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Prime Recipient Type:	Private Company
Project Title:	Solid State Li Ion Batteries Using Si Composite Anodes
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Prime Recipient DUNS Number:	078313639
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Abstract

Solid Power has teamed with Argonne National Laboratory (ANL) to develop an all solid-state lithium-ion battery (ASSB), enabled by a high-capacity Si anode and a solid state electrolyte (SSE). Replacing liquid electrolytes with solid electrolytes addresses the calendar life challenges that currently limit the widespread adoption of Si anodes.

In this project, Si-SSE composite materials have been developed with a specific capacity >1500 mAh/g (at electrode level). A Si anode was coated by using a roll-to-roll process. All-solid-state NMC-Si pouch cells have been assembled and tested. Cycle life of 1100 at 100% DOD has been demonstrated in the solid state Si pouch cell. Excellent calendar life is achieved in the cell via a high temperature storage test.

Background

Objectives The project objective is to develop all-solid-state Li ion batteries that implement high energy silicon anodes for EV application. The all solid state battery (ASSB) cell will be able to deliver > 350 Wh/kg specific energy, > 750 Wh/L energy density, > 1000 cycle life, and > 10 years calendar life.

Impact The project is enabling scalable production of large format all-solid batteries required by the vehicle market and building domestic battery manufacturers as leaders in the global vehicle ASSB production. The proposed technology addresses key limitations of state-of-the-art lithium batteries to meet DOE EV battery targets and accelerate their adoption as large-format EV batteries for sustainable transportation technology.

Approach The project develops a solid state electrolyte (SSE) for Si anode and synthesizes a Si-SSE composite anode. The solid state electrolyte system addresses the calendar life challenge of the Si anode batteries by forming highly stable SEI. A high-Ni content NMC cathode was selected to match the Si anode. The all-solid-state cell was assembled by scalable roll-to-roll processes developed by Solid Power.

Collaborations The proposed team consists of Solid Power and a subcontractor, Argonne National Laboratory (ANL). Solid Power (PI: Pu Zhang) has developed the high energy Si anode and other cell components, assembled cells, and conducted cell tests. ANL (Co-PI: Wenquan Lu) has carried out material characterization and cell failure mode analysis.

Milestones

Period	Milestone	Type	Status	Completion Date
BP 1	Raw materials and equipment secured	Technical	Complete	12/31/2020
	Anode capacity ≥ 1500 mAh/g	Technical	Complete	9/30/2021
	Cathode down-selected	Technical	Complete	3/31/2021
	15 x 0.2 Ah baseline cells delivered	Technical	Complete	12/31/2021
	Go/No-Go. Anode capacity ≥ 1500 mAh/g & cell cycle life ≥ 500	Go / No-Go	Complete	09/30/2021
BP 2	Si content > 70%	Technical	Complete	3/31/2022
	Separator coating ≥ 1m	Technical	Complete	6/30/2022
	Electrode loading ≥ 4.0 mAh/cm^2	Technical	Complete	9/30/2022
	15 x 1 Ah interim cell delivered	Technical	Complete	9/30/2022
	Go/No-Go. Anode capacity ≥ 2000 mAh/g & cell cycle life ≥ 750	Go / No-Go	Complete	12/31/2022
BP 3	Anode, cathode, and separator coating > 50 meters each	Technical	Complete	3/31/2023
	15 x 2 Ah final cell delivered	Technical	Complete	12/31/2023
	Specific energy > 350 Wh/kg and energy density > 750 Wh/L	Technical	Complete	12/31/2023
	Cost ≤ $100/kWh	Technical	Complete	12/31/2023
	Cell cycle life > 1000 and calendar life > 10 years	Technical	In progress	(Est.) 6/30/2024

Accomplishments:

1. Si anode development

The Si composite was synthesized by integrating a Si powder and a Solid Power's sulfide solid state electrolyte (SSE). The Si-SSE composite material was mixed with a binder, a conductive carbon additive and a selected solvent to form an anode slurry. The slurry was then coated to Cu foil to form an electrode.

Figure 1 shows the SEM images (i.e., elemental maps) of the anode, indicating a homogenous Si-SSE composite structure. The anode was coated by a slurry-cast method on an industrial slot-die coater, with >500 meters delivered. The coated anode is shown in Figure 2.

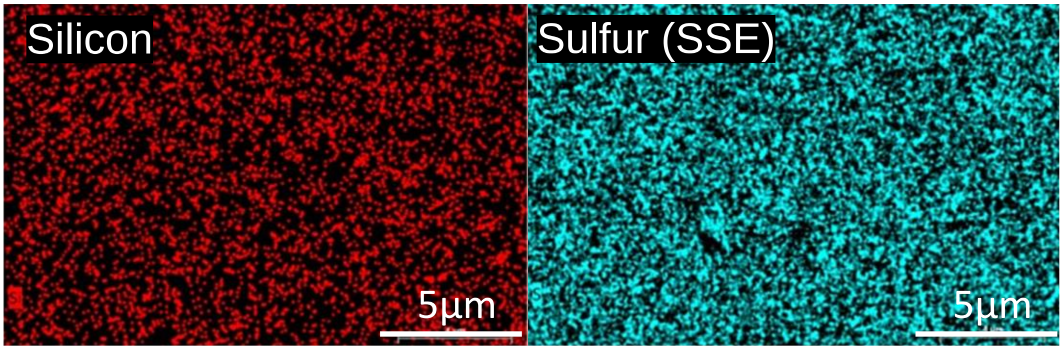


Figure 1. SEM elemental mapping of the Si-SSE composite anode. It confirms a homogenous dispersion of Si and SSE in the composite.

