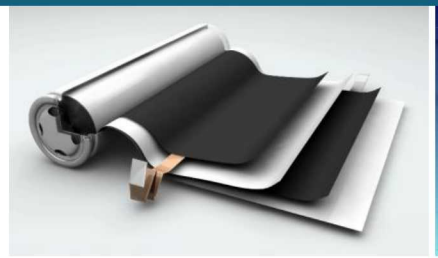
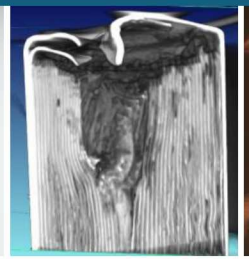
SAND2019-5906C

Sandia National Laboratories

Microcalorimetry of Silicon Anode Materials for Lithium-ion Batteries





PRESENTED BY

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235th ECS Meeting – May 26-30, 2019 – Dallas, TX

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Introduction – Silicon Anodes

Silicon is an alternative anode to the traditionally employed graphite, offering dramatically increased capacity.

However, silicon undergoes dramatic volume change during cycling and exhibits poor surface passivation. Both of these contribute to poor cycle life for silicon anodes.

Mitigation approaches to realize practical application of silicon anodes included

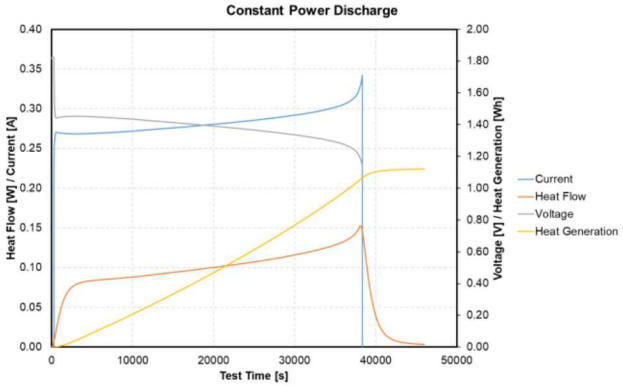
- Composites
- Nano
- Surface functionalization / artificial SEI
- Binders

Introduction - Microcalorimetry

TA Instruments TAM IV with three microcalorimeter options

20 mL calorimeter
- +/- 300 nW precision
- Isothermal testing

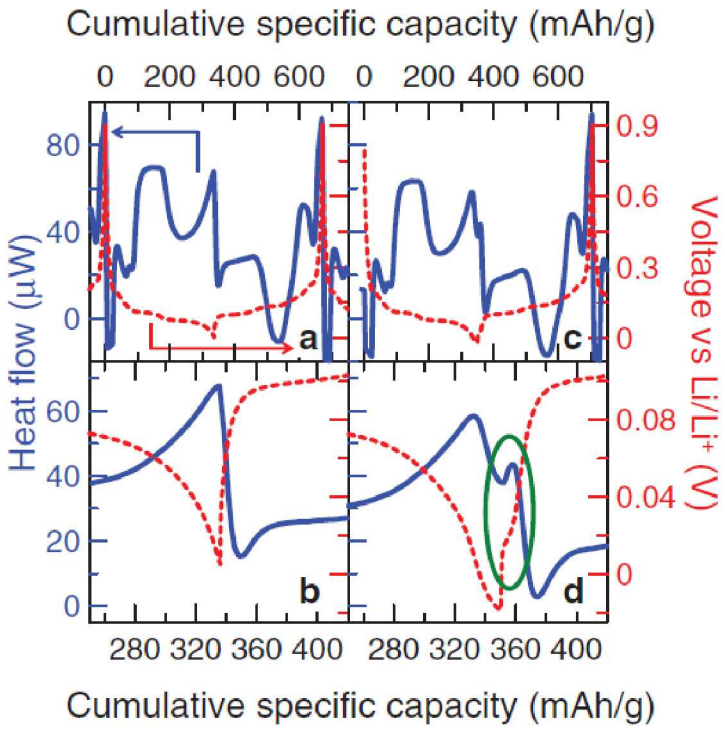
125 mL calorimeter
- +/- 3 µW precision
- Isothermal testing
- Battery cycling



4 mL calorimeter
- +/- 200 nW precision
- Isothermal testing
- Gas/liquid perfusion

This work focuses upon the use of the 20mL microcalorimeter to measure isothermal calorific output of silicon slurry pre-mixes soon after combination

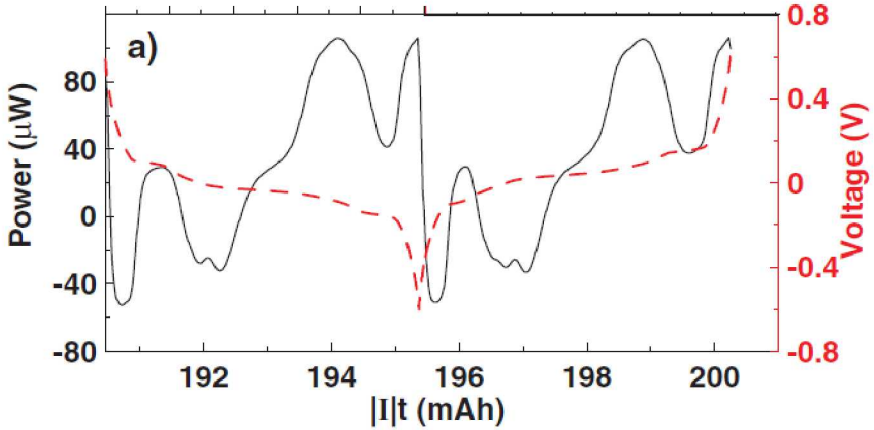
Microcalorimetry of Battery Electrodes



Heat flow from coin cells correlated to different lithiation mechanisms

- Green circle shows signature for lithium plating/stripping

** L.E. Downie, L.F. Krause, J.C. Burns, L.D. Jensen, V.L. Chevrier, J.R. Dahn. J. Electrochem. Soc. **160** (2013) A588-A594.



$$Q_p = \left[\int_0^{t_d} \frac{dQ_d}{dt}dt + \int_0^{t_c} \frac{dQ_c}{dt}dt\right] - \left[\int_0^{t_c} I_c V_c dt - \int_0^{t_d} I_d V_d dt\right] \quad (2)$$

Method to separate various sources of heat generation when cycling cells to isolate the parasitic heat signal

- Correlated to coulombic efficiency of cells

** L.J. Krause, L.D. Jensen, J.R. Dahn. J. Electrochem. Soc. **159** (2012) A937-A943.

Reactivity in Processing

Traditional PVDF binders are not conducive to good performance of Si electrodes and from and environmental and safety perspective there is a desire to move away from NMP as a solvent. Instead, aqueous binder systems such as CMC or LiPAA are employed for silicon anodes.

