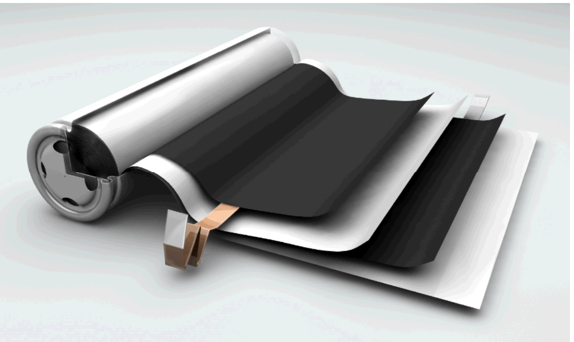
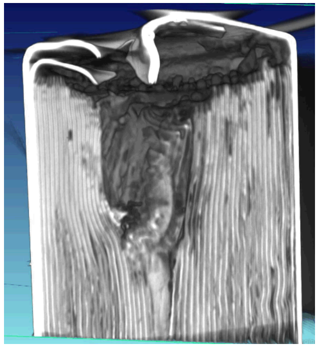
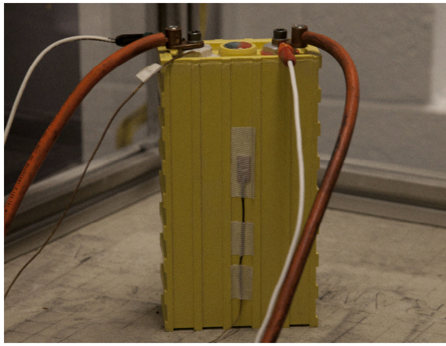
SAND2016-9799C

Exceptional service in the national interest

Sandia National Laboratories







Materials Safety Study of Practical Nano-Silicon + Graphite Anodes for Lithium-Ion Batteries

Eric Allcorn, Ganesan Nagasubramanian, Kyle Fenton

Sandia National Laboratories

ECS PRiME October 2-7, 2016

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

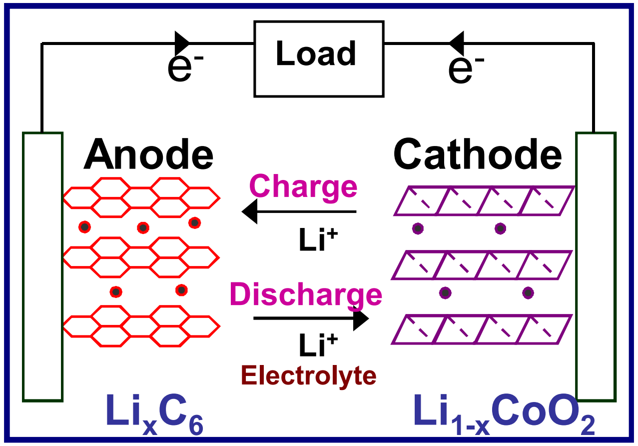
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

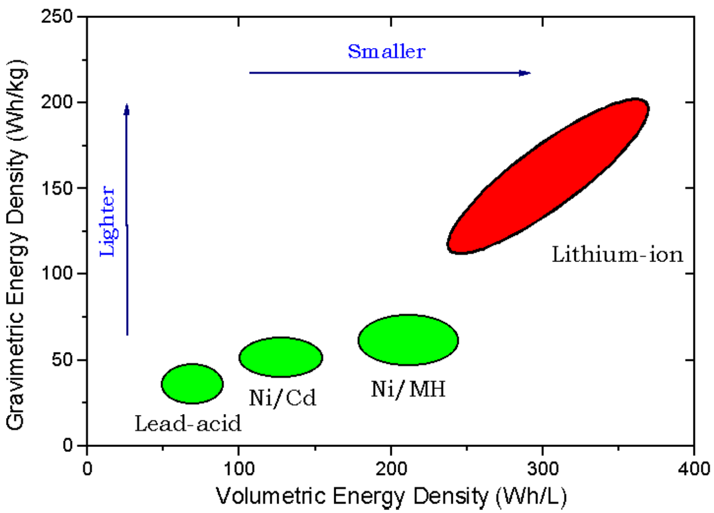
Introduction

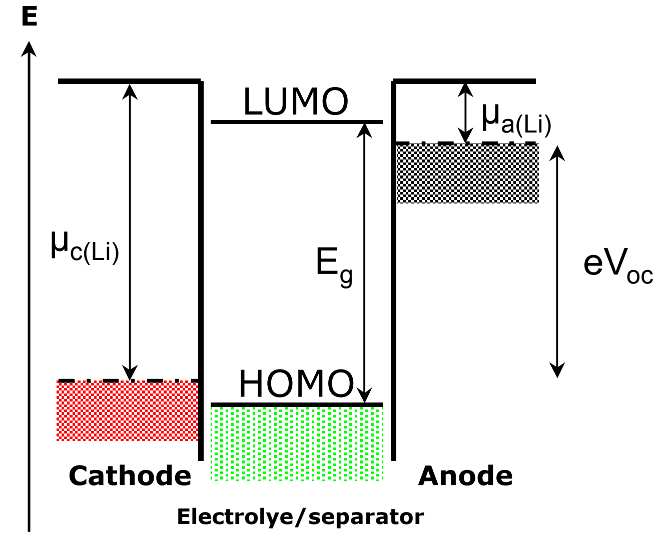
- Multi-lab Deep Dive on Silicon Anodes – Sandia investigates abuse performance
- Background & Motivation
  - Safety issues of Li-ion batteries
  - Silicon containing anodes
- Thermal studies of nSi + graphite anodes
  - DSC and ARC analysis of anode materials
  - Effects of silicon content, electrolyte additives, particle size, etc.

