DISCLAIMER

1. Cover Page

Federal Agency and Organization Element to Which Report is Submitted	Office of Energy Efficiency and Renewable Energy
Federal Grant or Other Identifying Number Assigned by Agency	DE-EE0009184 RF Award 89436
Project Title	Fully Fluorinated Local High Concentration Electrolytes Enabling High Energy Density Si Anodes
PD/PI Name, Title and Contact Information (e-mail address and phone number)	Amy C. Marschilok, Professor amy.marschilok@stonybrook.edu 631-632-8364
Name of Submitting Official, Title, and Contact Information (e-mail address and phone number), if other than PD/PI	Margaret Badon, Grants & Contracts Specialist, 631.632.9087, margaret.badon@stonybrook.edu
Submission Date	October 28,2024
Recipient Organization (Name and Address)	Research Foundation for SUNY Stony Brook University 100 Nicolls Road Stony Brook, NY 11794-3362
Project/Grant Period (Start Date, End Date)	10/1/2023 to 6/30/2024 (with NCTE)
Reporting Period End Date	9/30/2024
Report Term or Frequency (annual, semi-annual, quarterly, final, other)	Final

2. Executive Summary

Major Goals & Objectives:
The objective is to research, fabricate, and test lithium battery cells that implement ≥ 30% silicon content electrodes with commercially available cathode technology and have the potential to achieve cell performance identified in the table below.

Beginning of Life Characteristics at 30°C	Cell Level
Useable Specific Energy @ C/3	>350 Wh/kg
Useable Energy Density @ C/3	>750 Wh/L
Calendar Life (<20% energy fade)	>10 Years
Cycle Life (C/3 deep discharge to 350Wh/kg, <20%	>1,000

Technical Achievement(s) in Past Quarter [*Provide a terse summary of the major technical status and progress of the project in achieving objective and programmatic goals for the reporting period*]

The program is on track. The Q12 milestone – characterization of parasitic heat associated with LHCE interface formation using isothermal microcalorimetry – has been completed.

Project Schedule Status

The project is on schedule. Task 4.1 – Characterize FLHCE derived solid electrolyte interphase chemistry and associated evolved parasitic heat – is complete. Task 5.1 – Evaluate extended cycling performance of optimized FLHCE and benchmark against cells using conventional electrolyte with FEC additive – is underway. We have received a no cost time extension as some of the electrolytes are showing promising electrochemistry which merits collection of longer term data. In order to collect, analyze and interpret the data, an extension of time was needed.

Project Budget Status This is the final project report.

Changes/Problems:

None. The no cost time extension was helpful to be able to prepare the cells appropriately for the program. We are now at the end of the project.

Key Personnel Changes: [*Describe planned or actual changes in principal investigator, business contacts, or senior/key personnel and the impact to achieving project objectives.*]

There are no changes in key personnel or teaming arrangements at this time.

Scope Issues: [

There are no issues with completing the required project scope at this time.

Schedule Issues:.]

There are no changes to the schedule at this time.

Budget Issues: [*Describe changes during the reporting period that may have a significant positive or negative impact on expenditures or the overall budget.*]

There are no changes to the budget at this time.

3. Accomplishments of Planned Tasks and Milestone Update:

Task number and title:

Task 5.1 – Evaluate extended cycling performance of optimized FLHCE and benchmark against cells using conventional electrolyte with FEC additive

Planned Activities:

Planned activities for this task in this quarter were to optimize the Si content of the Si- graphite electrodes and the areal loading prior to preparation of 0.2 Ah cells with Si- graphite anodes and NMC811 cathodes for benchmarking extended cycling.

Accomplishments:

To complete the end of project goal, 12 multilayer pouch cells with either FEC10 control or Gen2 LHCE#1 electrolyte were fabricated. Cells were constructed with NMC811 cathodes and 20% Si / 55% graphite anodes, with an N/P ratio of 1.08. This design generated cells with a nominal capacity of 300 mAh based on a reversible capacity of 200 mAh/g for NMC811.

To generate an effective SEI, the cells received formation cycling in which they were charged to 4.3 V and then cycled four times from 3.0-4.3 V at 30 °C, C/10 (20 mA/g). The capacities are presented in **Table 1**. The cells exceed the 200 mAh target on the 4th discharge; the FEC10 electrolyte delivers slightly higher capacity than the LHCE.