Through this modification of processing observations of slurry gassing have been observed and reported on during scale-up efforts.

K.A. Hays, B. Key, J. Li, D. Wood, and G.M. Veith. *J Phys Chem C* **122** (2018) pp 9746-9754.

Testing Method

LiPAA binder mixture

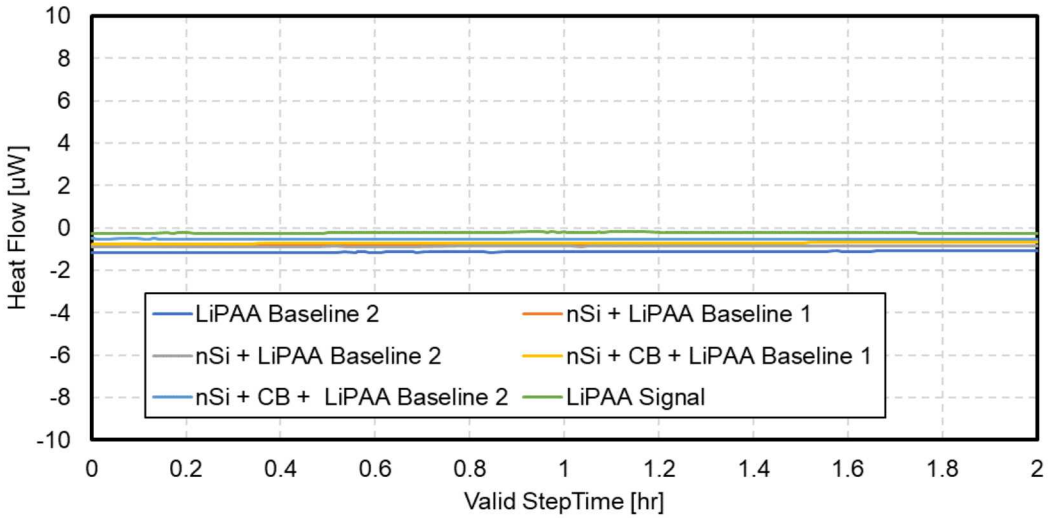
- Slurry with no heat generation

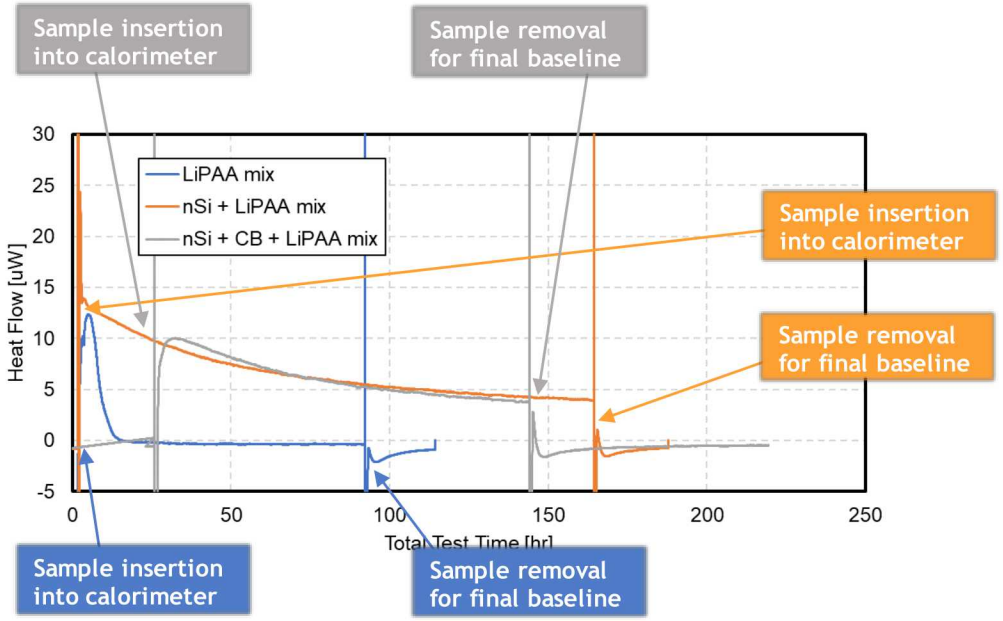
LiPAA binder with nSi

- Heat generation from nSi
- Vary nSi and correlate with surface chemistry/BET area