Background on Lithium-ion Batteries

- Energy storage needs are constantly driving for greater gravimetric and volumetric energy density
- High voltage of Li-ion system enables high energy density – necessitates the use of flammable organic electrolytes





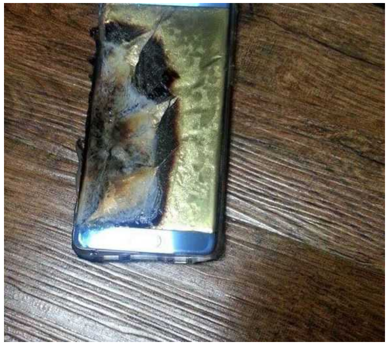


A. Manthiram, *J. Phys. Chem. Lett.* **2**, 176-184 (2011).

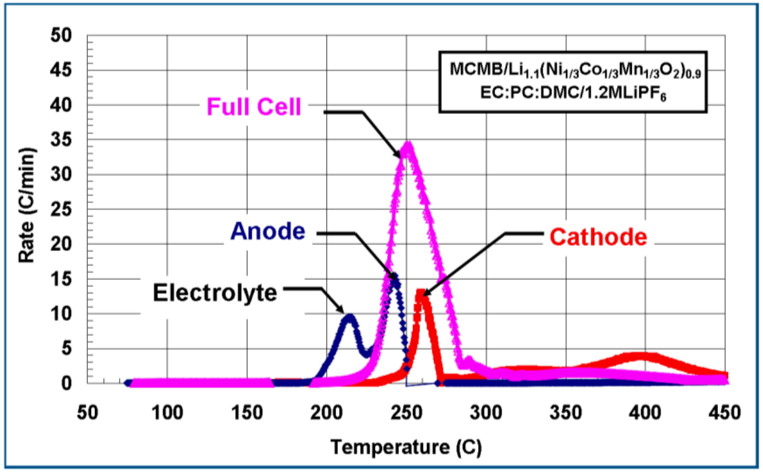
Issues of Battery Safety

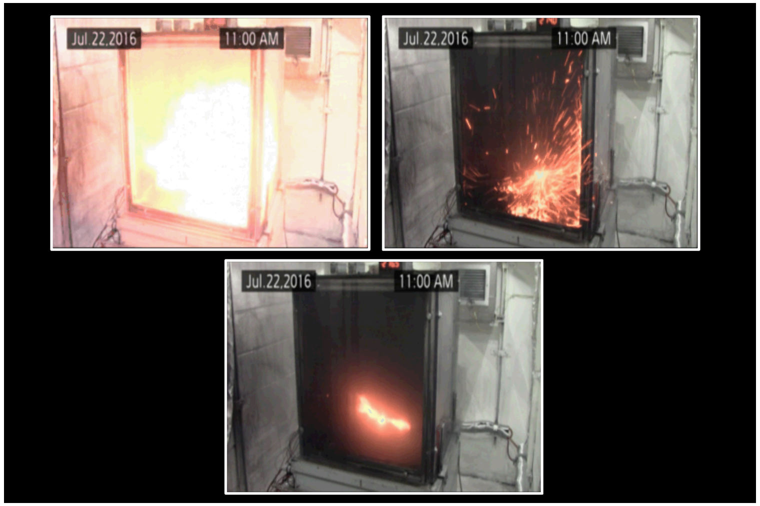
- Thermal runaway primarily caused by cathode and electrolyte reactions at high temperatures
- Anode degradation begins at lower temperatures and can lead to self sustaining temperature rise eventually causing thermal runaway

Samsung Galaxy S7 Recall



www.techproducts.com.ng





D. Doughty, E.P. Roth, *ECS Interface*, 37-44 (2012).

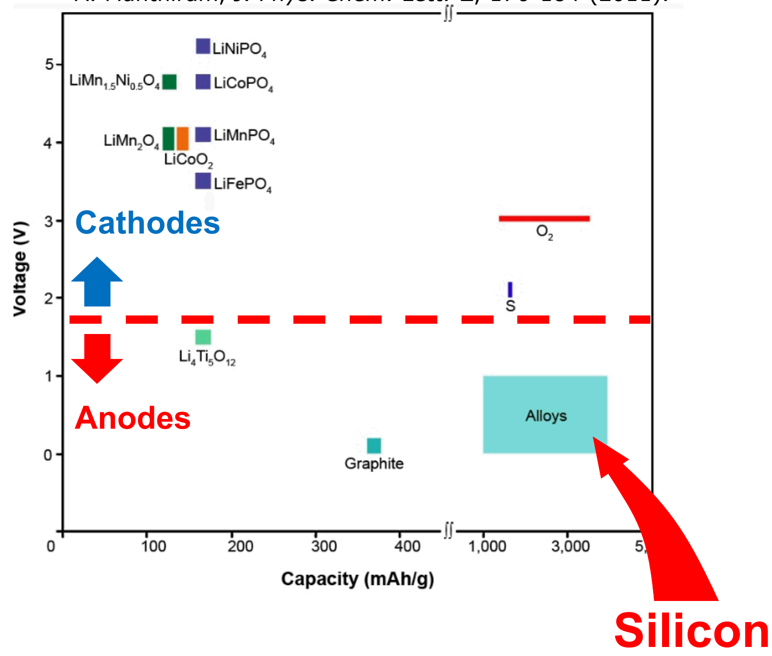
Silicon as Anode Background

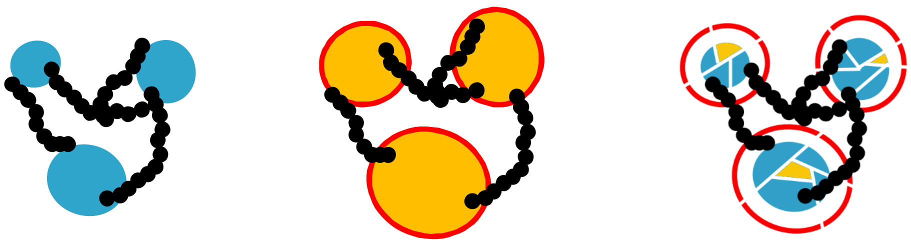
- Meets the need for greater energy density with order of magnitude capacity increase over graphite (~3500 mAh/g vs 372 mAh/g)
  - Alloying reaction with lithium

$$Si + xLi \rightarrow Li_xSi + (3.75 - x)Li \rightarrow Li_{3.75}Si$$

  - Cycle life issues
    - Volume change during lithiation/delithiation of >300%
    - Lack of surface passivation, exacerbated by changing particle size

A. Manthiram, *J. Phys. Chem. Lett.* **2**, 176-184 (2011).





Safety of silicon anodes and contribution to cell runaway are not well known but must be considered in any effort to develop new electrodes

* Y. Wang, J. Dahn. *ECS Solid State Lett.* **9**, A340-A343 (2006).
* Y.S. Park, S.M. Lee. *Bull. Korean Chem. Soc.* **32**, 145-148 (2011).