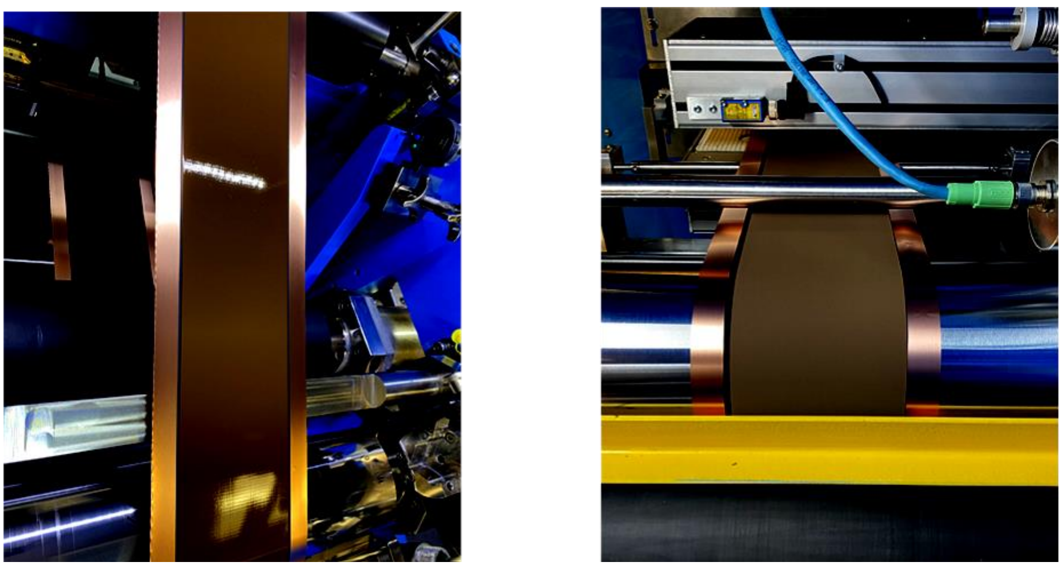


Figure 2. A roll-to-roll coating of Si composite anode on a slot-die coater: wet (left) and dry (right).

A baseline Si anode at 1000 mAh/g was established at the beginning of the project. Through the project, the Si anode composition was developed and optimized by Design of Experiments. All the anodes were coated at loadings ≥ 3 mAh/cm^2. Si-Li coin half cells were built and tested at C/5 – C/5, 0.05 – 1.0V and 45°C. Two new generations of the anodes have been developed with specific capacities of 1500 mAh/g and 2100 mAh/g at electrode level, respectively. The newly developed Si anodes achieve higher capacity, higher first cycle efficiency (FCE), and more stable cycle life than the baseline anode. The anode capacity and FCE are shown in Table 1 and Figure 3. The comparison of half cell cycle life is shown in Figure 4. The full cell cycle life of the Si anode is shown in the "full cell performance" section.

Table 1. Capacity and FCE of the Si materials

Property	Baseline Si Anode at Beginning of Project	High Energy Si Anode (Year 1)	Ultra-high Energy Si Anode (Year 2)
Si Anode Capacity (at Electrode Level)	1000 mAh/g	1500 mAh/g	2100 mAh/g
First Cycle Efficiency	87%	92%	92%

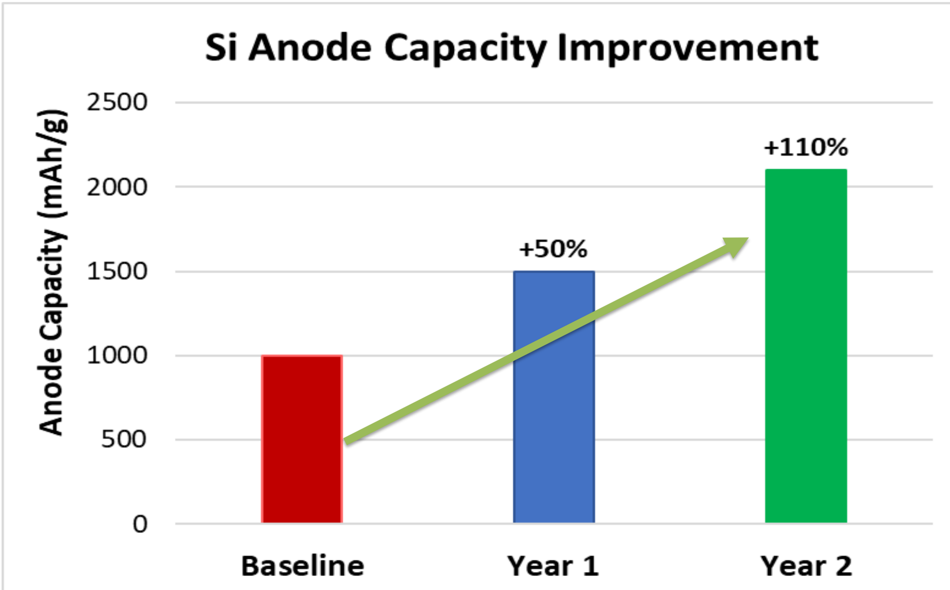


Figure 3. The newly developed Si composite anodes show significant improvement from the baseline.