LiPAA binder with nSi and CB

- Impact of CB inclusion on nSi reactivity

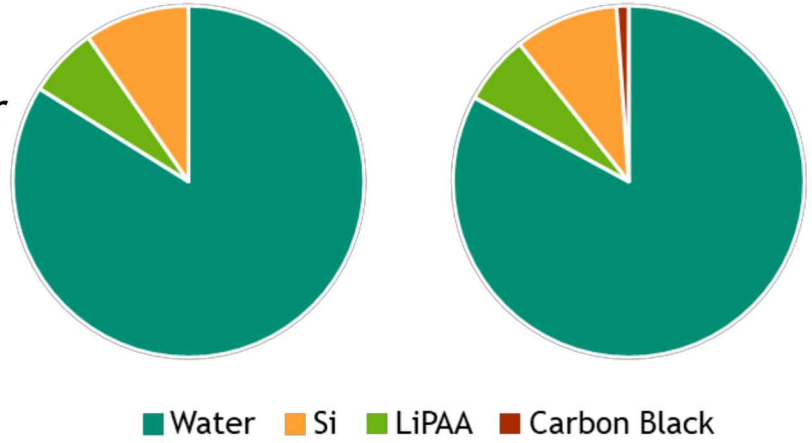




Materials Investigated

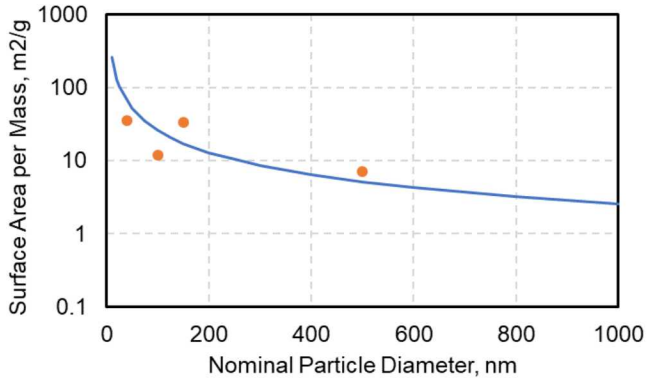
Premix slurries of 10wt% solution LiPAA (pH ~6.5) in DI water combined with nanosilicon and (sometimes) carbon black

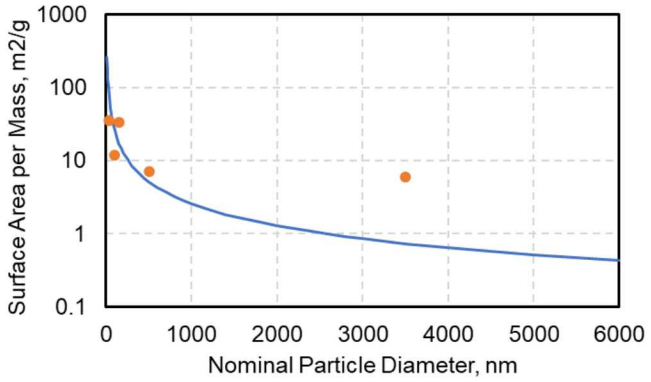
83.8% Water
9.7% Si
6.5% Binder



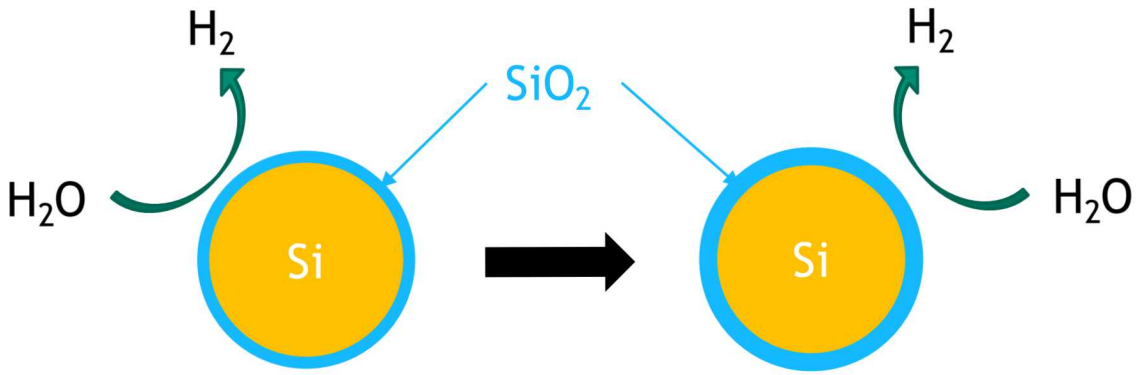
82.9% Water
9.6% Si
6.4% Binder
1.1% CB

Silicon	Nominal Particle Size, nm	BET Surface Area, m^2/g
S1	1000-5000	5.91
S2	500	7.19
S3	150	33.64
S4	70-130	11.99
S5	30-50	34.97

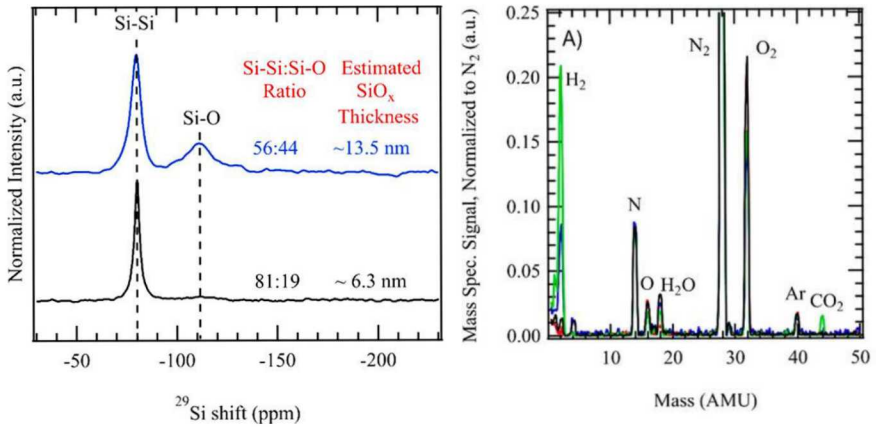




Assumed Reactions From Processing



Silicon interior with growing SiO_2 shell



K.A. Hays, B. Key, J. Li, D. Wood, and G.M. Veith. *J Phys Chem C* **122** (2018) pp 9746-9754.

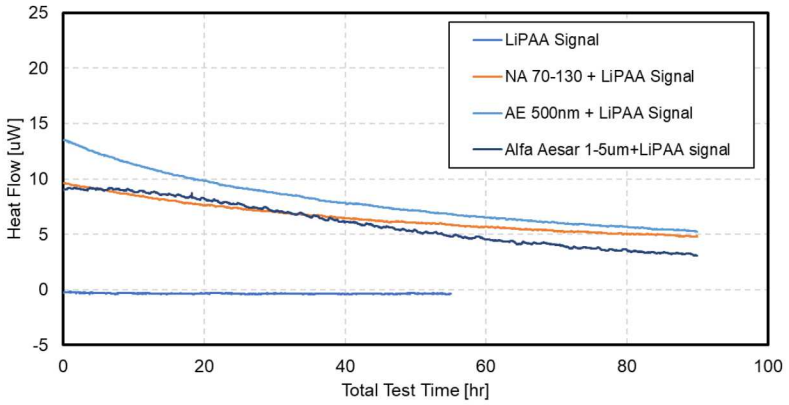
Reaction: $Si + 2\ H_2O = SiO_2 + 2\ H_2$