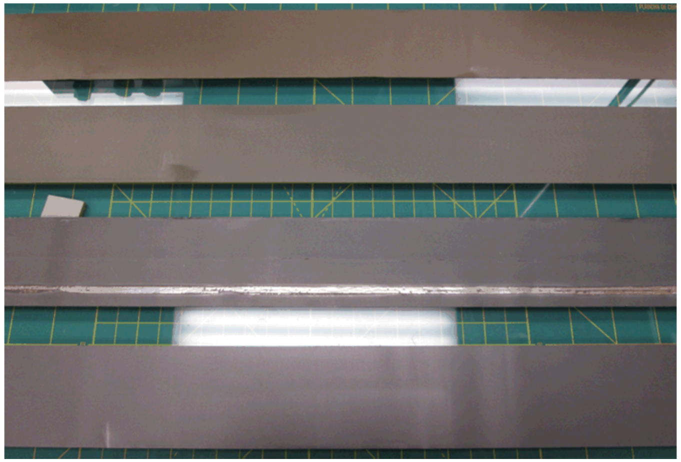
Silicon Material Studied

Mixture of nSi (Nanostructured & Amorphous Materials, Inc) + graphite (Hitachi MAG-E), LiPAA binder (MW= ~400,000), carbon black (Timcal C45)

- 88% active (nSi + graphite): 10% LiPAA: 2% CB

Varied Electrode Properties

- **0%, 5%, 10%, 15%** nSi content
- nSi nominal particle sizes of **30-50nm, 50-70nm, 70-130nm**
- Baseline electrolyte of **3:7 EC:EMC w/ 1.2M $LiPF_6$, baseline electrolyte + 10% FEC**



15% nSi

10% nSi

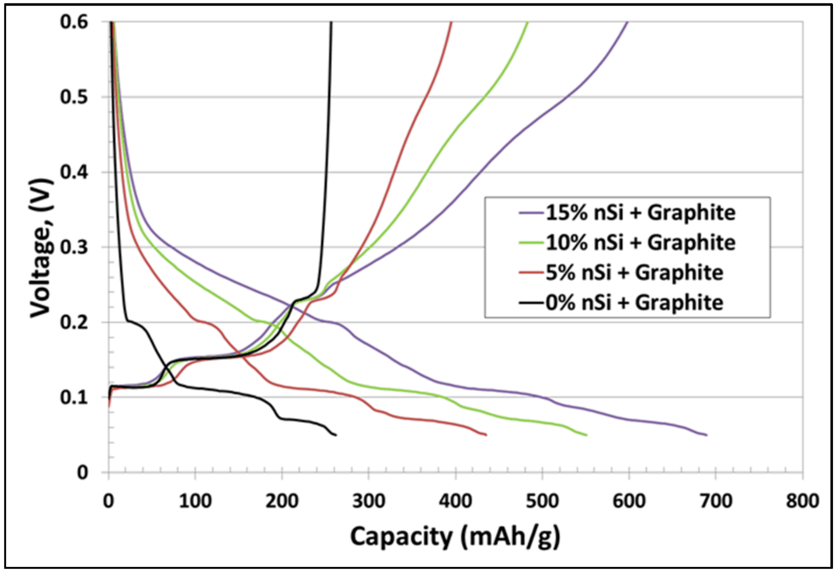
5% nSi

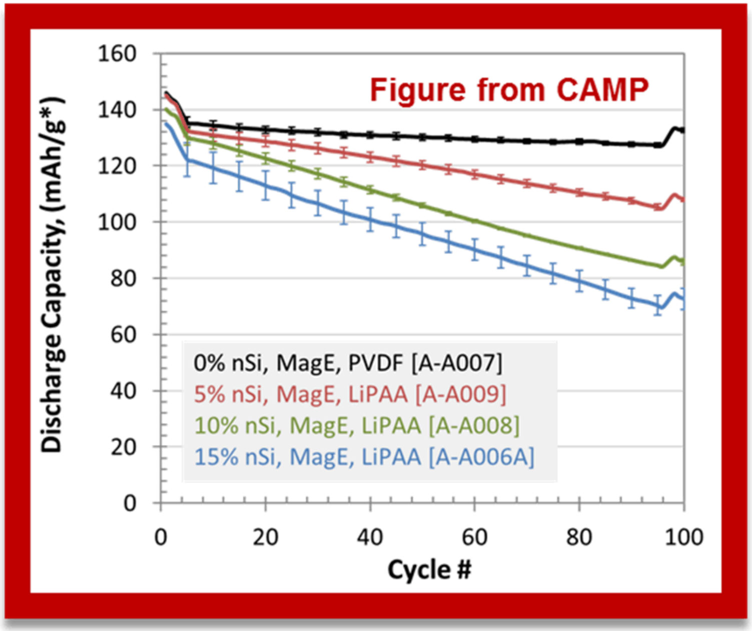
0% nSi

Electrochemical Performance of nSi/G Materials

- Performance trends with increasing nSi content
  - Increasing capacity with increasing content
  - Decreasing cycle life with increasing content

Electrode	Reversible Capacity (mAh/g)
0% nSi	330
5% nSi	430
10% nSi	550
15% nSi	660



