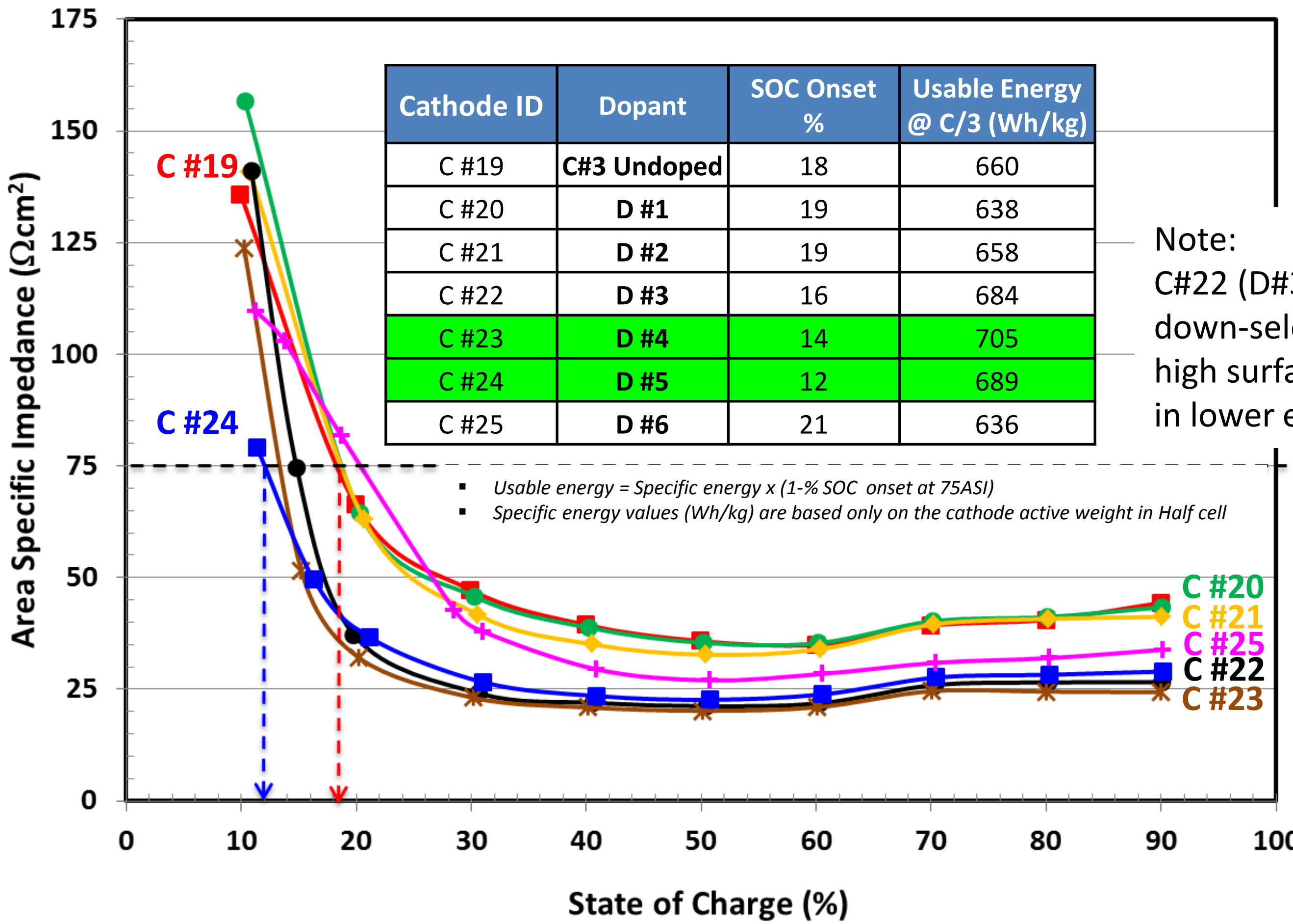






Half-cell coin-cell data tested from 2.0-4.6V and cycled at a C/3 rate

DC-Resistance Data



Cathode ID	Dopant	SOC Onset %	Usable Energy @ C/3 (Wh/kg)
C #19	**C#3 Undoped**	18	660
C #20	**D #1**	19	638
C #21	**D #2**	19	658
C #22	**D #3**	16	684
C #23	**D #4**	14	705
C #24	**D #5**	12	689
C #25	**D #6**	21	636

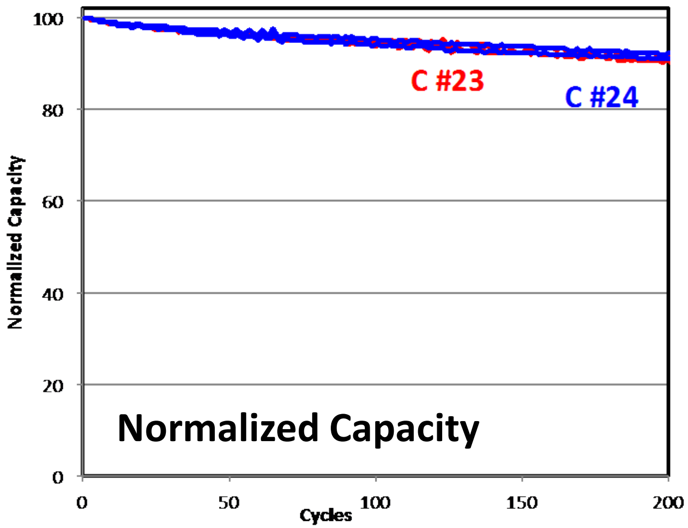
Single layer pouch cells

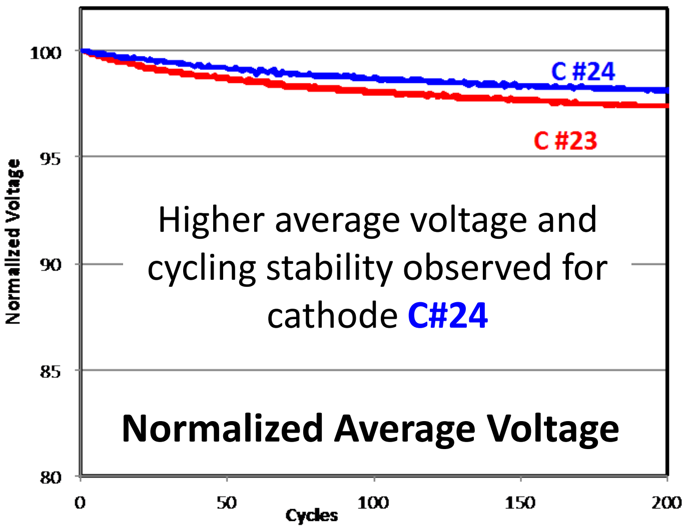
Note:
C#22 (D#3) cathode was not down-selected because it has high surface area that will result in lower electrode densities