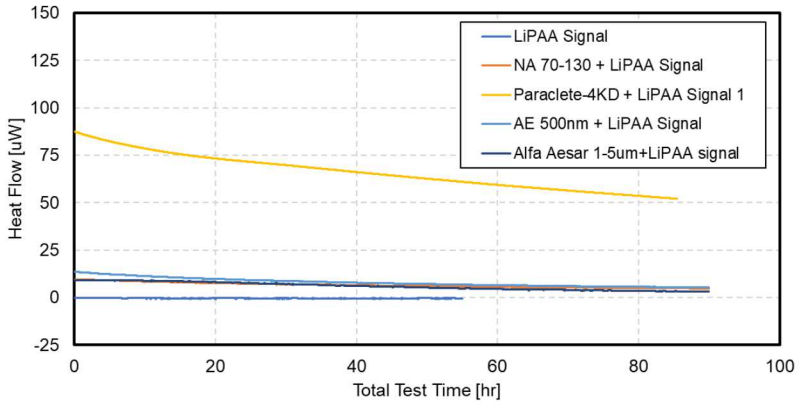
$\Delta H_{SiO2} = -287.8$ kJ/mol

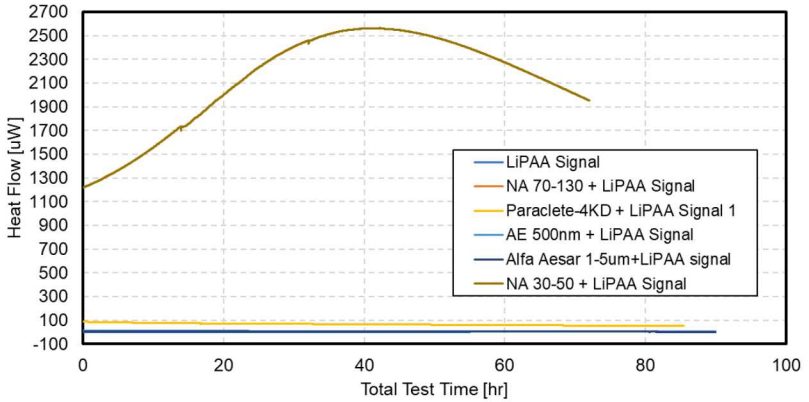
Assume full conversion to SiO_2, no SiO_x phases

Literature support for increased oxidation of Si and evolution of hydrogen gas after aqueous mixing.

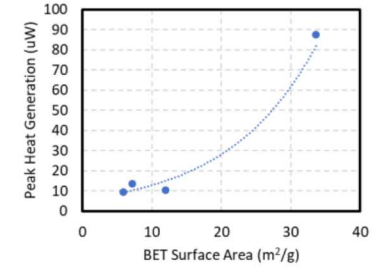
Measured Heat Generation of Silicon Pre-mix Slurries

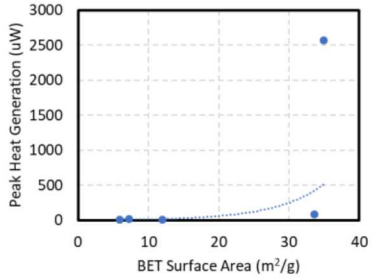




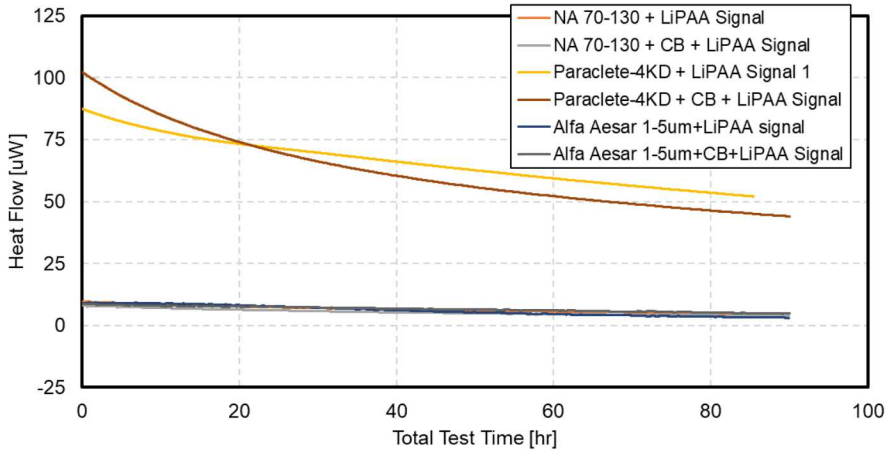


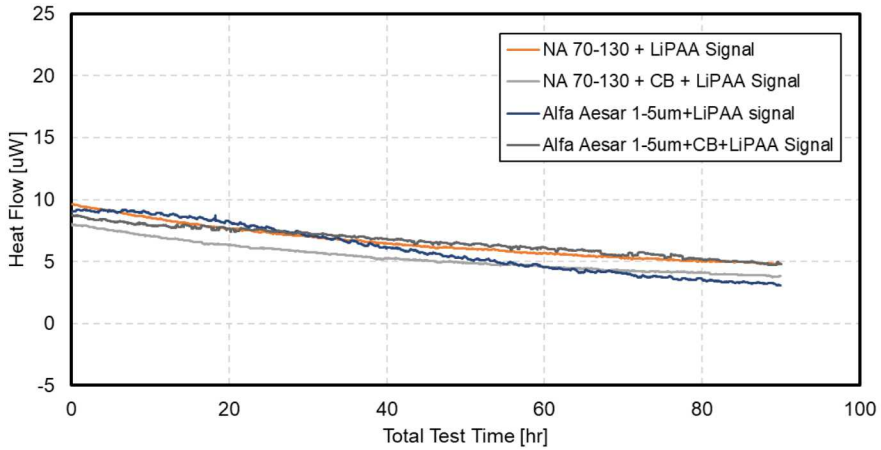
Sample	Peak Signal (μW)	Avg. Signal (μW)	Peak Signal (μW/g)	Peak Signal ($\mu W/m^2_{silicon}$)
LiPAA	0.83	0.65	0.40	N/A
S1 + LiPAA (1-5um)	9.43	6.21	4.56	7.96
S2 + LiPAA (500nm)	13.67	8.19	6.73	9.68
S3 + LiPAA (150nm)	87.60	66.42	41.52	12.75
S4 + LiPAA (70-130nm)	10.46	7.29	5.23	3.93
S5 + LiPAA (30-50nm)	2565.12	2113.67	1245.20	367.94