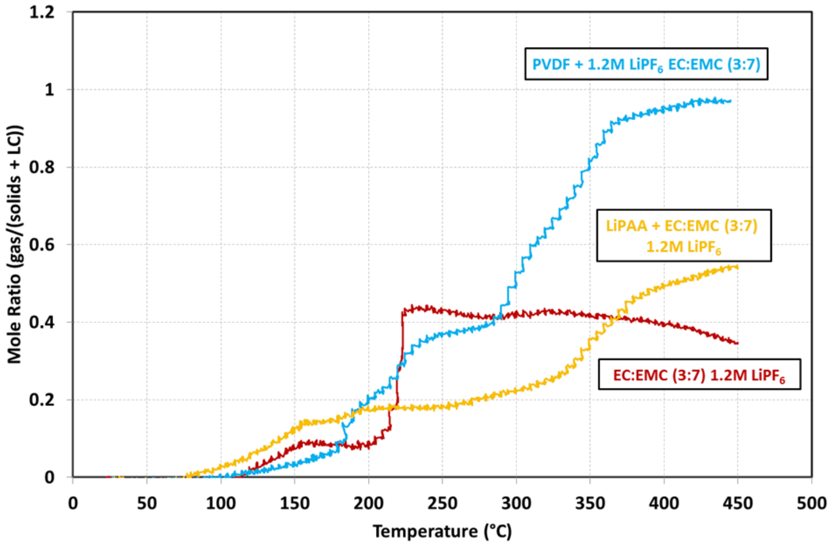


* Data from ANL CAMP Facility

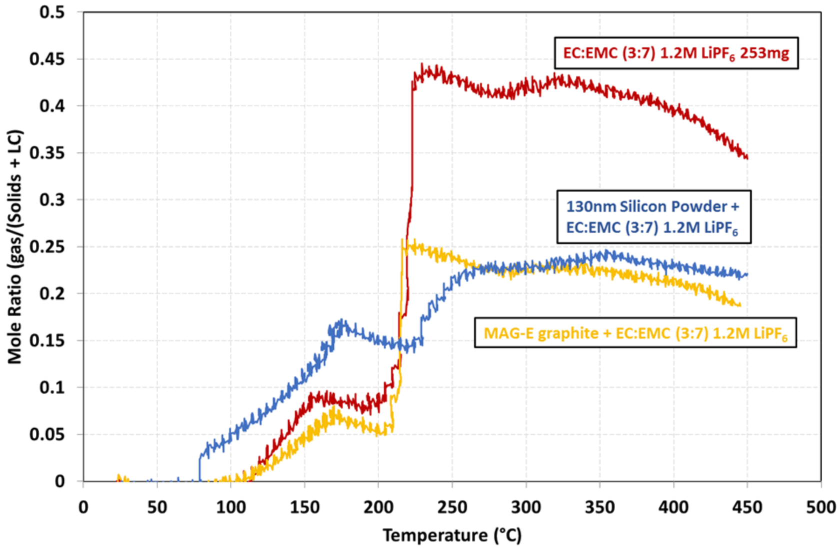
ARC Study of Binders and Active Materials

- Gas generation of individual electrode components combined with electrolyte
  - Effect of shift to LiPAA from baseline PVDF
  - Effect of inclusion of nSi in place of graphite

250 mg solids + 250 mg electrolyte



Additional gas generation from both PVDF and LiPAA



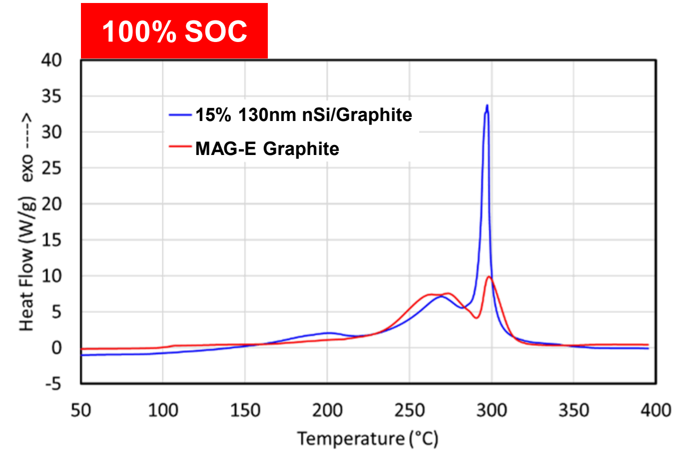
Almost no contribution from graphite or silicon

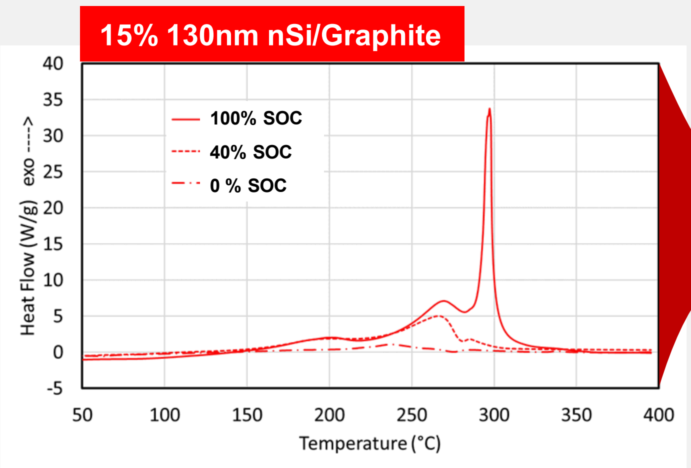
DSC of nSi Electrodes

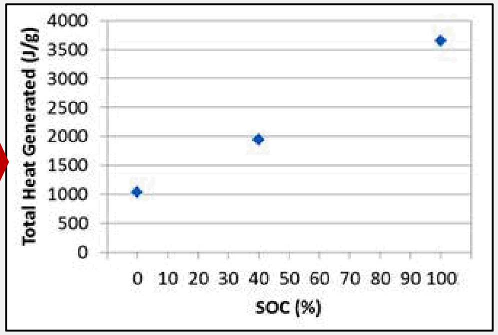
Cells undergo 4 formation cycles from 3.0-4.1V at C/10 followed by topoff or discharge to desired SOC, testing performed with 1:1 mass ratio of active material to electrolyte

- Similar peak locations, higher heat generation and significant exotherm present in silicon containing anodes at 100% SOC – **3800** J/g vs. **2300** J/g
- Large exotherm is only present at full SOC – reaction of $Li_{15}Si_4$?

