I. Chapter Heading

IV.D.7 Next Generation Anodes for Lithium-ion Batteries: Thermodynamic Understanding and Abuse Performance (Sandia National Laboratories)

Kyle Fenton (SNL PI), Eric Allcorn, and Ganesan Nagasubramanian
Sandia National Laboratories
PO Box 5800
Albuquerque, NM 87185
Phone: (505) 284-3377; Fax: (505)844-6972
E-mail: krfento@sandia.gov

Peter Faguy, DOE Program Manager
US Department of Energy
Phone: (202) 586-1022
E-mail: Peter.Faguy@ee.doe.gov

I.1.A.1. Abstract

Objectives

- Elucidate degradation mechanisms, decomposition products, and abuse response for next generation silicon based anodes.
- Understand the contribution of various materials properties and cell build parameters towards thermal runaway enthalpies. Quantify the contributions from various cell parameters such as particle size, composition, state of charge (SOC), electrolyte to active materials ratio, etc.

Accomplishments

- Double sided electrodes (for cylindrical cells) were fabricated and evaluated to show comparable response to baseline materials used throughout the program.
- Materials level thermal runaway was conducted on baseline materials through DSC, TGA, MS, and ARC evaluations.
- Larger format cylindrical cells (18650) were constructed and tested for electrochemical and thermal abuse response.
- A smaller capacity cell platform was developed for quantification of runaway enthalpy using ARC techniques. This allows for quantification and evaluation of runaway response with minimal risk of damage to equipment or facilities.
- Drying parameters, electrode design, state of charge, silicon particle size, binder selection, and solvent selection were investigated to understand abuse response and gas generation during runaway.

Future Achievements

- Develop fundamental understanding of gas generation mechanism and how it can be leveraged to keep next generation anode runaway response as benign as possible.
- Refine the understanding of materials level changes and how they contribute to runaway energy, full cell safety, gas generation during runaway, and overall enthalpy released during runaway.

✧ ✧ ✧ ✧ ✧

I.1.A.2. Technical Discussion

Introduction

As we develop new materials to increase performance of lithium ion batteries for electric vehicles, the impact of potential safety and reliability issues become increasingly important. In addition to electrochemical performance increases (capacity, energy, cycle life, etc.), there are a variety of materials advancements that can be made to improve lithium-ion battery safety. Issues including energetic thermal runaway, electrolyte decomposition and flammability, anode SEI stability, and cell-level abuse tolerance behavior. Introduction of a next generation materials, such as silicon based anode, requires a full understanding of the abuse response and degradation mechanisms for these anodes. This work aims to understand the breakdown of these materials during abuse conditions in order to develop an inherently safe power source for our next generation electric vehicles.

Approach

The effect of materials level changes (electrolytes, additives, silicon particle size, silicon loading, etc.) to cell level abuse response and runaway reactions will be determined using several techniques. Experimentation will start with base material evaluations in coin cells and overall runaway energy will be evaluated using techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and accelerating rate calorimetry (ARC). The goal is to understand the effect of materials parameters on the runaway reactions, which can then be correlated to the response seen on larger cells (18650). Experiments conducted showed that there was significant response from these electrodes. Efforts to minimize risk during testing were taken by development of a smaller capacity cylindrical design in order to quantify materials decision and how they manifest during abuse response.

Results

This work continues the efforts from last year, which aimed to evaluate electrochemical and abuse response for electrodes provided from the CAMP facility at Argonne National Laboratory. This included evaluation of anodes containing between 0 and 15 wt% silicon from NanoAmor. Investigations were completed on coin cell and 1.25 Ah 18650 form factors. Several experiments showed a high level of gas generation and overall runaway for cells containing silicon electrodes. To further understand the response of these materials, this work focused on understanding the effect of several factors to runaway response and gas generation including solvent selection, electrode processing, silicon content, and the effect of water. The primary reaction believed to be resulting in significant contribution to runaway reaction is the water reaction. This is particularly interesting in systems using polyacrylic acid (PAA) binders as one of the products during degredation of PAA is water, which could lead to increase runaway energetics. During degradation of PAA, water is evolved at the expected temperature of 100 °C as well as a second peak around 250 °C, which is presumably from polymer degradation reactions.