Based on % SOC onset (reaching 75 Ω.cm^2) cathode **C#23, C#24** with dopants D#4, D#5 shows lower DC Resistance compared to other dopants studied

Cycle Life & Next Steps

Full cells vs Graphite
Voltage: 4.35-2.2V
Rate: C/2-C/2





Based on capacity, average voltage, DC-R, usable energy and cycle life, cathode **C#24** with dopants D#5 has been down-selected for coating and composite development

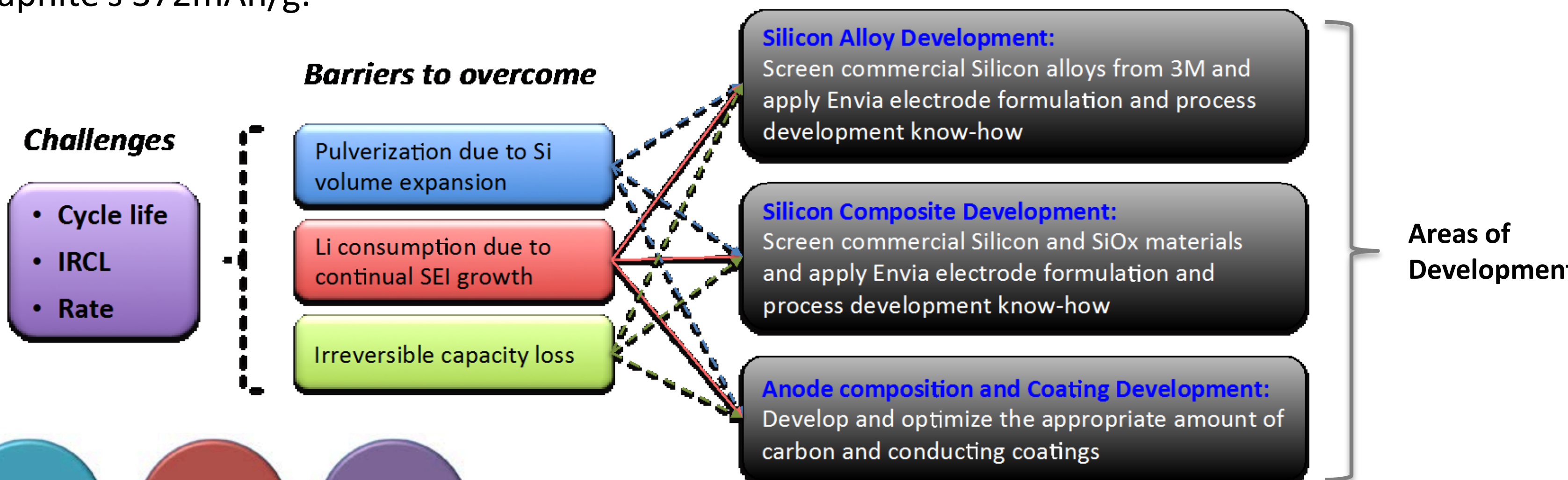
NEXT STEPS (Cathode Development):

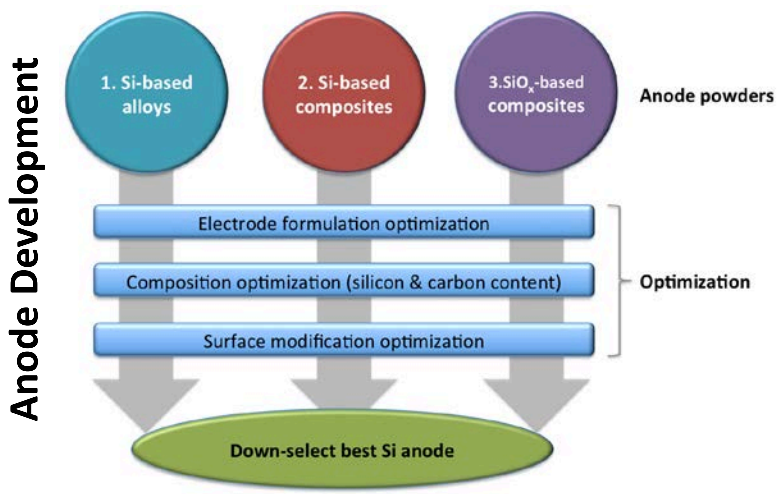
1. Screen conductive polymer coatings on down-selected HCMR^{TM} cathode (C#24)
2. Model and optimize cathode composites incorporating C#24 cathode
3. Down-select and scale-up HCMR^{TM} cathode for large capacity cell builds

Si-based Anode Challenges & Development

Si-based anode Advantages:

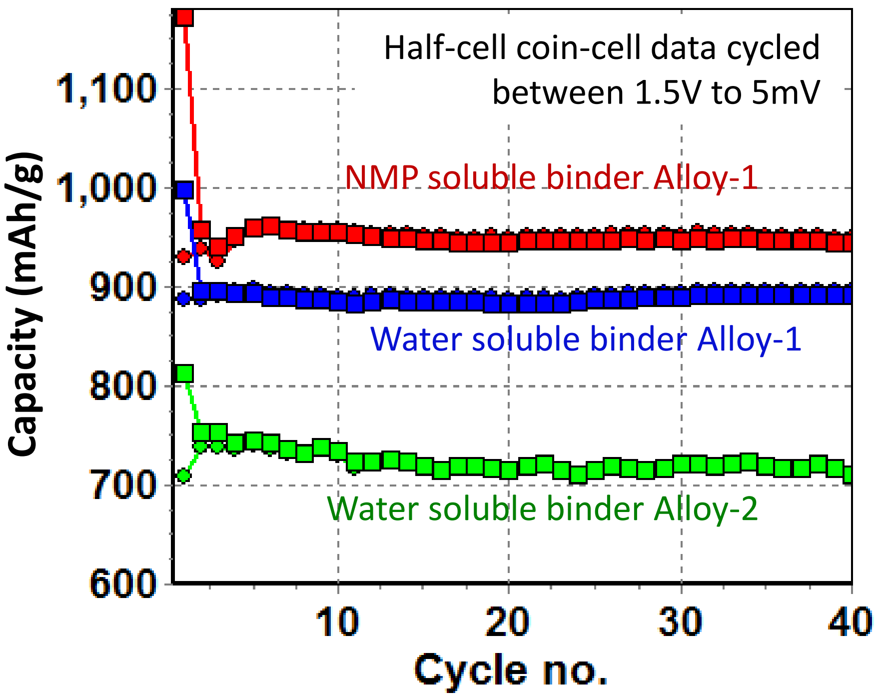
Silicon-based anodes are attractive alternatives to graphite because Silicon can alloy 4.4 Lithium ions per silicon ($Li_{4.4}Si$) resulting in an extremely large theoretical capacity of 4200mAh/g versus graphite's 372mAh/g.