* Y.S. Park, S.M. Lee. *Bull. Korean Chem. Soc.* **32**, 145-148 (2011).



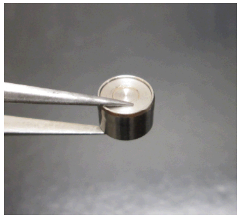




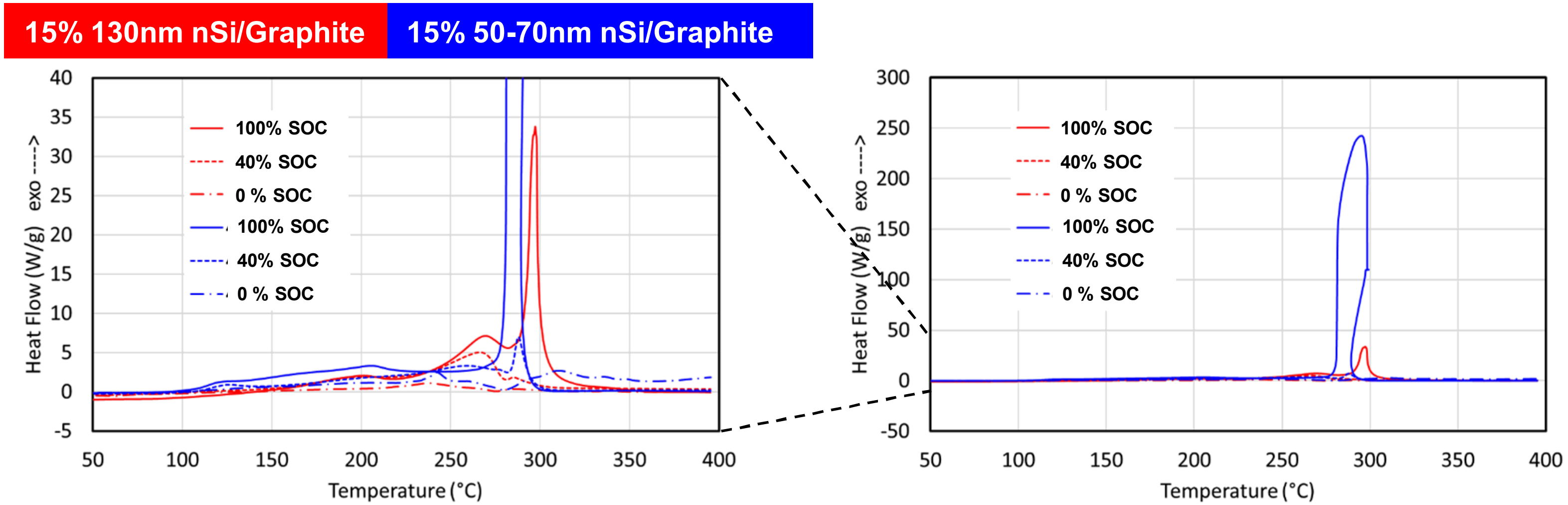
M. Klett, J.A. Gilbert, S.E. Trask, B.J. Polzin, A.N. Jansen, D.W. Dees, D.P. Abraham. *J. Electrochem. Soc.* **163,** A875-A887 (2016).

Extreme Exothermic Reactions Observed

- Testing of CAMP produced electrodes with higher loading and smaller particle sizes resulted in dramatic exothermic peaks, very high kinetics in 100% SOC electrodes
  - Surpassed equipment capability to accurately record heat flow with no observable leakage
- Smaller particle size lowers initiation temperature of large exotherm

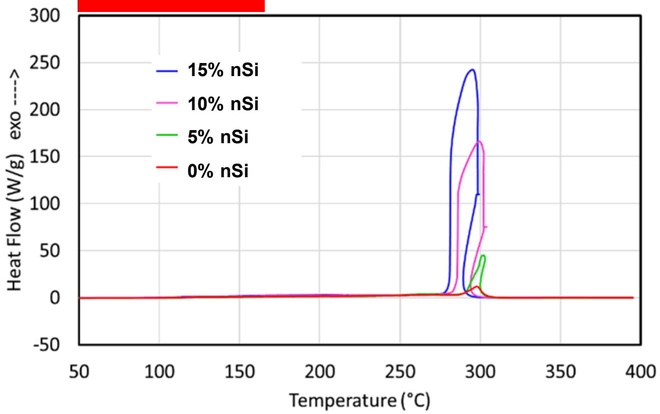


No observed pan leakage



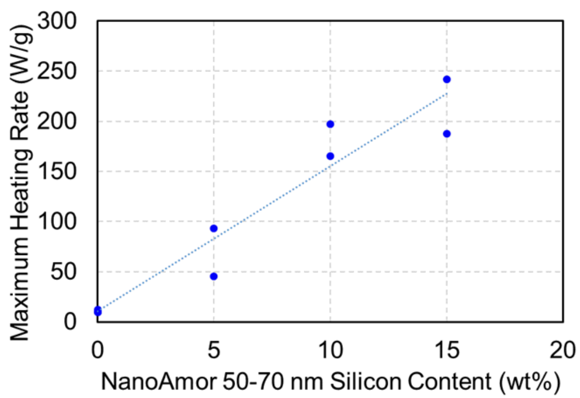
Trending of Heat Generation with Si Content