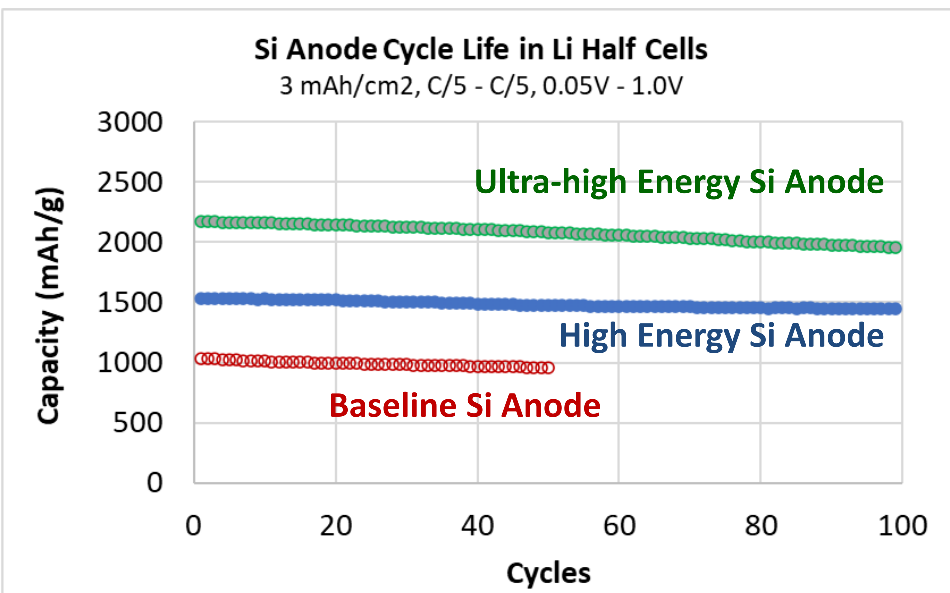


Figure 4. Cycle life of baseline and newly developed Si anodes in Li half cells. The anode loading is at 3 mAh/cm^2 loading. The cells are tested at C/5 – C/5, 0.05 – 1.0V, and 45°C

2. Cathode and separator integration

A high Ni content NMC cathode has been developed under an internal project and applied to this project. The NMC active material was mixed with SSE, binder, conductive carbon additive, and solvent to form a cathode slurry. The slurry was then coated to Al foil to form an electrode. A roll-to-roll cathode has been coated for the large format cell assembly. Figure 5 shows a R2R cathode picture.

Figure 5. Slurry cast NMC cathode by R2R process

Both the cathode formulation and fabrication process were optimized to match the Si anode. A comparison of newly developed and baseline cathodes is shown in both Table 2 and Figure 6. The cathodes were tested in full Si pouch cells at C/5 and 45°C. Gen 2 (NMC 622) cathode was selected for the project based on its performance advantage.

Table 2. Comparison of the NMC cathodes

Cathode Materials	Development Focus	Discharge Capacity (mAh/g)	Full Cell First Cycle Efficiency (%)
Gen 1	Baseline material at beginning of project	140	90%
Gen 2	Optimized formulation and process	152	90%

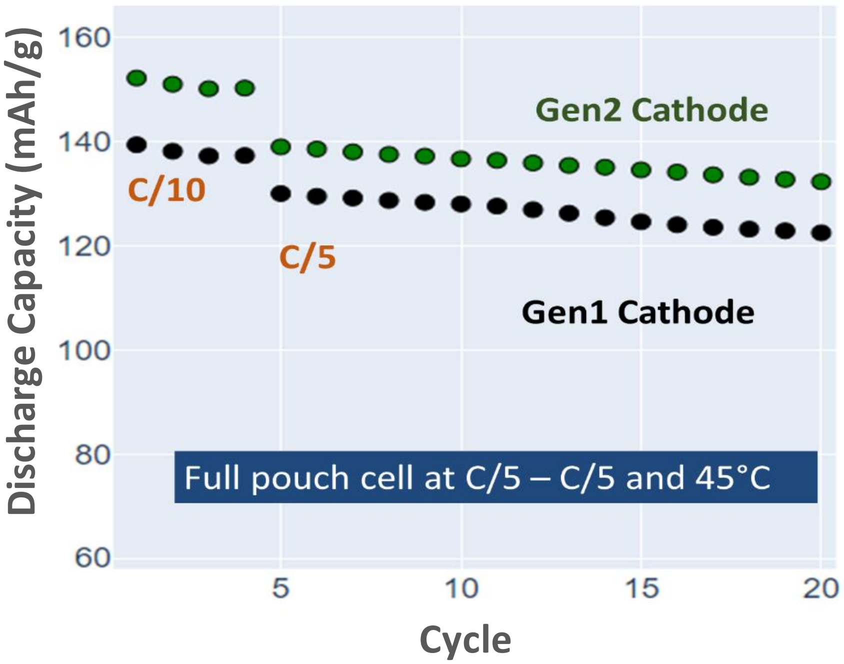


Figure 6. Cycle life of the three generations of NMC cathodes in Si-NMC full pouch cells (at 3 mAh/cm^2 loading, C/5 – C/5, 2.5 – 4.1V, 45 °C).