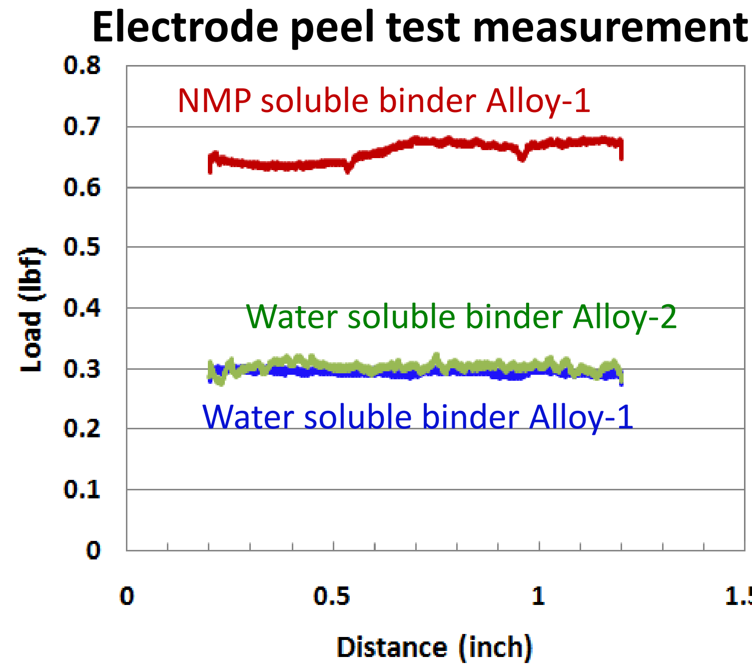




Envia develops Si anodes by using commercially available Si-based materials (Si-based alloys & nSi- and SiO_x-based composites) and applies its electrode formulation, processing, and coating know-how to further improve the performance of the silicon anodes

1. Silicon-based Alloy Anodes



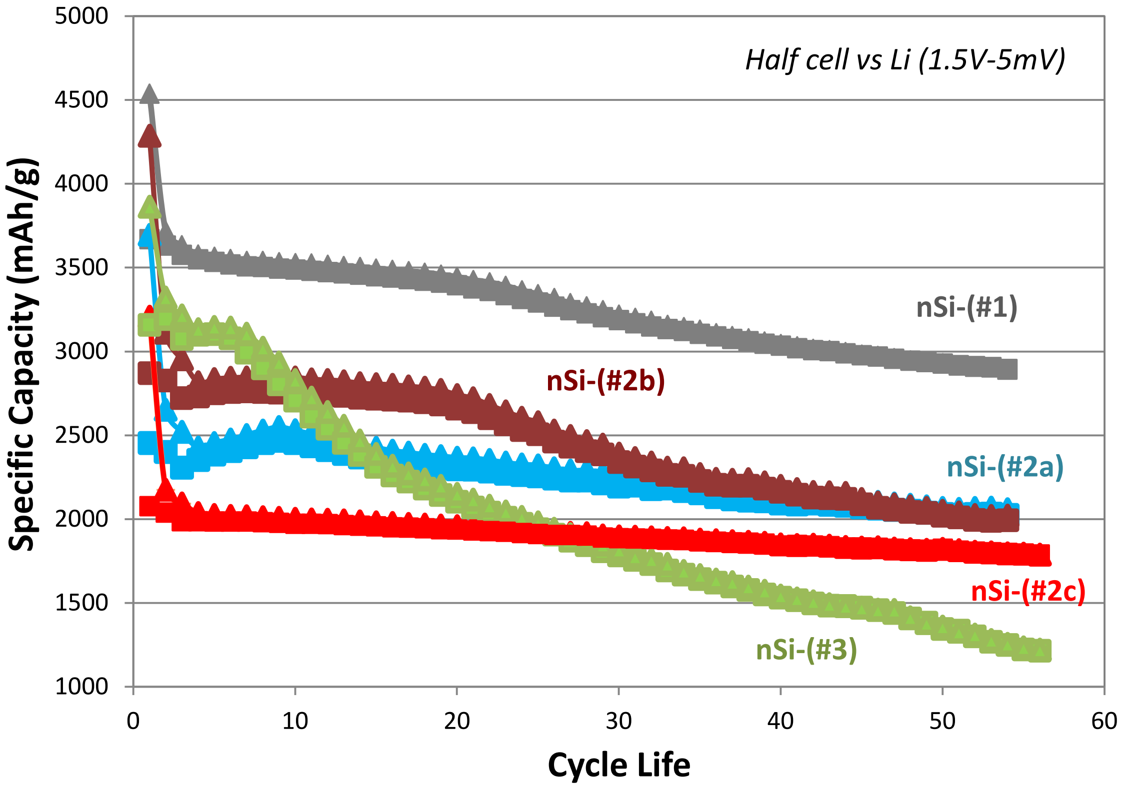


Material	Binder	C/20 Li insertion (mAh/g)	C/20 Li deinsertion (mAh/g)	First cycle IRCL (%)	C/3 Li deinsertion (mAh/g)
Alloy-1	NMP soluble	1172	929	20.7	940
Alloy-1	Water soluble	997	887	11	890
Alloy-2	Water soluble	812	708	11	737