100% SOC

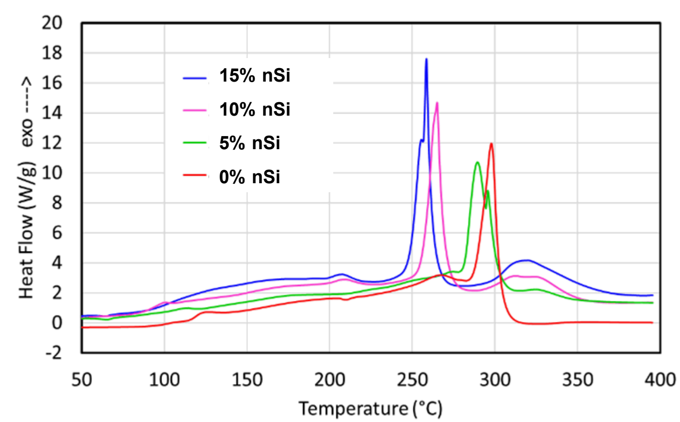


- Large exotherms are repeatable and trend with silicon content
  - Greater peak heating rate
  - Lower exotherm onset temperature
- Exotherm can be mitigated by reducing electrolyte ratio
  - Trends hold in this case but reaction peaks are quite altered

Exotherm values aren't true but qualitative comparison shows trending with silicon content



Testing with reduced electrolyte ratio

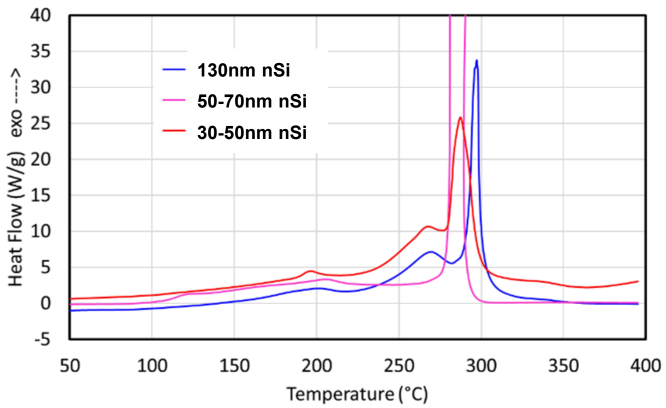


Effect of nSi Particle Size

- Electrolyte clearly participates in highly exothermic reaction, suggests that greater surface area (ie. Smaller particle size) will lead to greater reaction rates
  - Anticipated trends of greater peak heating rate / lower reaction onset with smaller particle size

Observed Trends

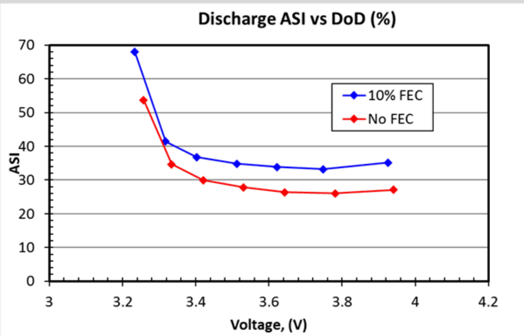
- High loading CAMP electrodes do not follow trends
  - Extreme exotherms may be associated with greater material loading
- In lower loading electrodes smaller particles show:
  - Stronger SEI peak, lower temperature peak onset, minimal change to peak heating rate and total heat generation
  - Conclusions are tentative due to limited data points, limited characterization of nSi particles



Effect of FEC on Electrode Performance

- FEC is widely demonstrated to improve capacity and cycle life of Si electrodes
  - Formed SEI is more passivating / robust

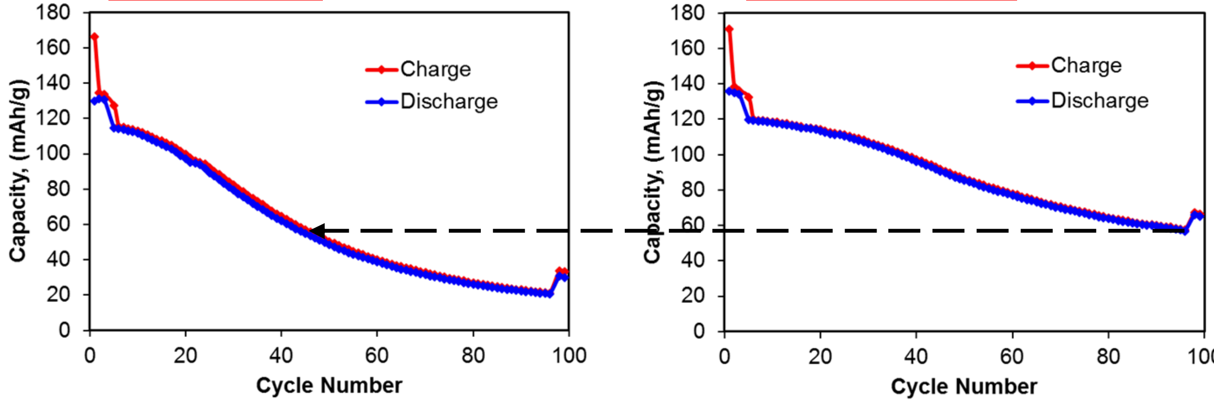
    * N.S. Choi, K.H. Yew, K.Y. Lee, M. Sung, H. Kim, S.S. Kim. *J. Power Sources* **161,** 1254-1259 (2006).