The SSE separator coating process is similar to the electrode process. A separator slurry was prepared by mixing the SSE powder, binder, and solvent by using a planetary mixer. The slurry was cast on a carrier film on a slot-die coater. Figure 7 shows SSE film coated by R2R process.

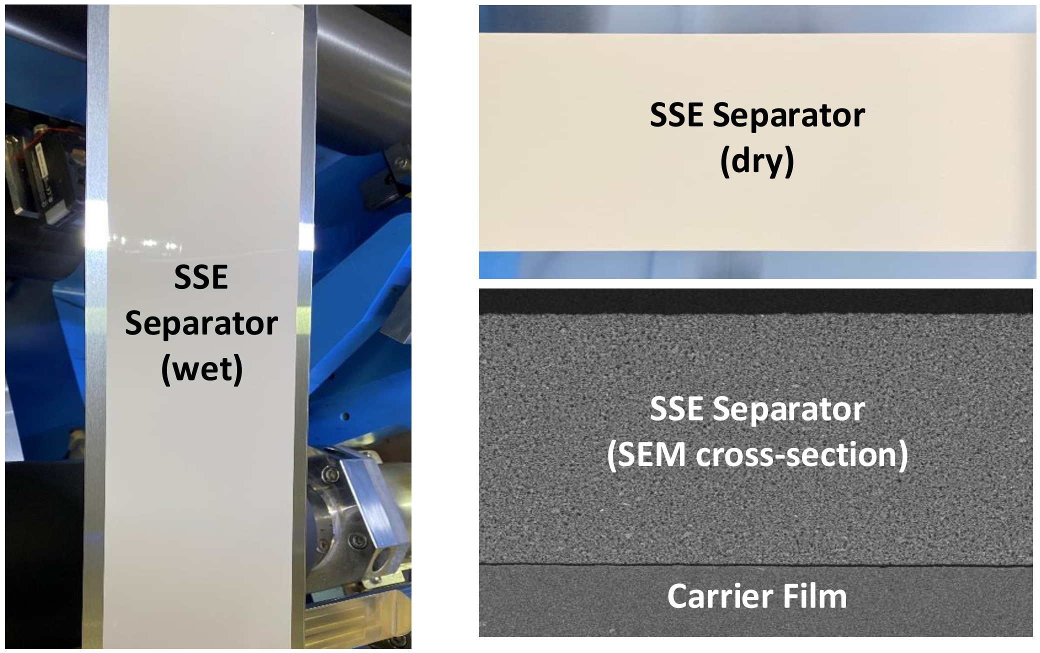


Figure 7. A slurry-cast SSE separator film by R2R process

3. Cell assembly

Three types of all-solid-state cells have been developed in the project. (1) A Si // Li half-cell is used to evaluate the Si anode performance at material level. (2) A single-layer pouch cell contains Si anode, NMC cathode, and SSE separator. It is used to evaluate the full cell performance at both material level and process level. (3) A multilayer pouch cell (> 2Ah) is developed as the large format cell demonstration at pilot scale.

A Si-SSE-NMC tri-layer stack is the core of a full pouch cell. The tri-layer stack fabrication process has been developed and optimized in the project. The focus of the investigation was to minimize the interface resistance among the component layers. A single-layer pouch cell is formed by welding tabs to the stack and sealing the tabbed stack in a pouch. A multilayer pouch cell is assembled by tabbing and pouching repeated units of the tri-layer stacks. Figure 8 shows an integrated single tack (SEM cross-section) and large format pouch cells containing multilayer stacks.