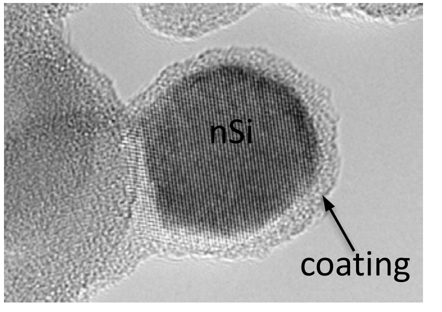
- Silicon-based alloys are being screened with various electrode formulations
- Stronger electrode adhesion (~0.65lbf) is observed for the NMP soluble binder compared to water soluble binder (~0.3lbf)
- Lower IRCL is observed for the water soluble binder (~11%) versus NMP soluble binder (~21%)
- Full cell cycling evaluation is underway

envia SYSTEMS

2. nSi-based Composite Anodes



Anode	Particle Size (nm)	Surface area (m^2/g)	First cycle IRCL (%)
nSi #1	Large	Low	19
nSi #2a	Smallest	Highest	33-38
nSi #2b	Smaller	High	33
nSi #2c	Smaller	High	35
nSi #3	Largest (<100nm))	Low	19



- Screening various supplier nSi-based materials with varying particle size, surface area and crystallinity
- Anode materials are tested in a HC configuration incorporating similar electrode formulation and loading levels
- nSi materials will further undergo composition optimization to reduce capacity and optimize cycle life
- nSi (#1) shows the highest specific reversible capacity (>3000mAh/g)

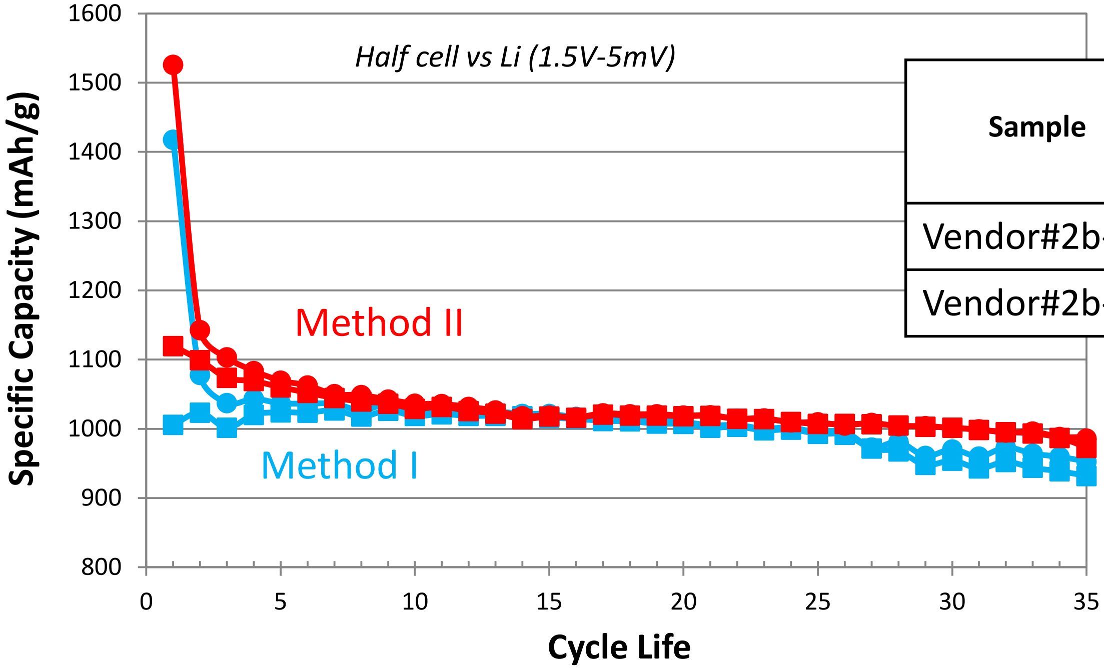
envia SYSTEMS

2. nSi-based Composite Anodes

High capacity nSi-based material + Carbon

1. **Method I** (physical)
2. **Method II** (physical-chemical)

→ ~1000mAh/g n-Si – C anode composite

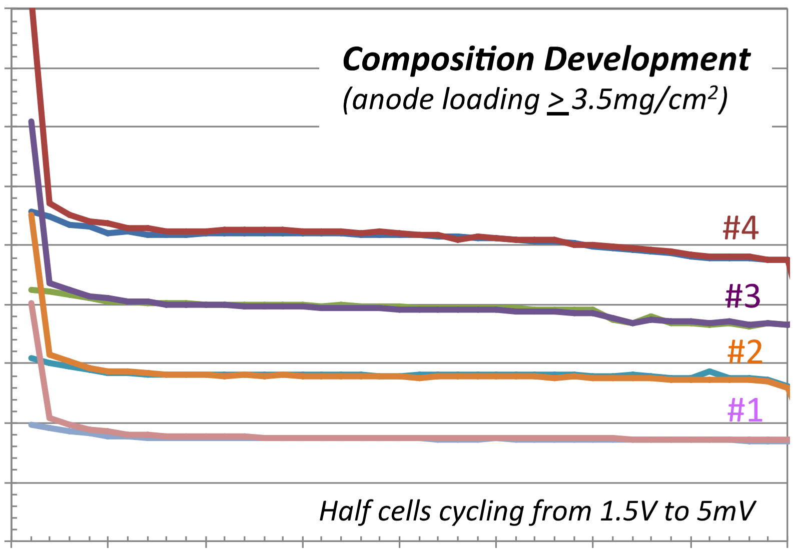


Sample	C/20 Dis Cap. (mAh/g)	C/20 Charge Cap. (mAh/g)	IRCL (%)	C/3 reversible cap. (mAh/g)
Vendor#2b-I	1526	1119	26	1078
Vendor#2b-II	1418	1006	32	1000

- Carbon content optimization by both physical (I) and physical-chemical (II) methods can control the reversible specific capacity to ~1000mAh/g to improve cycle life
- Full cell cycling evaluation is underway