HPPC shows higher ASI – more resistive SEI

No FEC

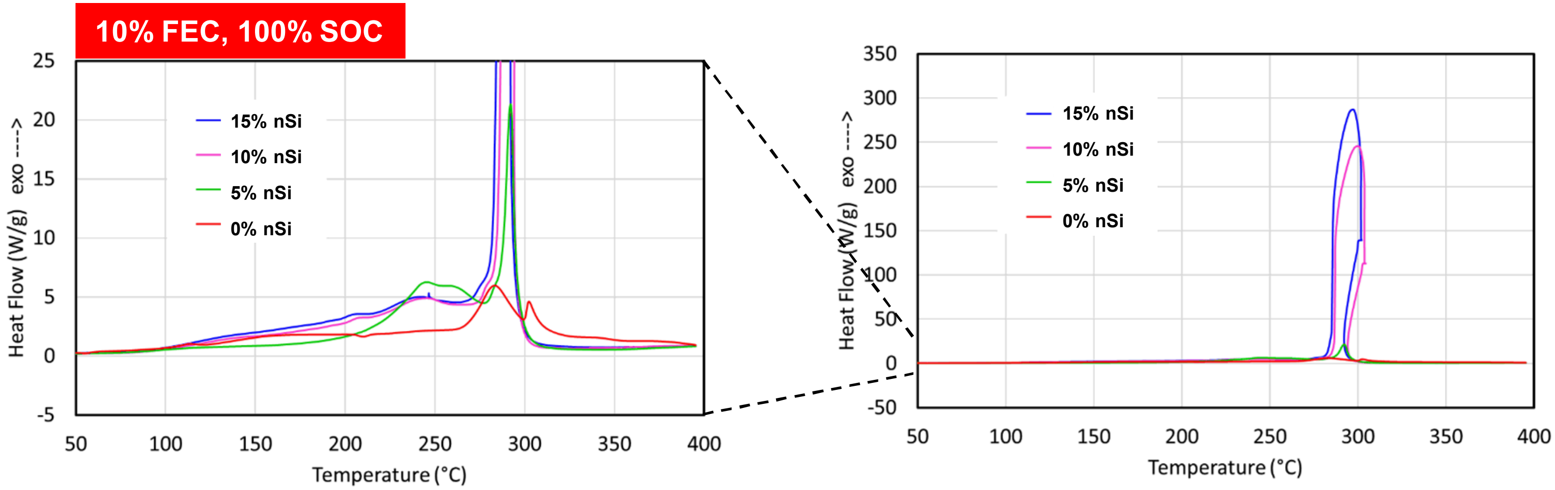
10% FEC



Addition of 10% FEC to electrolyte more than doubles cycle life at a given capacity

Effect of FEC on Thermal Performance

- Testing after cycling with and in the presence of 10% FEC shows thermal performance is not significantly affected by FEC addition
  - Extreme exotherms still present and still trend with nSi content



Scale Up to Larger Format Testing

- Purpose of materials level study is to correlate observations with full scale testing (18650 full cells)
  - Accurate thermal abuse performance requires larger cell capacities
  - ARC, thermal abuse testing, electrical abuse testing, etc.
- As discussed in previous presentation, observed issues with thermal reactivity of nSi translate to full scale performance

Conclusions

- Silicon is an appealing substitute for graphite as an anode in lithium ion batteries
  - Challenges include limited cycle life and difficulty in achieving high silicon loading
- This materials thermal performance study suggest that thermal instability is another issue that needs to be addressed before silicon becomes a viable substitute
  - These conclusions agree with full cell study observations

Acknowledgements

Sandia National Labs

- Lorie Davis
- Jill Langendorf
- Chris Orendorff

Argonne National Lab – CAMP Facility

- Andrew Jansen
- Bryant Polzin
- Steve Trask

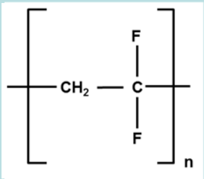
Thanks to Peter Faguy and the U.S. Department of Energy – Vehicle Technologies Office for financial support of this work.

Extra Slides

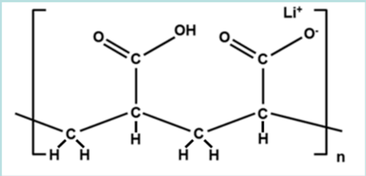
TO EXTRA SLIDES

- Silicon shows good performance in mixtures, in nano-architecture, and with low loadings
  - Difficulty in achieving practical areal energy density while maintaining high specific capacity and/or cycle life
- Proper binder and electrolyte selection are crucial for optimized silicon performance