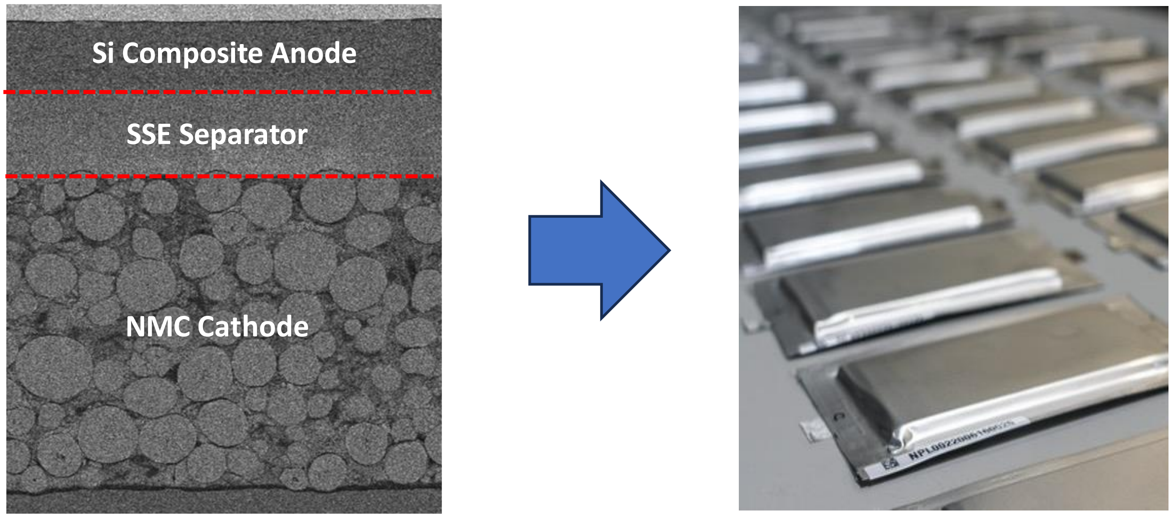


Figure 8. Cross-section image of a single cell stack by SEM

Table 3 lists the key parameters of the large format cell (as final delivery).

Table 3. Multilayer Pouch Cell Key Parameters

Parameter	Value
Cathode type	NMC622
Cathode loading	3.3 mAh/cm^2
Anode type	Si composite, 1500 mAh/g
A/C ratio	1.1
Number of electrode pairs	9
Rated capacity (at C/10 and 45°C)	2.50 Ah

The large format pouch cells show consistent performance during the formation cycles. Table 4 shows the capacity, First Cycle Efficiency (FCE), and resistance from the 10 cells tested internally.

Table 4. Pouch Cell Capacity, FCE, and Resistance at 45°C

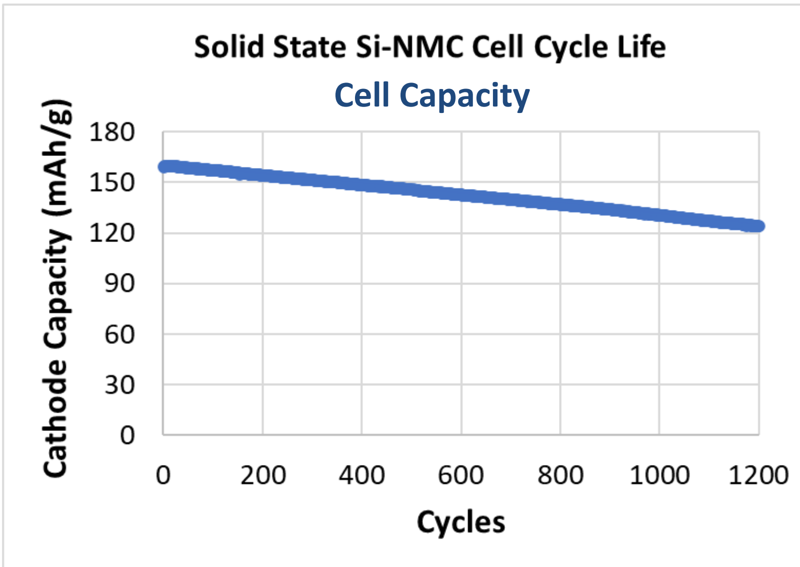
Cell Number	C/10 Capacity (Ah)	FCE (%)	Resistance (Ohm)
1	2.53	90.1	0.129
2	2.52	90.3	0.133
3	2.52	89.6	0.135
4	2.49	89.8	0.136
5	2.55	90.4	0.130
6	2.48	89.7	0.138
7	2.56	90.0	0.132
8	2.56	90.0	0.130
9	2.55	89.7	0.131
10	2.53	90.1	0.131
Average	**2.53 ± 0.03**	**90.0 ± 0.3**	**0.133 ± 0.003**

4. Full cell performance

As described in the previous sections, a high energy Si composite anode has been successfully developed with a reversible capacity >1500 mAh/g at electrode level and an NMC cathode >150 mAh/g has been selected to match the anode in a full pouch cell. The solid state pouch cell was assembled with Si composite anode, NMC cathode, and SSE separator.

4.1. Single-layer pouch cell performance

When cycled at C/5 – C/5, 2.5 – 4.1V (100% DOD), and 45°C, the cell shows 90% first cycle efficiency and retains 80% capacity after 1100 cycles (Figure 9).