3. SiO_x-based Composite Anodes

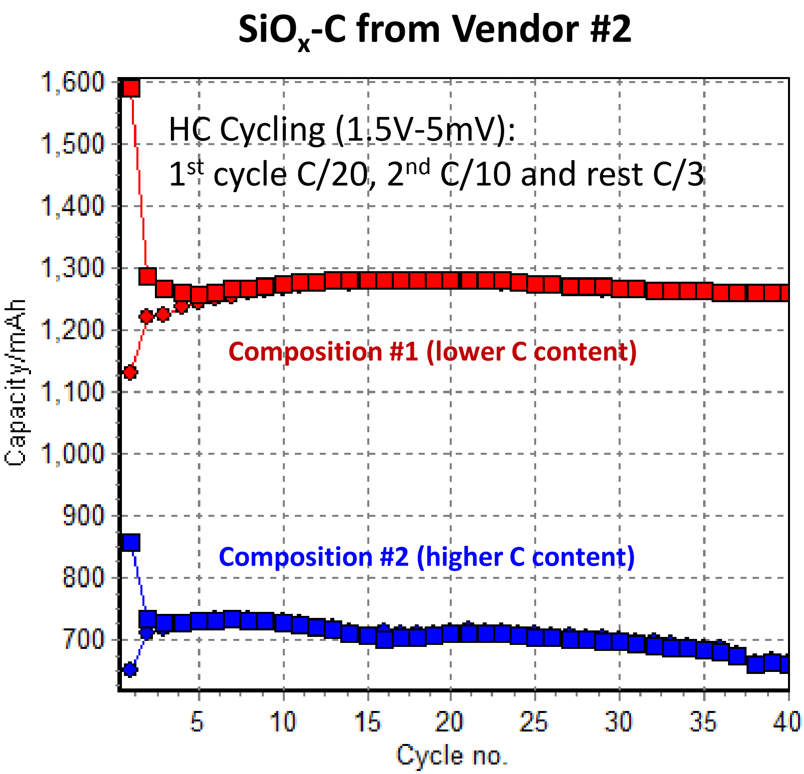
- Screening two types of commercially available SiO_x-based materials
- Optimized the carbon content to reduce capacity from the SiO_x-based material to enhance the cycle life



Anode composition development (Si, SiO & C content) from SiOx-based vendor #1

- Specific capacity is greatly affected by tuning the Si, SiO and C content of the Si-based anode composite
- Cycle life can be improved by tuning the Si, SiO and C content, which also affects the morphology of the Si-based anode composite

SiO_x-Carbon Composition Development



Electrode formulation	C/20 Li insertion	C/20 Li deinsertion	First cycle IRCL	C/3 Li deinsertion
Composition 1	1591	1132	29%	1223
Composition 2	856	650	24%	715

Down-selected SiO_x-C material from vendor #2 with lower carbon content (composition #1) for the baseline cell build

NEXT STEPS (Anode Development):

1. Full cell cycle life evaluation of the various promising Si-based anode materials
2. Conducting polymer coating of promising Si-based anode materials to further improve cycle life
3. Electrode formulation optimization to maintain high capacity, low IRCL and improve cycle life
4. Down-select Si-based anode materials for large capacity cell builds

Pre-lithiation of Si-based Anodes

Advantages of Pre-lithiation:

1. Pre-lithiation enables the integration of high capacity Si-based anodes, by precisely compensating the high irreversible capacity loss (IRCL)
2. In the absence of pre-lithiation, compensation of the IRCL would come from the cathode which is the priciest component in the cell
3. Pre-lithiation has also been shown to improve the cycle life in various materials

Challenges of Pre-lithiation Processing:

1. Low cost
2. Scalable and manufacturable
3. Robust and reproducible

Nanoscale Components

Envia has partnered with Nanoscale Components to use their low cost, roll-to-roll manufacturable and reproducible electrochemical pre-lithiation process to fabricate large capacity pouch cells

Pre-lithiation Development Status

1. Envia has selected a SiO_x-based anode for the baseline cell build and has used SLMP (from FMC Lithium) as the lithium source during pre-lithiation
2. Nanoscale used its roll-to-roll process to successfully pre-lithiate SiO_x-based anodes, which Envia assembled into 1Ah pouch cells and are currently testing
3. In order to reduce stress in the electrode and enable the required high Silicon pre-lithiation dose, an optimized thermal processing step and precisely tailored electrode formulations are required
4. Nanoscale designed, built and is qualifying a large scale roll-to-roll pre-lithiation pilot line which is 5x wider and 10x faster throughput than existing prototype line with capability of supporting large format high capacity (>20Ah) pouch cells

NEXT STEPS:

1. Select best Si-based material and electrode formulation to further reduce the electrode stress
2. Pre-lithiation development to optimize process conditions for future cell builds
3. Qualify large scale roll-to-roll pre-lithiation pilot line
4. Continue to pre-lithiate sufficient Silicon anodes to support cell development and large cell builds