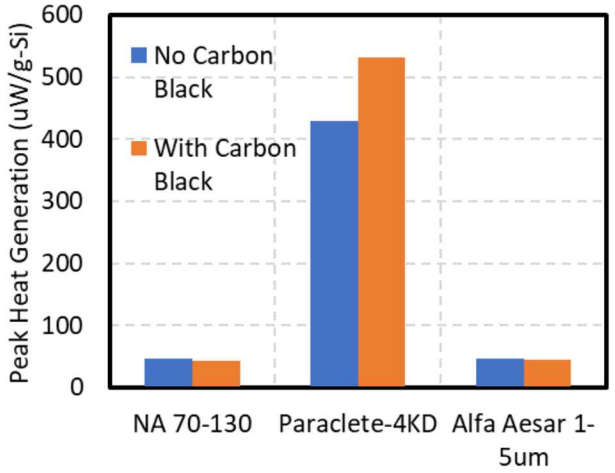
Impact of Carbon Black on Reaction Severity

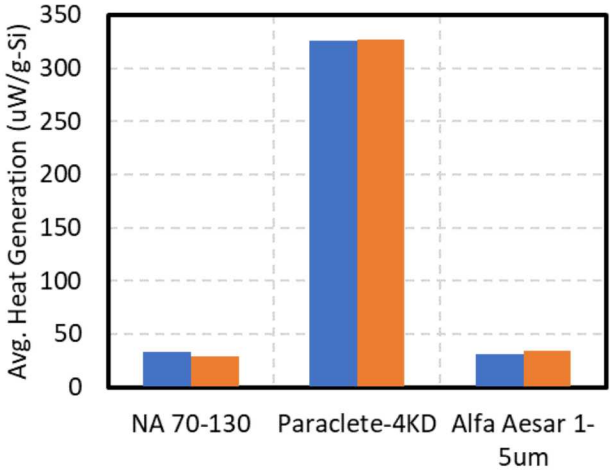




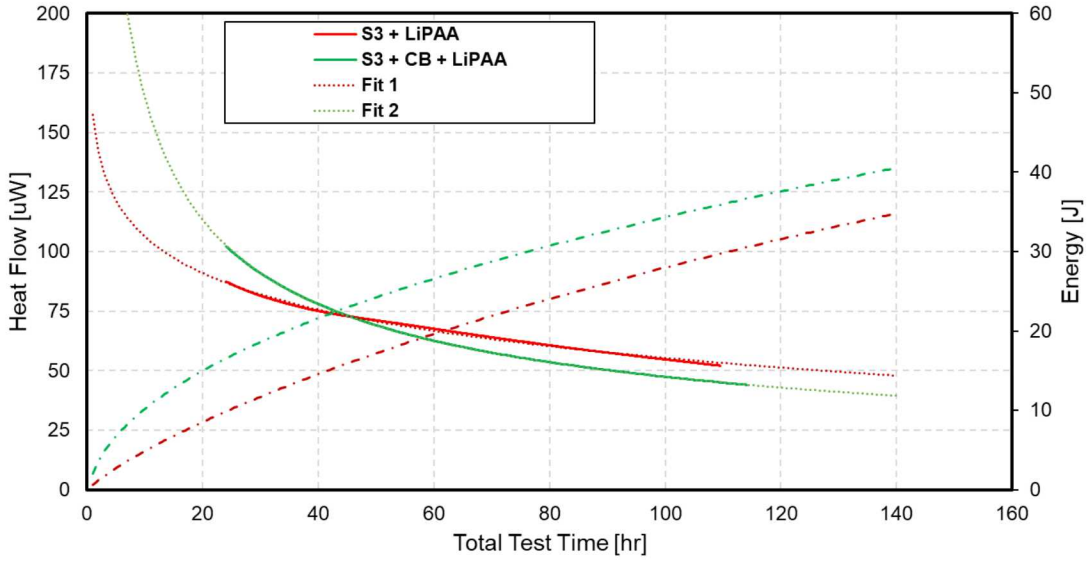
Hays et. al. reported dramatic increase in reactivity during processing with the addition of carbon black, thought to facilitate electron transfer between water and the silicon particle cores

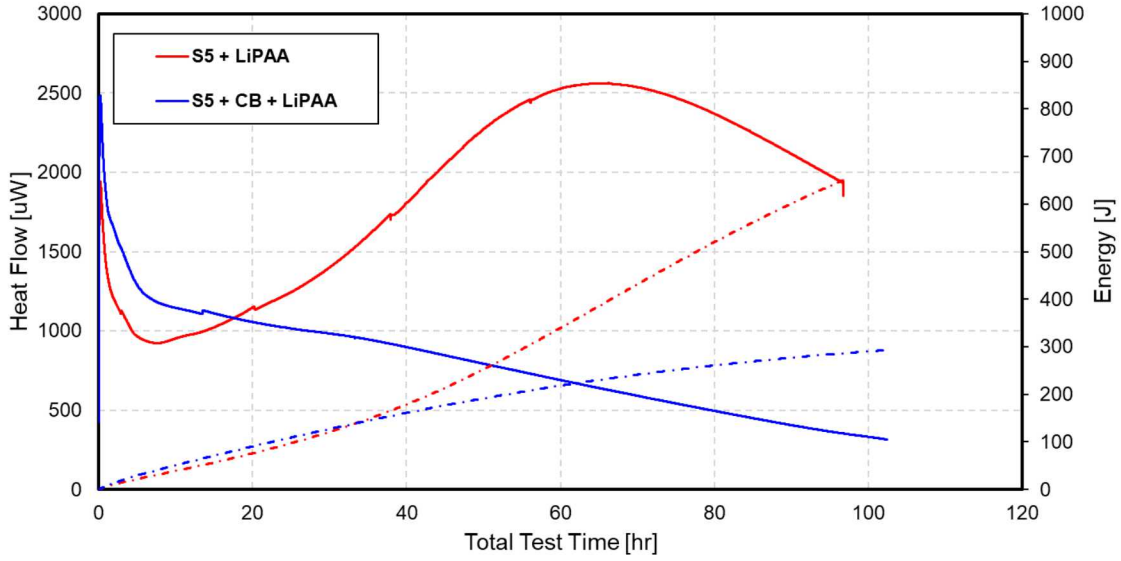
- Our observations show minimal impact from carbon black addition
- Literature slurries had higher carbon black contents and milling of slurries to break up agglomerates