In order to investigate the effect of binder during runaway, electrodes were prepared with several process to identify the contribution to overall runaway enthalpy based upon water content during processing and during high temperature breakdown. Figure I-1 shows the electrodes used to evaluate runaway energetics. Electrodes were made with nanoamor 70-130 nm silicon, Hitachi Mag-E graphite, Timcal C45 carbon, and several different binders in weight percentage ratios of 15/73/2/10 respectively. Electrodes parameters were 45 µm thickness, 45 % porosity, and areal capacity of 1.9 mAh/cm^-2.

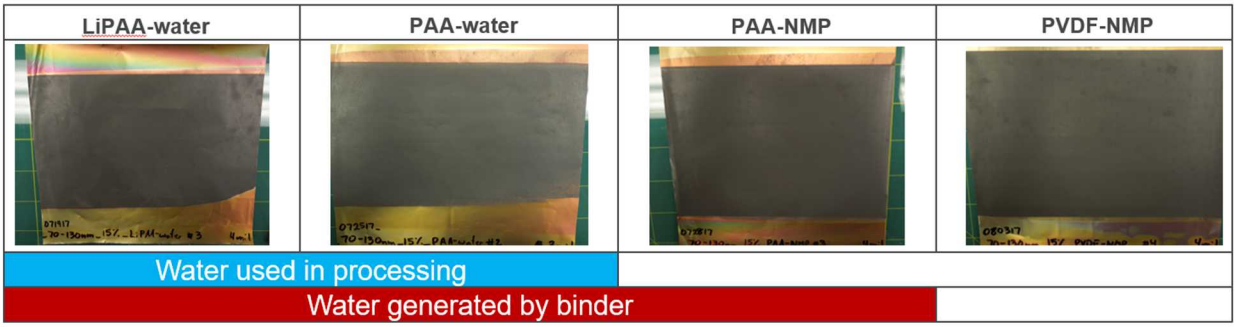

Figure I-1: Prepared electrodes processed with water (blue) and that will have water present during runaway reactions (red) in comparison to normal non-aqueous systems (right).

Coin cells were assembled and formation cycling was conducted on all electrodes. After 5 cycles, each cell was held at 100 % state of charge and disassembled for differential scanning calorimetry (DSC) to evaluate the head generated during thermal abuse conditions. Each sample had an additional amount of electrolyte added to make a 1:1 wt% ratio between active material and electrolyte. All cells performed similarly under formation conditions, as seen in Figure I-2 left, with the exception of the PVDF, which was expected as it is known to be a slightly lower performing binder for the silicon system. DSC results can be seen in Figure I-2 right, which all show similar responses with a slight exotherm around 225 °C with full material runaway occuring near 275 °C.

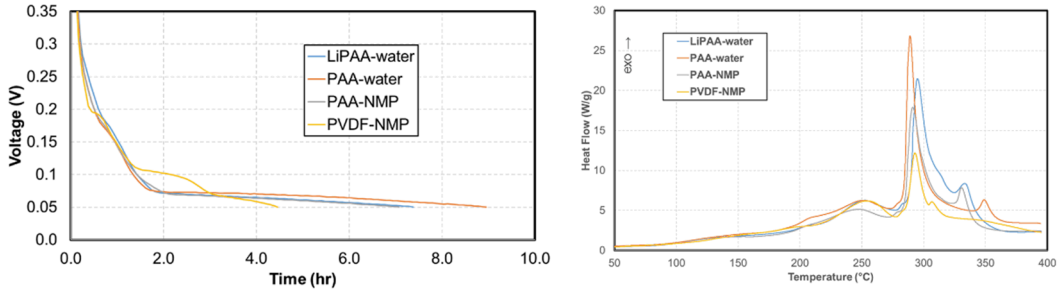

Figure I-2: Selected material level evaluations for next generation anodes. Panels show the effect of silicon content on heating rate (A) and material decomposition (B), and gas generation based on electrolytes and binder (C) and with the addition of active electrode materials (D).