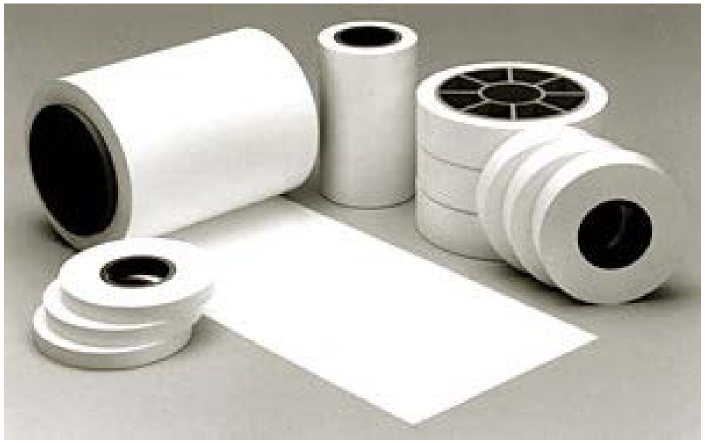
Nanoscale Components

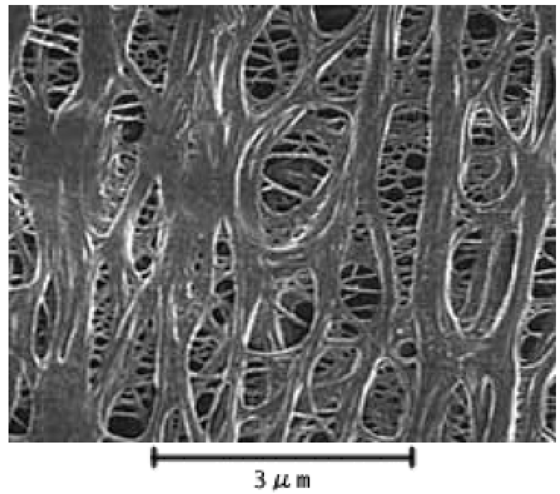
envia SYSTEMS

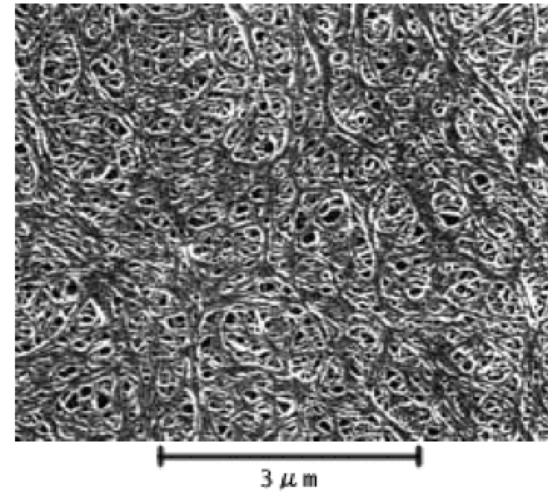
Separator Development

AsahiKASEI
ASAHI KASEI E-MATERIALS

Asahi Kasei's Hipore™ polyolefin membranes





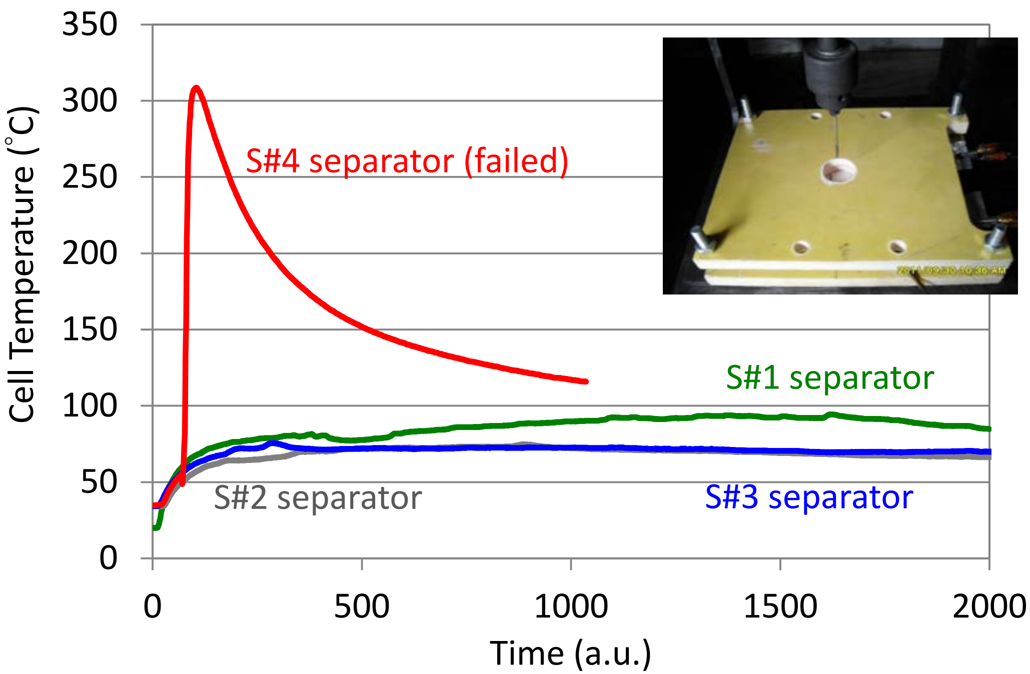


- Selecting the proper separator is critical for meeting the electrochemical cell targets, passing abuse testing and meeting cost targets
- Ceramic coated separators have been used in high capacity automotive pouch cells enabling meeting the cell targets
- Four separators (S#1, S#2, S#3 & S#4) from Asahi Kasei have been received as possible candidates for future cell builds

envia SYSTEMS

Separator Development Status

Separator screening by nail penetration test



Separator requirements:

1. Pass nail penetration test
2. Support EC cell performance (energy, power, endurance, etc.)
3. Desirable physical properties (thin, light, strong, low porosity, low heat shrinkage, good permeability)
4. Low cost

Ceramic coated separator
PASSING nail penetration test

Standard separator
FAILING nail penetration test

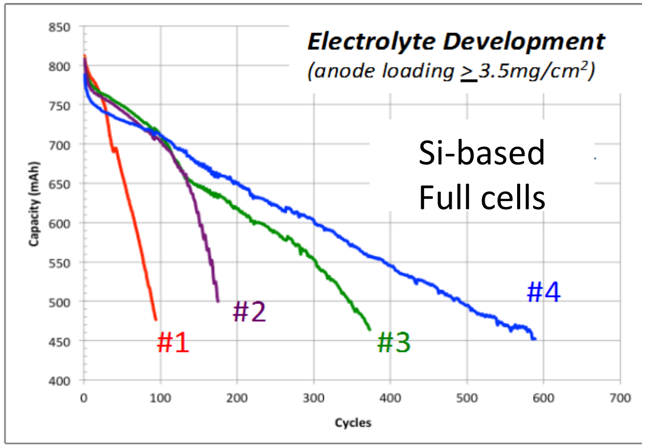
- Nail penetration tests were performed on 20Ah cells to screen the 4 separators
- Separator S#1, S#2, & S#3 passed the Nail penetration tests performed on 20Ah cells making them potential candidates for future cell builds
- Promising separators will be integrated in large capacity pouch cells to evaluate EC performance

envia SYSTEMS

AsahiKASEI
ASAHI KASEI E-MATERIALS

Electrolyte Development

Electrolyte Development:



Pouch cells cycling to 4.35V

Controlling the Si-based anode surface interaction with the electrolyte by engineering the electrolyte formulation (additives, solvents and salts) has shown significant impact on cycle life

- Envia has partnered with Daikin America to develop fluorinated electrolyte formulations that will improve the electrochemical stability of Si-based cells
- The optimal electrolyte formulation should stabilize the SEI formation on the Silicon surface thus reducing the consumption of Lithium during cycling
- Criteria for electrolyte:
  1. Support high voltage operation
  2. Compatible with Silicon-based anodes
  3. Compatible with Li-rich cathodes
  4. Able to support electrochemical, cycle life & temperature cell targets