Eight of the multilayer pouch cells were cycled 1000 times. The cells were cycled from 3.0 to 4.3 V at 30 °C; the cells were discharged at a C/3 (67 mA/g) rate and charged at a C/3 rate and then the voltage was held for 20 minutes. The cells are divided into two populations where each contains two cells with each electrolyte. The first population received two recovery cycles every 100 cycles where the recovery cycling was performed at a C/10 rate with no voltage hold. The second population received two recovery cycles every 250 cycles. At C/3, the cells all exceeded the target capacity of 200 mAh (236 +/- 5 mAh for FEC10 and 228 +/- 2 mAh for LHCE). The FEC10 cells fade more quickly with a retention of 39% at cycle 200 *vs*. 49% for the LHCE cells. This may relate to the more resistive interface generated by the FEC10 electrolyte as observed with EIS. Over cycling, the fading becomes extremely significant for both electrolytes and by cycle 1000 they have similar retention values (~13%). The graphical data were provided in the last quarterly report.

To test the calendar aging of the cells, four cells (two with each electrolyte) were calendar aged at 3.5 V, 30 °C after formation. Every 28 days, they were charged to 4.3 V at C/10, EIS was collected, they were then cycled once from 3.0-4.3 V and discharged back to 3.5 V. The final results are presented in **Figure 1** and **Table 1**. After 1 month, the capacity had declined by 4% for FEC10 and 7% for the LHCE. After 2 months, there were only been small additional declines, 5% and 7% total for FEC10 and the LHCE. There have been minimal changes to the EIS. After 3 months, there were only small additional declines, 6% and 9% total for FEC10 and the LHCE. After 6 months, there were only small additional declines, 7% and 9% total for FEC10 and the LHCE. There have been minimal changes to the EIS overall under the calendar aging protocol.

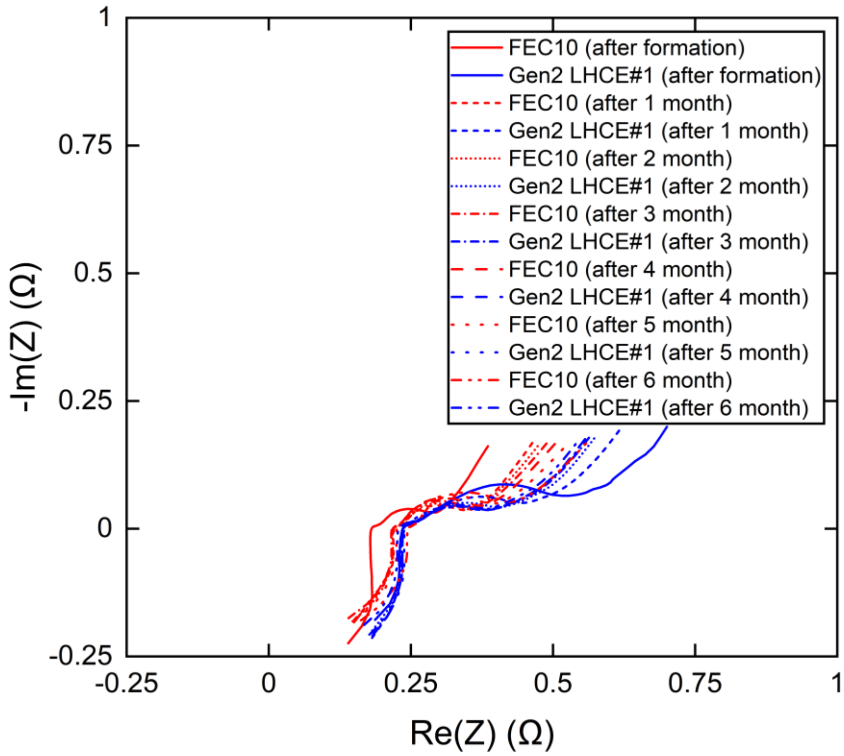

Figure 1. EIS of multilayer NMC811/Si-graphite pouch cells with FEC10 or Gen2 LHCE#1 electrolyte after formation, 1, 2, 3, 4, 5, and 6 months of calendar aging.

Table 1. Capacities of multilayer NMC811/Si-graphite pouch cells with FEC10 or Gen2 LHCE#1 electrolyte after calendar aging test post cycling.