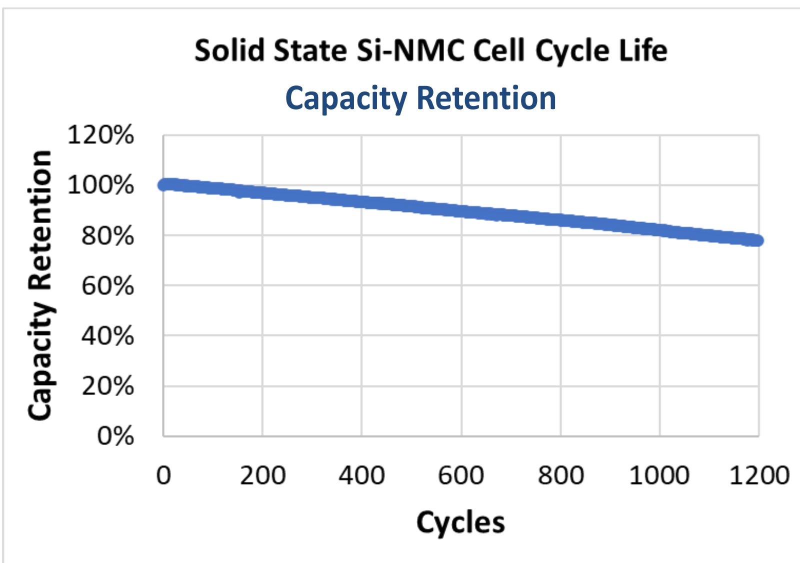


Figure 9. Cycle life of Si-NMC full pouch cell (3.3 mAh/cm^2 loading, C/5 – C/5, 100% DOD, 45 °C): (top) NMC cathode capacity vs. cycle; (bottom) capacity retention vs. cycle.

The pouch cell was also evaluated for high temperature storage stability. The cells were charged to 4.1V at C/10 and stored at 25, 45, or 60 °C, respectively. After the storage, the capacity is checked at C/10, 2.5 – 4.1V, and 45 °C. Over a storage period of 20 weeks, the cell energy loss is 6%, 11%, and 18% at the storage temperature of 25°C, 45°C, and 60°C, respectively (Figure 10). It confirms excellent storage stability of the all-solid-state Si anode cell, comparable to a baseline graphite anode Li ion cell. Long calendar life > 10 years is projected for the ASSB Si cell.

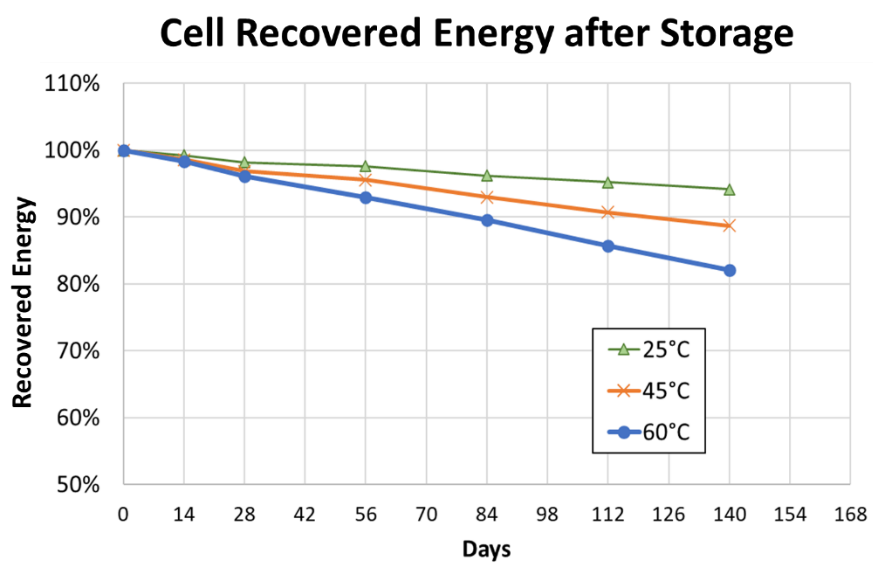


Figure 10. Storage testing at various temperatures. The cell is charged to 4.1V at C/10 and stored at 25, 45, or 60 °C. After the storage, the capacity is checked at C/10, 2.5 – 4.1V, and 45 °C.

4.2. Multilayer pouch cell performance

Multilayer pouch cells (>2 Ah) were assembled and tested at the end of the project. Fifteen (15) of the large format cells have been delivered to DOE to conclude the project. The long term performance data is not yet available, but the initial data indicates good quality of the cells.

4.2.1. Initial cycle life performance

The cells show 94% capacity retention after 100 cycles (Figure 11), with the following test protocol.

- C/3 – C/3, 2.5 – 4.1V, and 45°C
- NMC622 cathode and Si anode, A/C = 1.1

4.2.2. Initial calendar life (60°C storage) performance

The cells show 98% energy recovery after 15 days of storage at 60°C (Figure 12), with the following test protocol.

- Charged to 4.1V and stored at 60°C
- Capacity check at 2.5 – 4.1V, C/10, and 45°C