DAIKIN

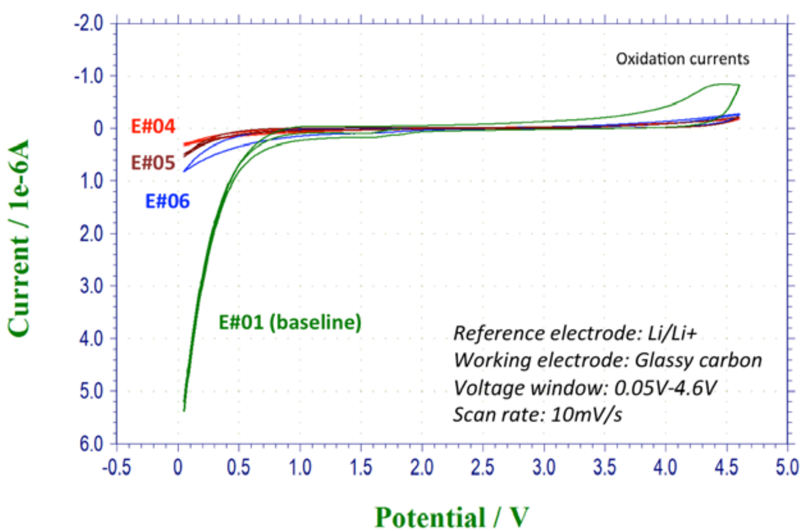
envia SYSTEMS

Electrolyte Development Status

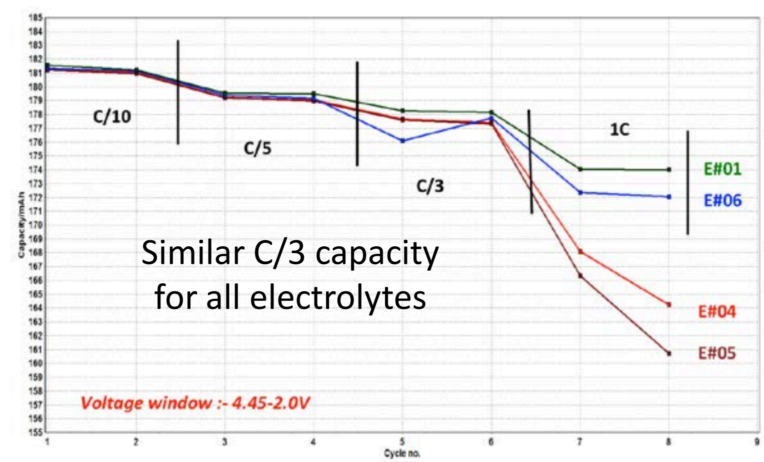
1. Three electrolyte formulations (E#04, E#05 & E#06) have been received from Daikin
2. Preliminary characterization (CV and half-cell compatibility tests) was completed with cycle life to be tested in large capacity cells

NEXT STEPS:

Integrate promising electrolyte formulations into large capacity cells and test cycle life and other cell metrics (power, energy, safety, etc.)



Electrochemical stability: E#04 > E#05 > E#06 > E#01



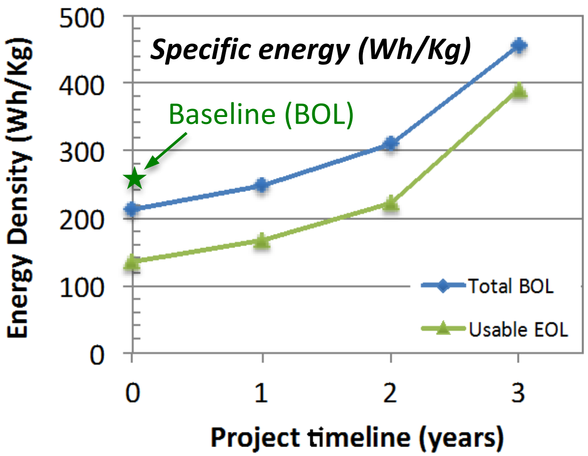
Rate capability: E#01 > E#06 > E#04 > E#05

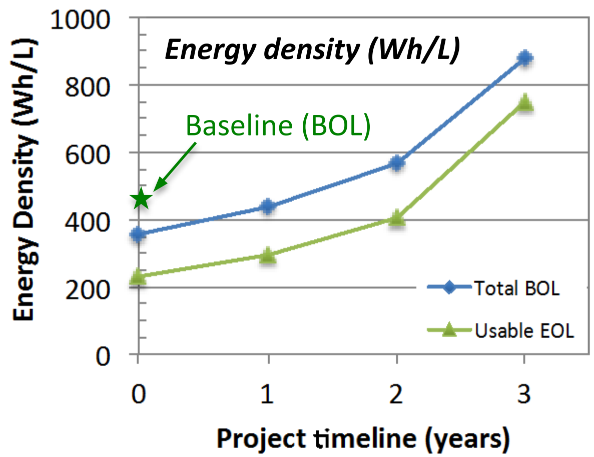
Cell Development

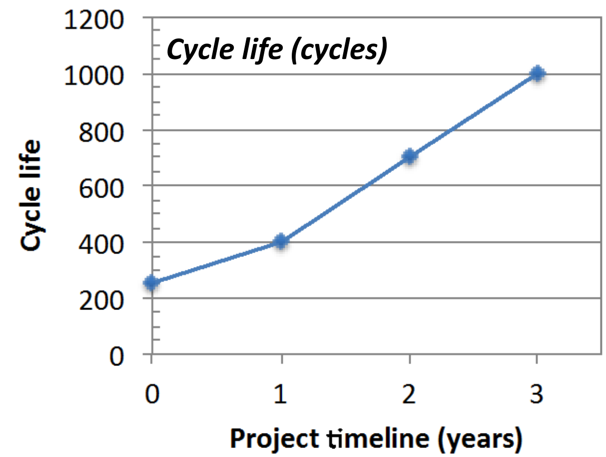
Program Goals:

Develop, optimize and integrate advanced materials, cell components and pre-lithiation process into high capacity pouch cells meeting the USABC EV battery goals for 2020

Cell Development Progression:







Cell Development Status:

- 245Wh/Kg cell design was down-selected and baseline cells were built and delivered with testing ongoing at both Envia and INL
- Developing 275Wh/Kg energy cells for cell build #1 (year 1 of the program)