Discharge	**FEC10**		**Gen2 LHCE#1**	
	Capacity (mAh/g)	**Capacity (mAh)**	**Capacity (mAh/g)**	**Capacity (mAh)**
4th Formation	163.0 +/- 0.2	243.2 +/- 0.3	155.3 +/- 0.1	231.3 +/- 0.7
After 1 Month	156.3 +/- 0.8	233 +/- 1	145 +/- 4	218 +/- 7
After 2 Month	154.5 +/- 0.7	231 +/- 1	144 +/- 5	215 +/- 9
After 3 Month	153.2 +/- 0.7	229 +/- 1	142 +/- 7	211 +/- 11
After 5 Month	151.9 +/- 0.7	227 +/- 1	142 +/- 6	211 +/- 9
After 6 Month	150.8 +/- 0.8	225 +/- 1	142 +/- 4	211 +/- 7

Plans for Next Quarter:

None. This is the final report for the program.

Task table:
(see following page)

Task Number	Planned Activities	Accomplishments	Explanation of Variance	Plans for Next Quarter
1.1	(a) Procure and determine water content of electrolyte solvents, (b) Electrode material characterization (c) Preparation of Si-graphite composite electrodes (d) Measure physical properties (viscosity and contact angle) of Gen1 electrolytes (e) Measure electrochemical properties (ionic conductivity and voltage stability) of Gen1 electrolytes	(a) Electrolyte solvents procured with water content <50 ppm (b) Nano-Si electrode material characterized by XPS, XRD, SEM (c) Si-graphite composite electrodes prepared and characterized in half cells and full cells (d) Viscosity and contact angle of Gen1 electrolytes characterized (e) Ionic conductivity and voltage stability measurements of electrolytes characterized (f) Single salt LHCEs and mixed salt LHCEs with varying salt concentration prepared, conductivity, contact angle, voltage stability characterized	Single salt (LiFSI) and mixed salt ($LiPF_6$ + LiFSI) LHCEs were prepared at different salt concentrations to understand impact of salt on stability and electrochemical behavior.	Task complete
2.1	(a) Testing of Gen1 electrolyte formulations in half cell configurations (b) Testing of Gen1 electrolyte formulations in full cell configuration	(a) Half cell electrochemical behavior of Gen1 formulations based on single salt and mixed salt LHCEs characterized (b) Full cell electrochemical behavior of Gen1 formulations based on single salt and mixed salt LHCEs characterized (c) Calendar aging tests performed	Calendar aging tests in a half cell configuration were performed in addition to galvanostatic cycling tests XPS studies of recovered electrodes from full cells were performed Isothermal microcalorimetry	Task complete

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3.1	(a) Preparation of Gen 2 electrolyte formulations with varying hydrofluoroether diluent chemistry and concentration (b) Measure physical properties (viscosity and contact angle) of Gen2 electrolytes (c) Measure electrochemical properties (ionic conductivity and voltage stability) of Gen2 electrolytes (d) Testing of Gen2 electrolyte formulations in half cell configurations (e) Testing of Gen2 electrolyte formulations in full cell configuration (f) Calendar life testing of Gen2 electrolyte formulations	(a) Gen2 electrolyte formulations with varying hydrofluoroether diluent chemistry and concentration were prepared. (b) Viscosity and contact angle of Gen2 electrolytes were characterized (c) Ionic conductivity and voltage stability of Gen2 electrolytes were characterized. (d) Testing of Gen2 electrolyte formulations in half cell configurations (e) Testing of Gen2 electrolyte formulations in full cell configuration (f) Calendar life testing of Gen2 electrolyte formulations		Task complete
4.1	(a) Characterize morphology of LHCE derived interfaces from cycled electrodes (b) Characterize chemical composition of LHCE derived interfaces (c) Isothermal microcalorimetry characterization of LHCE derived interfaces	(a) Characterize morphology of LHCE derived interfaces from cycled electrodes (b) Characterize chemical composition of LHCE derived interfaces (c) Isothermal microcalorimetry characterization of LHCE derived interfaces		Task complete
5.1	(a) Preparation of full cells in pouch cell format to benchmark extended cycling and calendar life of LHCE vs. conventional electrolyte with FEC additive (b) Demonstrate 0.2 Ah cells with optimized LHCE with 50% improvement in capacity retention compared to cells with control electrolyte			Task complete