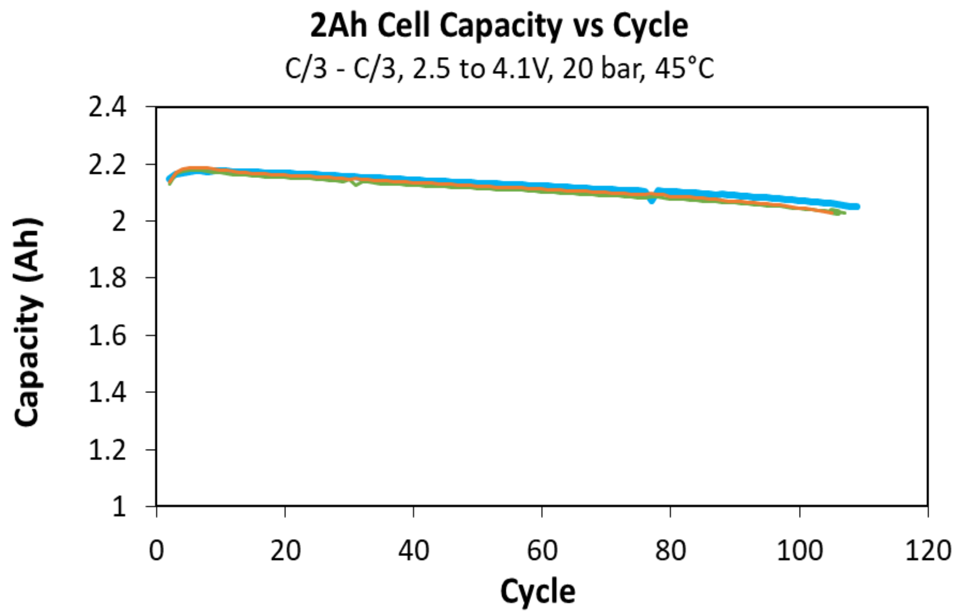


Figure 11. Cycle life of 2Ah pouch cells. The cells are tested at 2.5 – 4.1V, C/3 – C/3, and 45 °C.

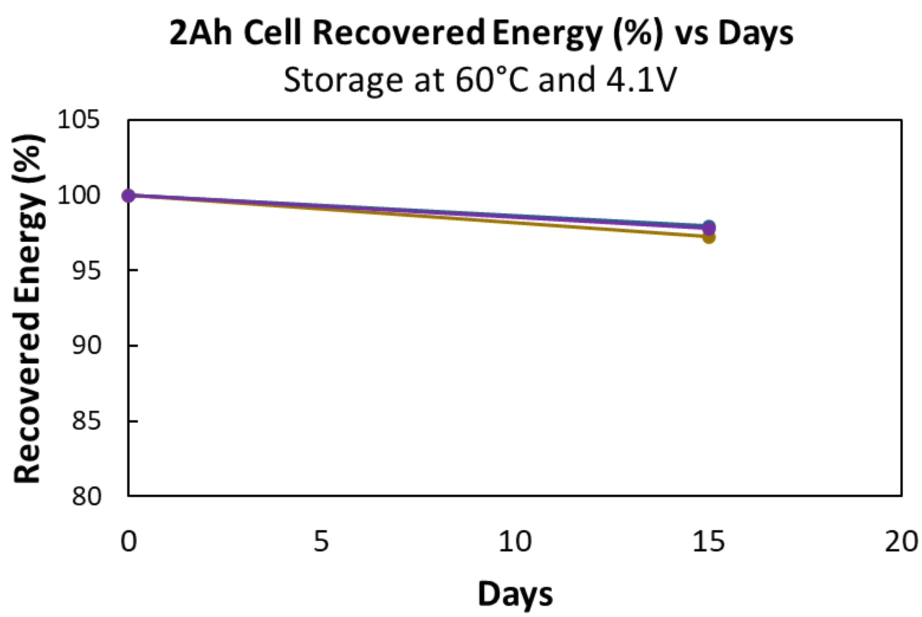


Figure 12. Calendar life of 2Ah pouch cells. The cells are charged to 4.1V at C/10 and stored at 60 °C. After the storage period, the capacity is checked at C/10, 2.5 – 4.1V, and 45 °C.

5. All-solid-state battery (ASSB) Si cell design and modeling

5.1. ASSB cell platform

Several cell designs are possible under the all-solid-state umbrella. Solid Power's SSE materials enable an entire new cell platform that can incorporate a wide variety of existing and future anode and cathode materials (Figure 13).

On the anode side, although Li metal is an ultimate solution as it stores ultra-high energy per unit mass long-term, silicon is attractive as it offers the quickest path to meeting the charge rate and low temperature cycling requirements for future electric vehicles in low-cost EV scale cells. It can deliver similar volumetric energy density to Li metal if enough Si material can be packed into the anode layer.

On the cathode side, the sulfide electrolytes can be paired with the same lithium nickel-manganese-cobalt oxide (NMC) cathode materials being used today in EVs, which is important for near-term market introduction. Conversion reaction type cathode chemistries such as iron sulfide and sulfur, paired with Li anode, would provide further gains in specific energy while being inexpensive and sustainable long term.