Total Energy Loss from Processing Degradation





Use of fit curve to estimate heat generation over first 24 hours for S3 (150nm) material, add in measured generation over remaining test duration

For S5 (30-50nm) sample the signal strength dramatically outweighed any residual heat from sample introduction to the chamber so the actual signal was used to measure heat generation for the duration of testing

Quantification of Silicon Degradation

S3 (150nm) + CB + LiPAA

Duration	Total Energy (J)	SiO_2 formed (mol)	Si Loss	Specific Capacity
0 hr	0	0	0%	**100%**
24 hr	16.52	5.7409e-5	0.79%	**98.31%**
48 hr	23.37	8.2461e-5	1.13%	**97.58%**
96 hr	33.66	.000117	1.61%	**96.57%**

S5 (30-50nm) + CB + LiPAA

Duration	Total Energy (J)	SiO_2 formed (mol)	Si Loss	Specific Capacity
0 hr	0	0	0%	**100%**
24 hr	105.55	.000366	5.04%	**90.30%**
48 hr	185.96	.000646	8.88%	**84.07%**
96 hr	285.26	.000991	13.63%	**77.39%**

Sample sizes of approximately 2g slurry

- **At approximately 10% nSi loading translates to ~0.2g silicon per sample**

For S3 (150nm) material the predicted performance impact is quite small, remaining below 4% predicted loss even after 4 days aging

For the more reactive S5 (30-50nm) material the impact is more significant, approaching 25% losses at 4 days aging.

Worth noting is that the rate of reaction for actively mixing vs static aging would likely be appreciably higher.

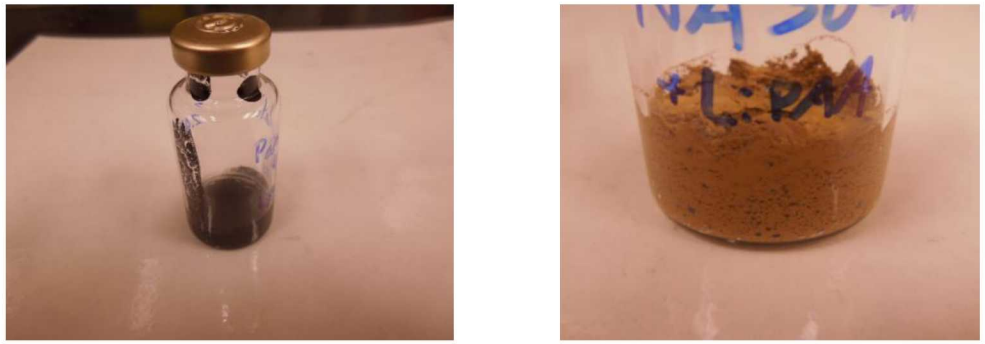
Quantification of Gas Generation During Degradation

S3 (150nm) + CB + LiPAA

Duration	H_2 formed (mol)	H_2 formed (mL - RTP)	H_2 formed (mL/g-Si)
0 hr	0	0	0
24 hr	.000115	2.76	13.62
48 hr	.000165	3.96	19.54
96 hr	.000234	5.62	27.74

S5 (30-50nm) + CB + LiPAA

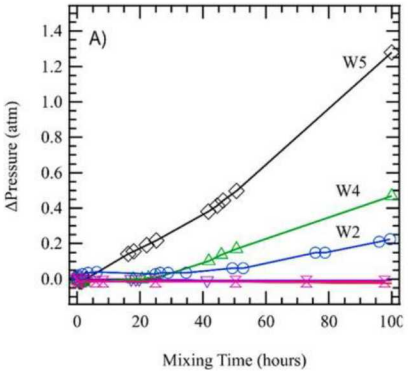
Duration	H_2 formed (mol)	H_2 formed (mL - RTP)	H_2 formed (mL/g-Si)
0 hr	0	0	0
24 hr	.000733	17.59	86.82
48 hr	.001292	31.01	153.06
96 hr	.001982	47.57	234.80



Post analysis images of S3 + CB + LiPAA (left) and S5 + CB + LiPAA (right) with greater observation of gassing for S5 sample

For similar material in literature:

- N2/N1 = P2/P1 = 1.44
- 0.5L = 20.83 m-mol at RTP = 9.17 m-mol H_2 formed at 100hr
- Roughly 220 mL of gas generated
- H_2 generation of roughly 22 mL/g-Si, in agreement with our values



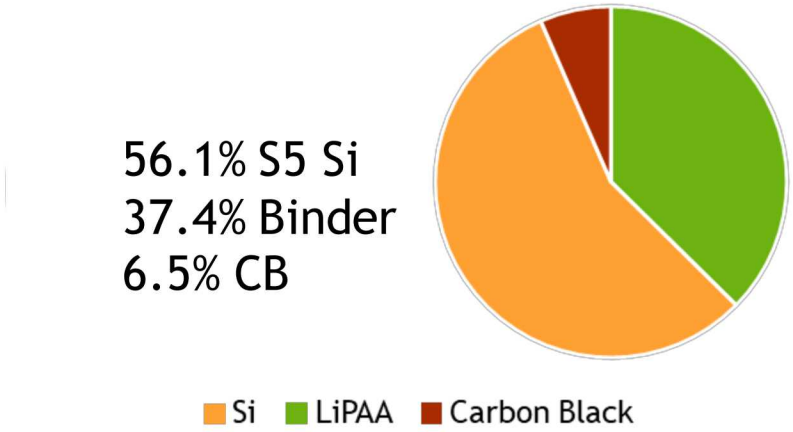
K.A. Hays, B. Key, J. Li, D. Wood, and G.M. Veith. *J Phys Chem C* **122** (2018) pp 9746-9754.