Milestone Table:

Milestone Number	Milestone Title	Milestone Completion Date			Explanation of Variance
		Original Planned Date	Revised Planned Date	Actual Completion Date	
M1	Procurement of solvents	12/31/2020	N/A	12/31/2020	N/A
M2	Physical properties of Gen1 FLHCEs characterized	3/31/2021	N/A	3/31/2021	N/A
M3	Electrochemical properties of Gen1 FLHCEs characterized	6/30/2021	N/A	6/30/2021	N/A
M4	Half cell performance of Gen1 FLHCEs characterized	9/30/2021	N/A	9/30/2021	N/A
M5	Demonstration of full cells using Gen1 FLHCE capable of 100 cycles at C/3 rate with delivered capacity > control cells	12/31/2021	N/A	12/31/2021	N/A
M6	Physical properties of Gen2 FLHCEs characterized	3/31/2022	N/A	3/31/2022	N/A
M7	Electrochemical properties of Gen2 FLHCEs characterized	6/30/2022	N/A	6/20/2022	N/A
M8	Half cell performance of Gen2 FLHCEs characterized	9/30/2022	N/A	9/30/2022	N/A
M9	Demonstration of full cells using Gen2 FLHCE capable of 100 cycles at C/3 rate with 20% improvement in capacity retention compared to cells with control electrolyte	12/31/2022	N/A	9/30/2022	The milestone was achieved in advance of the planned date.
M10	Morphology of FLHCE derived interphases characterized	3/31/2023	N/A	3/31/2023	N/A
M11	Chemical composition of FLHCE derived interfaces characterized	6/30/2023	N/A	6/30/2023	N/A
M12	Parasitic heat associated with FLHCE interface formation characterized	9/30/2023	N/A	9/30/2023	N/A
M13	Demonstration of 0.2 Ah cells utilizing FLHCE compared to cells with control electrolyte (≥500 cycles, C/3 rate)	12/31/2023	N/A	9/30/2024	N/A

3. Products:

a. Publications

Lutz, D. M.; McCarthy, A. H.; King, S. T.; Singh, G.; Stackhouse, C. A.; Wang, L.; Quilty, C. D.; Bernardez, E. M.; Tallman, K. R.; Tong, X.; Bai, J.; Zhong, H.; Takeuchi, K. J.; Takeuchi, E. S.; Marschilok, A. C.; Bock, D. C., Progress Towards Extended Cycle Life Si-based Anodes: Investigation of Fluorinated Local High Concentration Electrolytes. Journal of The Electrochemical Society 2022, 169 (9), 090501.

b. Books or other non-periodical, one-time publications

Nothing to report.

c. Conference proceedings, papers, and presentations

Nothing to report.

d. Website(s)

Nothing to report.

e. Inventions, patent applications, and/or licenses

Nothing to report.

f. Other products

Nothing to report.

4. Participants & Other Collaborating Organizations:

1. Name: Amy Marschilok
2. Total Number of Months: 0.5
3. Project Role: PI
4. Researcher Identifier:
5. Contribution to Project: Dr. Marschilok has been responsible for overall project planning and task reallocation.
6. State, U.S. territory, and/or country of residence: New York, U.S.A.
7. Collaborated with individual in foreign country: No
8. Country(ies) of foreign collaborator: N/A
9. Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: N/A

1. Name: Esther Takeuchi
2. Total Number of Months: 0.2
3. Project Role: Co-PI
4. Researcher Identifier:
5. Contribution to Project: Dr. Takeuchi has led efforts on cell characterization and testing.
6. State, U.S. territory, and/or country of residence: New York, U.S.A.
7. Collaborated with individual in foreign country: No

8. Country(ies) of foreign collaborator: N/A
9. Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: N/A

1. Name: Kenneth Takeuchi
2. Total Number of Months: 0.25
3. Project Role: Co-PI
4. Researcher Identifier:
5. Contribution to Project: Dr. Takeuchi has mentored graduate students contributing to the project.
7. Collaborated with individual in foreign country: No
8. Country(ies) of foreign collaborator: N/A
9. Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: N/A