Binder Materials

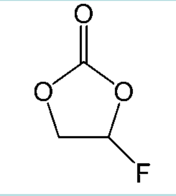


PVDF

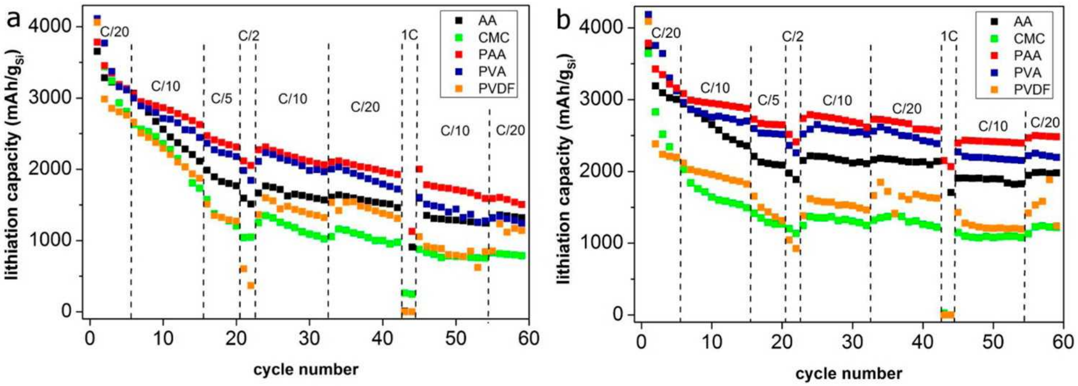


LiPAA

Electrolyte Additives



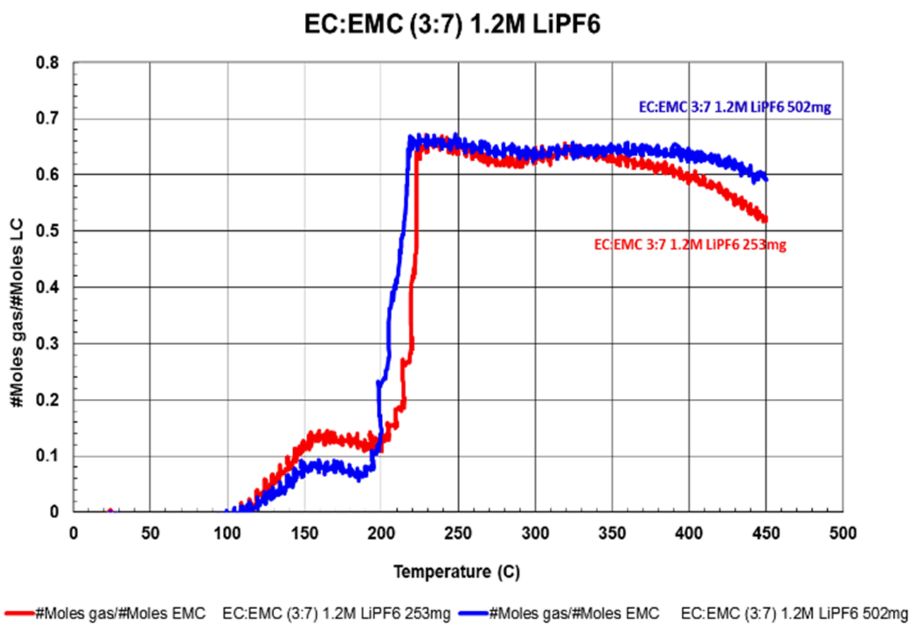
FEC

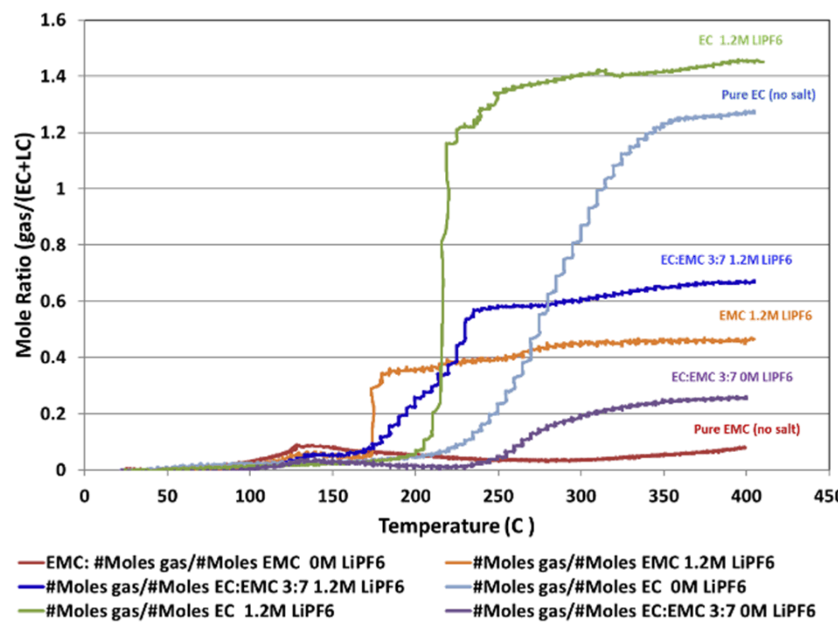


C. Erk, T. Brezesinski, H. Sommer, R. Schneider, J. Janek, *ACS Appl. Mater. Interfaces* **5**, 7299-7307 (2013).

Electrolyte ARC Data

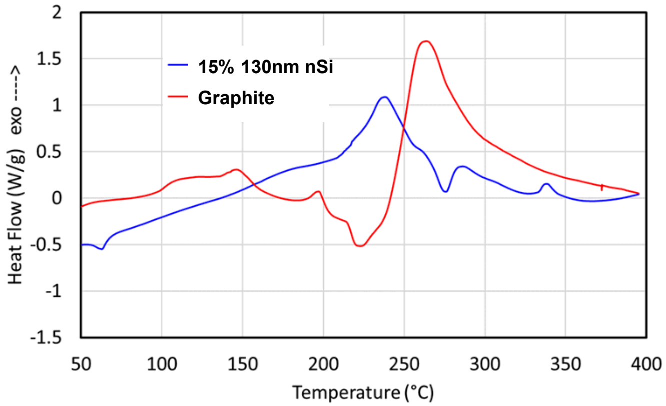
- Trend is independent of mass tested (250mg v 500mg)



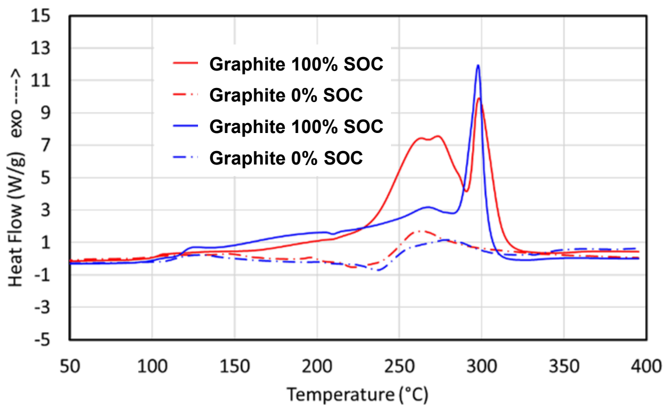


Additional DSC Curves

- 0% SOC comparison of graphite and nSi/graphite

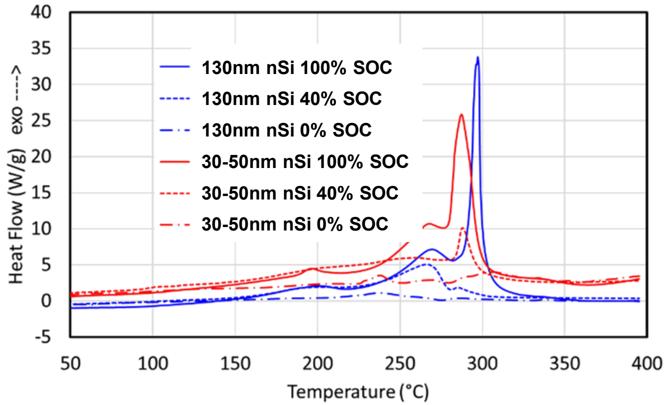


- Graphite DSC comparison of SNL-130nm to CAMP-50-70nm



Additional DSC Curves

- All SOC comparison of 130nm and 30-50nm nSi



- All SOC comparison of no FEC and 10% FEC in the electrolyte