Aging of Electrodes for Electrochemistry

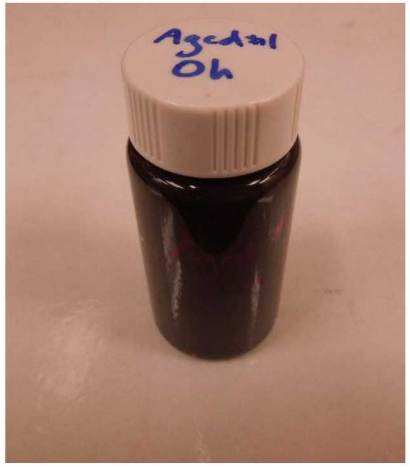
The same silicon slurry pre-mix as analyzed via microcalorimetry was prepared and coated at 0hr, 24hr, and 96hr after initial mixing.

S5 silicon was selected as it had the greatest measured reaction within the slurry and should therefore have the most easily quantified impact on electrochemical performance.

Electrodes were coated on copper foil and assembled into half-cells vs lithium foil.

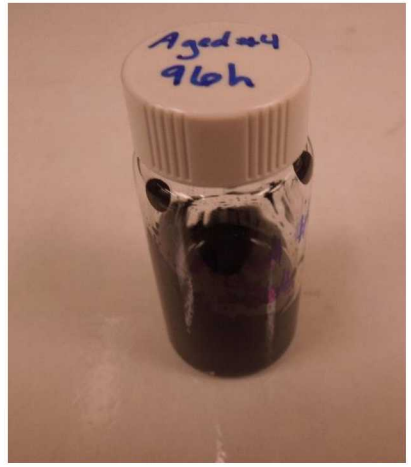


0hr Aged

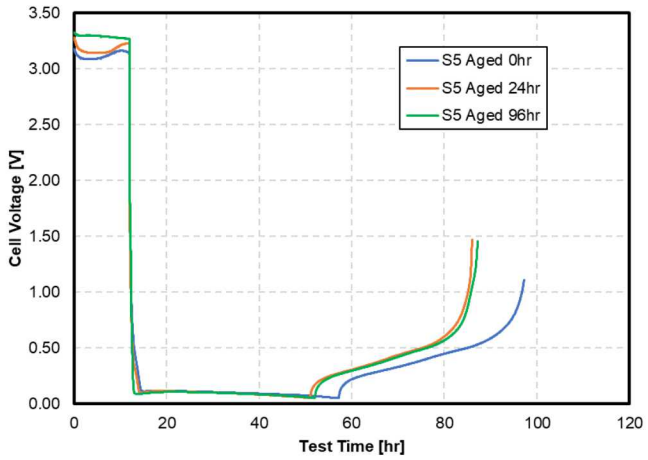


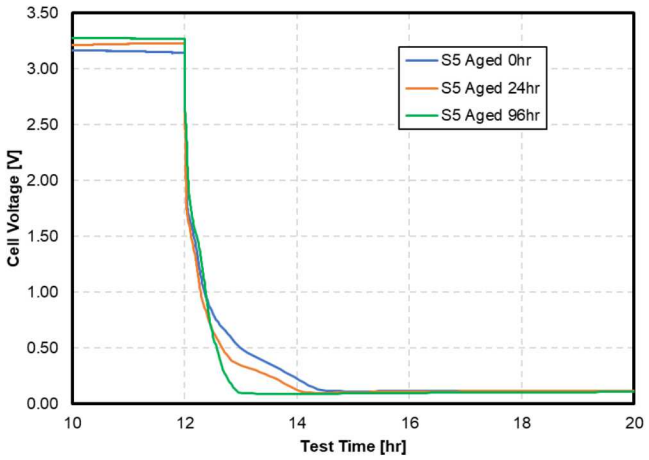
24hr Aged

96hr Aged



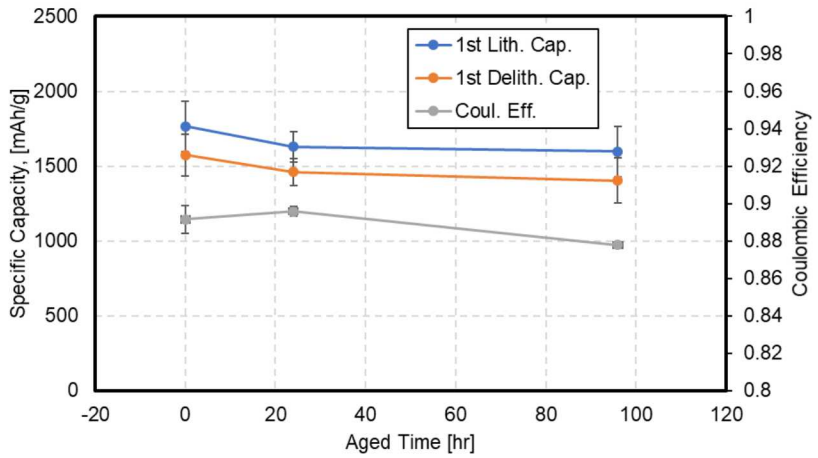
Measured Performance Impact



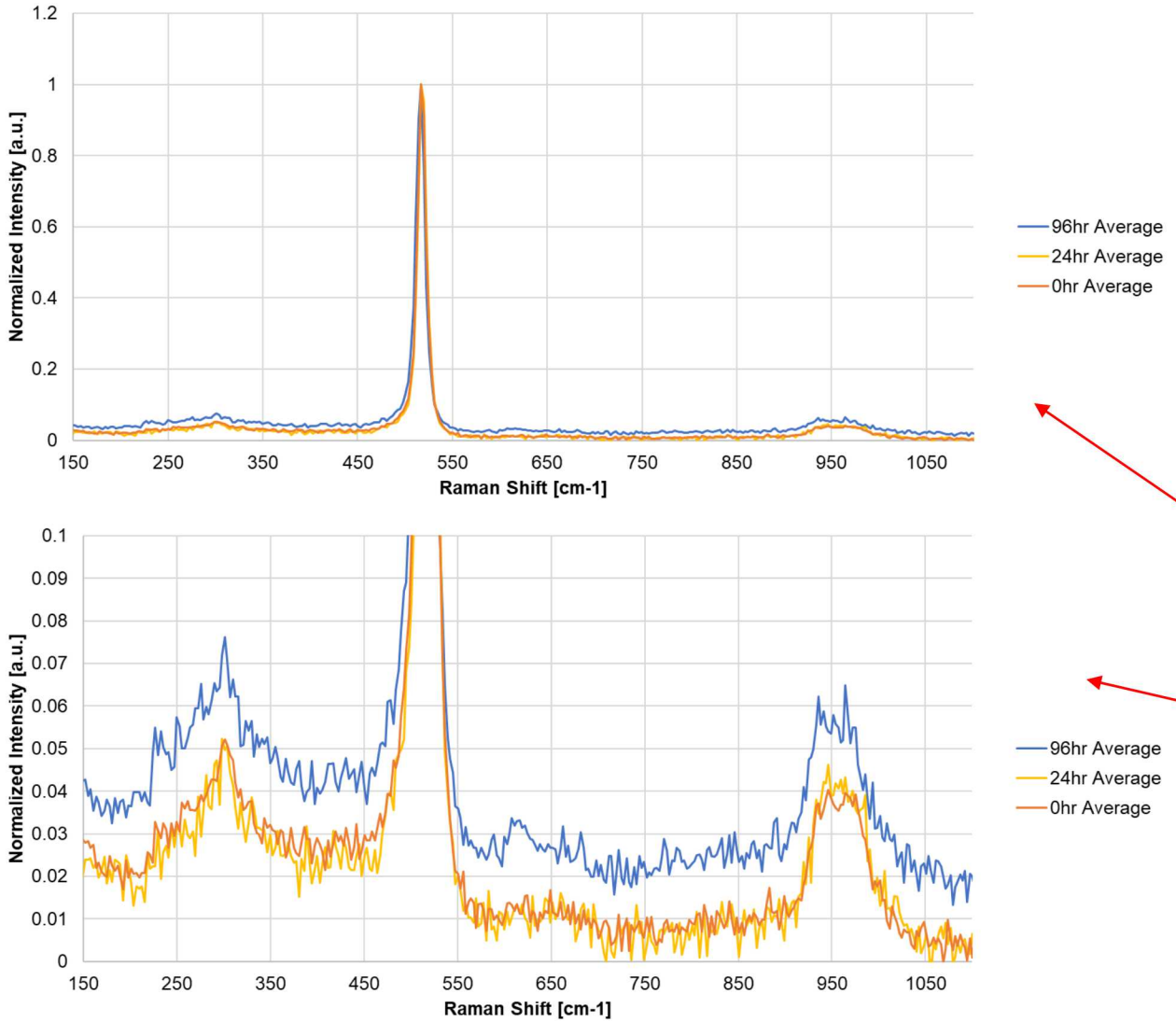


Overall behavior is similar between electrodes aged 0hr up to 96hrs. Our calculations predict a capacity loss of 10% after 24 hours and 22.6% after 96 hours. While the general trend is observed we only see losses of 7.2% and 10.9%.

Initial lithiation curves also suggest more resistance at active surfaces due to deeper initial voltage. Also suggests that formed SiO_2 is not electroactive due to shrinking capacity at higher voltages and minimal change to coulombic efficiency

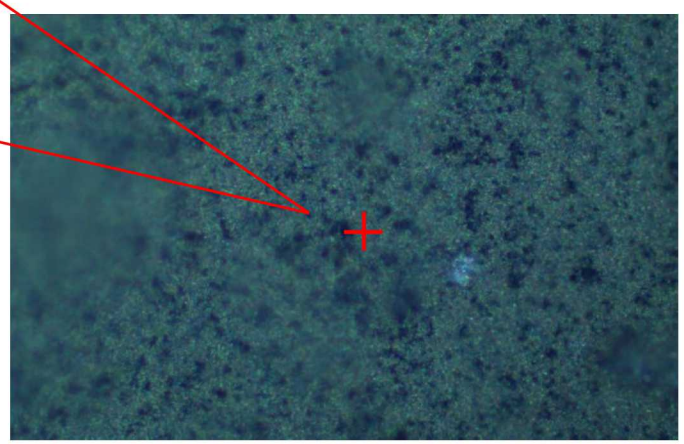


Supporting Characterization – Raman Spectroscopy



Raman analysis shows anticipated peak at 520 cm^{-1} corresponding to crystalline silicon. No peaks for amorphous silicon are present.

SiO_2 associated peaks can be observed from 250 – 450 cm^{-1} and 925 – 975 cm^{-1}, but the signal is too weak to quantify growth of SiO_2 with aging



Summary and Conclusions

Measurable and appreciable reactions occur when preparing silicon-containing anodes in aqueous binder systems, assumed (with literature support) to be the oxidation of Si to SiO_2, with concurrent evolution of H_2. The severity of reaction tends to increase with larger surface area / smaller particle size silicon materials. The incorporation of conductive carbon into the slurry samples is not observed to significantly impact the reaction.

Total energy generation from reaction predicts up to 22.6% capacity loss for more reactive materials after 96hrs of aging. Electrochemical data partially supports this prediction, though additional testing and secondary analysis is needed to fully confirm.

Future Work

Additional characterization of silicon samples to both confirm SiO_2 formation / rates of reaction and identify surface differences that may explain different severity of reactions between materials.

Incorporate electrolyte introduction and perfusion analysis to capture reactions between pristine and/or lithiated silicon electrodes and electrolytes.

In-situ electrochemical analysis to capture different reaction / degradation processes during silicon electrode cycling.

Acknowledgements

Colleagues at Sandia: Harry Pratt, Josey McBrayer, Brian Perdue

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