1. Name: Edelmy Marin Bernardez
2. Total Number of Months: 0.5
3. Project Role: Graduate student
4. Researcher Identifier:
5. Contribution to Project: Ms. Bernardez has worked on electrolyte development and characterization
7. Collaborated with individual in foreign country: No
8. Country(ies) of foreign collaborator: N/A
9. Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: N/A

1. Name: Alexis Pace
2. Total Number of Months: .15
3. Project Role: Graduate Student
4. Researcher Identifier:
5. Contribution to Project: Ms. Pace has performed work on electrolyte development and characterization.
7. Collaborated with individual in foreign country: No
8. Country(ies) of foreign collaborator: N/A
9. Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: N/A

Personnel Table:

Name (Last, First)	Hours worked During Reporting Period (>160 Hours)	State, U.S. Territory, or Country of Residence	Role	Contribution to Project (Note also collaboration with foreign country, travel to foreign country, country, and duration of travel)
Marschilok, Amy	160	New York	PI	Contribution: overall project planning and task reallocation. No collaboration with or travel to foreign countries.
Takeuchi, Esther	160	New York	Co-PI	Contribution: led efforts on cell characterization and testing. No collaboration with or travel to foreign countries.
Takeuchi, Kenneth	160	New York	Co-PI	Contribution: mentored graduate students contributing to the project. No collaboration with or travel to foreign countries.
Marin Bernardez, Edelmy		New York	Graduate Student	Contribution: performed work on electrolyte development and characterization

c. What other organizations have been involved as partners?

Organization Name	Location (If Foreign location list country)					Contribution to Project
	Street Address	City	State	Zip Code	Country	
Brookhaven National Laboratory	98 Rochester Street	Upton	NY	11786	USA	BNL engages in collaborative research with SBU researchers to complete the project tasks. SBU researchers utilize BNL facilities.

Have other collaborators or contacts been involved?

Nothing to report.

h. What percentage of the award's budget was spent in foreign country(ies)?

No part of the award budget was spent in foreign countries.

7. Special Reporting Requirements:

Not applicable.

8. Budgetary Information:

a. Cost Summary

Object Class Categories Per SF-424A	Approved Budget	Project Expenditures this Quarter	Cumulative to Date FINAL	% Spent to Date
a. Personnel	$259,095	$0	$280,015	108.07%
b. Fringe Benefits	$35,406	$0	$53,732	151.76%
c. Travel	$10,000	$1,980	$11,441	114.41%
d. Equipment	$133,389	$0	$125,413	94.02%
e. Supplies	$153,450	$696	$127,440	83.05%
f. Contractual	$0	$0	$0	0.00%
g. Construction	$0	$0	$0	0.00%
h. Other - Tuition and publishing	$36,180	$0	$28,919	79.93%
i. Total Direct Charges (sum of a. to h.)	$627,520	$2,676	$626,960	
j. Indirect Charges	$272,480	$1,592	$270,133	
k. Totals	$900,000	$4,268	$897,093	
(sum of i. and j.)				
DOE Share	$900,000	$4,268	$897,093	

b. Spend Plan:

Quarter	From	To	Updated Actuals & Estimated Federal Share of Outlays	Cumulative Federal Share
4Q20	Start	9/30/2020	$-	
1Q21	10/1/2020	12/31/2020	$6,013	$6,013
2Q21	1/1/2021	3/31/2021	$17,268	$17,268
3Q21	4/1/2021	6/30/2021	$34,605	$34,605
4Q21	7/1/2021	9/30/2021	$64,084	$64,084
1Q22	10/1/2021	12/31/2021	$150,175	$150,175
2Q22	1/1/2022	3/31/2022	$230,273	$230,273
3Q22	4/1/2022	6/30/2022	$342,055	$342,055
4Q22	7/1/2022	9/30/2022	$388,055	$388,055
1Q23	10/1/2022	12/31/2023	$470,751	$470,751
2Q23	1/1/2023	3/31/2023	$506,961	$506,961
3Q23	4/1/2023	6/30/2023	$553,700	$553,700
4Q23	7/1/2023	9/30/2023	$761,619	$761,619
1Q24	10/1/2023	12/31/2023	$806,004	$806,004
2Q24	1/1/2024	3/31/2024	$816,921	$816,921
3Q24	4/1/2024	6/30/2024	$897,093	$897,093
Totals			$897,093	$897,093