Normalization of heat flow to mass of active material shows fairly consistent results for overall runaway energy of between 40 - 55 W/Ah peak heating rates. While the reaction with water, both residual from processing and produced during runaway, plays a role in runaway it is not the sole contributing factor. Previous work has shown clear correlations to silicon content, silicon particle size, and state of charge.

Full cells were built using the 0, 5, 10, and 15 wt% silicon electrodes and built into 18650 format cells for larger cell evaluation of decomposition and abuse response. To mitigate potential safety issues, electrodes were made to be approximately half the normal length for construction into an 18650 cell. The resulting void volume within the case was taken up by either a tube of copper or a length of current collector foil wrapped to make the right jelly roll diameter. Either case, the extra copper component was then attached to the copper current collector of the anode to ensure proper electrical continuity to the negative case. All cells were formed with five formation cycles, held at 100 % SOC, and then evaluated using ARC.

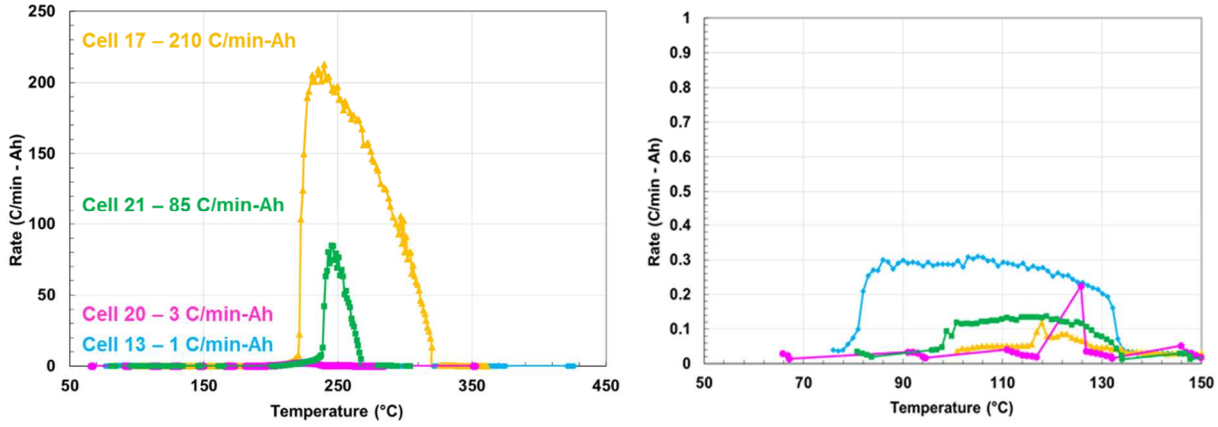

Figure I-3: ARC evaluations for several sample 18650 cells containing undersized electrodes.

No clear trend was observed for electrodes of half-length using both extra current collector (Figure I-3 yellow and blue) or solid copper tubing inserts (Figure I-3 green and pink). To make sure that the differences seen were not due to residual electrolyte degradation for extended periods of time, inspection of ARC data between 50 and 150 °C shows no appreciable difference between the two cells types, as seen in Figure I-3 right panel.

During ARC evaluations, a gas samples system was assembled that would actuate a valve at 275 °C to open and take a grab sample of vapor. This would then allow for isolation after full runaway of the cell, which was sent for gas sampling evaluation and chemical analysis. This was done for baseline NMC 523 vs Conoco Phillips G8 graphite using a standard sample bottle, 15 wt% Nanoamor silicon using a standard sample bottle, and 15 wt% Nanoamor silicon using a cleaned and sealed sample vial. Figure I-4 shows the results of analysis for organic components (Figure I-4A), hydrocarbons (Figure I-4B), and gases (Figure I-4C).