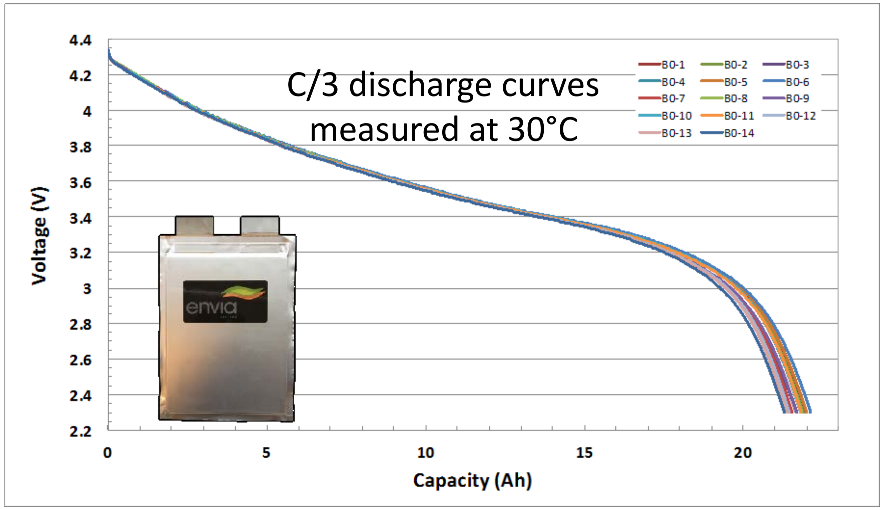
envia SYSTEMS

Baseline Cell Results

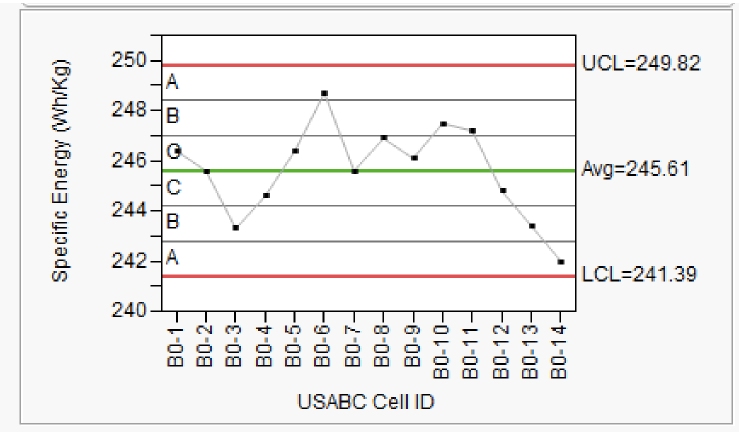
Baseline Cell Design:

		Units	Design #2
Positive	Active Material	N/A	HCMR™-XP Blend
	Cathode ID	N/A	C#8 + Commercial blend
	Electrode area	mm^2	26696
	Electrode density	g/cc	High (>3)
Negative	Active Material	N/A	SiO_x-C Composite
	Anode ID	N/A	Vendor #2, Composition #1
	Electrode area	mm^2	27360
	Electrode density	g/cc	Medium (~1)
Separator		N/A	S#1
Cell Weight		g	298.7
Estimated Capacity, C/3-Rate		Ah	21.4
Energy Density, C/3-Rate		Wh/L	419
Specific Energy, C/3-Rate		Wh/kg	**249**

Specific Capacity (Ah)



Specific Energy (Wh/Kg)



- 21Ah capacity baseline cells are currently testing for capacity, energy, power, cycle life, calendar life & temp performance at both Envia and INL
- Preliminary results suggest baseline cells met the target design and show reproducible capacity (21.7 +/- 0.2Ah) and energy (245.6 +/- 1.8Wh/Kg)

Summary

- Down-selected best Li-rich HCMR™ cathode composition (amount of Li, Ni, Co, Mn and Li_2MnO_3) and dopants to be integrated into 1Ah cell builds
- Anode development is ongoing with respect to composition, coatings and electrode morphology engineering to down-select between Si-based materials (Si-based alloys and/or nSi- & SiO_x-based composites)
- Successful electrochemical pre-lithiation of A#6 SiO_x-based anode electrode rolls with 1Ah cells made and starting testing
- Performed preliminary screening on possible electrolyte formulations and separator types to be integrated into upcoming large capacity cell builds
- 21Ah capacity baseline cells have been made and are currently testing for capacity, energy, power, cycle life, calendar life & temp performance at both Envia and INL with preliminary results matching the cell design and showing reproducibility in capacity (21.7 +/- 0.2Ah) and energy (245.6 +/- 1.8Wh/Kg)

Acknowledgements

- This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under the Award No. DE-EE0006250, under the United States Advanced Battery Consortium (USABC)
- This work was performed under the guidance and support from the USABC technical work group: Oliver Gross (program manager), OuJung (OJ) Kwon, Meng Jiang, Jack Deppe, Jon Christophersen, Matthew Keyser and Chris Orendorf
- This work was performed with processes, materials, cell components and guidance from the various partners: 3M, DuPont, Asahi Kasei, Daikin America, Nanoscale Components and A123 Systems

Technical Back-up Slides

Si-SiO_x-C Anode Process Flow

SiO_x + MO + Graphite

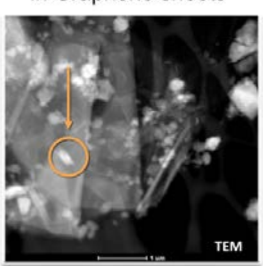
⇩

Envia's Process

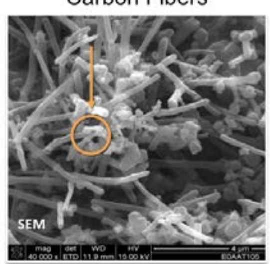
⇩

nSi-nSiO_x-Graphene

Embedded Si-SiO particles in Graphene sheets



Electrodes with Carbon Fibers



- Envia has developed an anode powder synthesis process using low cost precursors like SiO_x & Gr
- Patented process results in precise control of the anode material structure & morphology with Si & SiO_x particles between graphene sheets improving resistance against pulverization
- The stability and electronic conductivity of the Si-SiO_x-C composite anodes is further enhanced by incorporating a network of CFs and CNTs
- Process is cheap, scalable and available in kg quantities