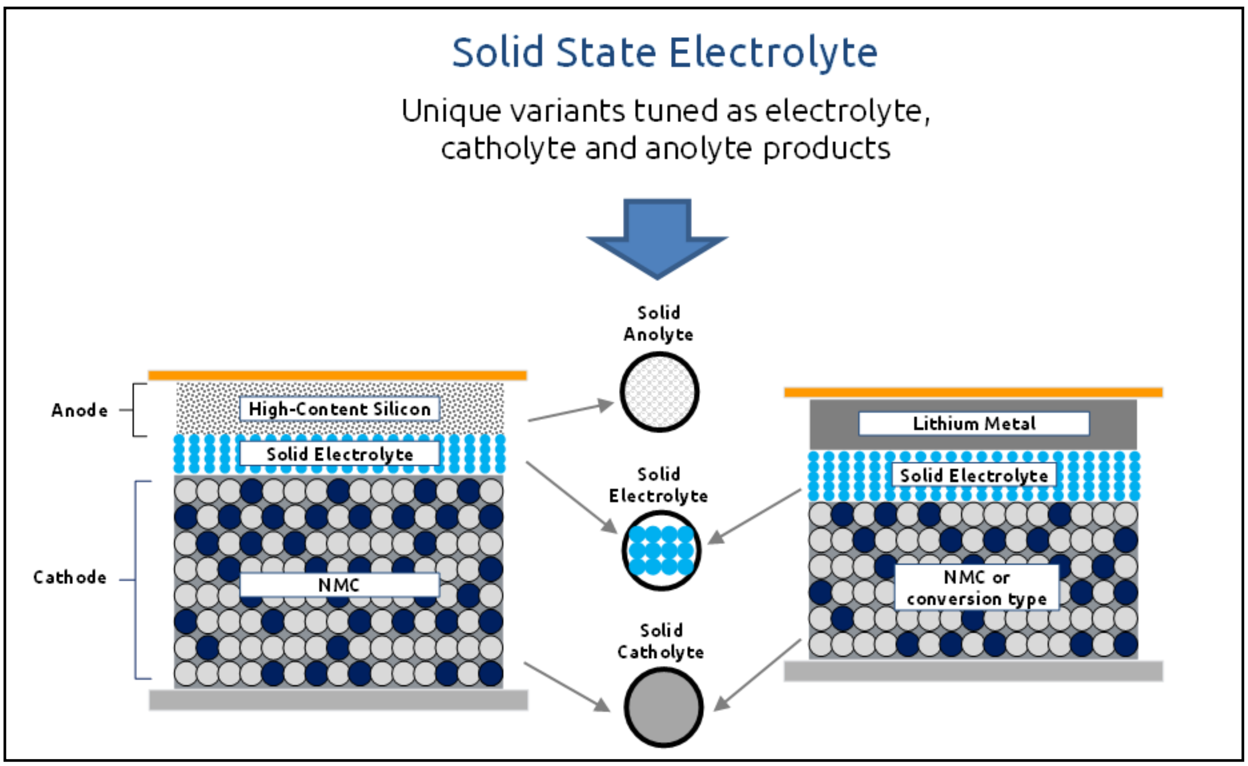


Figure 13. A flexible platform that incorporates a variety of anode and cathode materials for a high energy and low cost all-solid-state-battery cell

5.2. ASSB Si cell energy projection

In this project we have demonstrated a Si anode with 1500 mAh/g capacity, an NMC 622 cathode with 150 mAh/g capacity and 3.3 mAh/cm^2 loading, and an SSE separator at 30 µm in a full pouch cell.

By applying the current cell parameters to an EV-relevant pouch cell at 100 Ah, the cell specific energy and energy density are projected to be 314 Wh/kg and 715 Wh/L, respectively.

In future development beyond the project, we plan to apply an NMC 811 cathode at 3.5 mAh/cm^2 loading and reduce the separator thickness to 20 µm. An EV cell with specific energy at 355 Wh/kg and energy density at 836 Wh/L is projected.

The key cell design parameters and projected EV cell specific energy & energy density in the current generation and next generation technologies are summarized in Table 5.

Table 5. ASSB Li pouch cell design parameters and projected energy densities

Timeline	Key Cell Design Parameter				100 Ah EV Cell Specific Energy and Energy Density (Projected)	
	Cathode Type	Cathode Loading (mAh/cm^2)	Si Anode Capacity (mAh/g)	Separator Thickness (µm)	Specific Energy (Wh/kg)	Energy Density (Wh/L)
End of Project (2023)	NMC 622	3.3	1500	30	**314**	**715**
Next Generation (2024)	NMC 811	3.5	1500	20	**355**	**836**

5.3. ASSB Si cell cost projection

Rhomotion cell cost model has been used to calculate the cost of an ASSB Si-NMC EV cell at 100 Ah. The ASSB Si cell costs $76/kWh at material level, comparable to a baseline liquid electrolyte Li-ion cell. 68% of the material cost comes from the NMC cathode. DOE's current efforts to reduce the cathode cost by developing low cost synthesis processes and cathode recycling processes will lower the cathode cost and thus the cell cost further. Cell process cost is expected to similar to a conventional Li ion cell as Solid Power is using similar processes for the ASSB assembly. Solid Power is currently working with SK On (Tier-1 cell partner) on the process cost model. The final cell cost model will be updated once the process information is available.

Conclusion

In this project, Si-SSE composite materials have been developed with a specific capacity >1500 mAh/g (at electrode level). The Si anode has been successfully coated by using a roll-to-roll process. All-solid-state NMC-Si pouch cells have been assembled and tested. Cycle life of 1100 at 100% DOD has been demonstrated in an all-solid-state Si pouch cell. Calendar life > 10 years is projected in the cell.