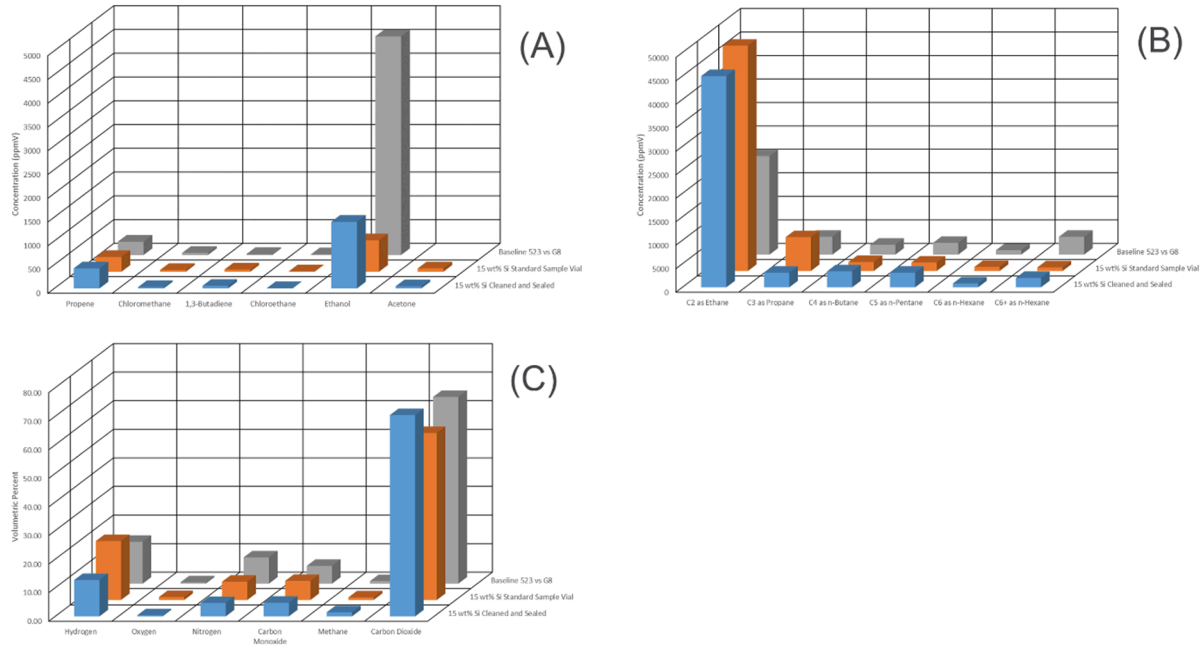

Figure I-4: Gas sampling results for electrodes containing baseline G8 graphite and 15 wt% silicon using both standard sample vials and cleaned and sealed bottles. Data is shown for analysis completed on organic species (A), hydrocarbons (B), and gases (C).

The primary differences seen in the gas sampling data are that there is a significantly larger amount of ethanol in the baseline samples without silicon but a significantly larger amount of ethane in the samples that do contain silicon. This is particularly interesting in light of the significant gas generation seen previously for

larger cells evaluated with ARC. These evaluations were done by an independent lab, which requires transportation time for the samples. Many of the reactive species that could be present during cell runaway are likely to have already reacted in this scenario. Efforts will continue to work towards the ability to analyze gas generation in real time for a more complete understanding of reaction chemistry during runaway for these next generation materials.

Conclusions

This work demonstrates that there is an impact on safety response with nanoscale silicon materials compared to graphite based anodes. Changes to material and cell level properties can have impact on safety and thermal response characteristics. We have reported thermal runaway properties of cells (coin cells and cylindrical cells) containing nanoscale silicon up to 15 percent by weight. We continue to develop the understanding of abuse response for these anodes to better understand how these next generation negative electrode materials will impact cell and battery-level abuse tolerance.

I.1.A.3. Products

Presentations/Publications/Patents

1. Eric Allcorn, Ganesan Nagasubramanian, Kyle Fenton. "Materials Safety Study of Practical Nano-Silicon + Graphite Anodes for Lithium-Ion Batteries." Prime 2016, Honolulu, HI, Oct. 2 - 7, 2016.
2. Kyle Fenton, Chris Orendorff, Ganesan Nagasubramanian, Josh Lamb, Eric Allcorn. "Impact of next Generation Electrode Materials on Abuse Response." Prime 2016, Honolulu, HI, Oct. 2 - 7, 2016.

I.1.A.4. Acknowledgement

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.