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I. Chapter Heading

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

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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 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 bomb 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.

Future Achievements

- Complete evaluation of cylindrical cells during abuse conditions and compare with baseline materials (both from this program and with historical data).
- 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.

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I.1.A.2. Technical Discussion

Background

Text (0APR_para STANDARD Paragraphs)

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 abuseresponse 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). Cylindrical cells were fabricated using a variety of baseline materials with varying silicon loading to understand full cell response. Our approach that spans from the materials level through large cells aims to understand both properties and scale effects that will be important in the development of an inherently safe power source utilizing next generation silicon based anodes.

Results

Initial efforts for the program focused on the fabrication and electrochemical evaluation of double sided electrodes that showed identical performance to the CAMP developed materials. Electrode evaluations were conducted in 2032 coin cells to validate electrode performance is comparable across the program and across laboratories, as seen in Figure I-1.

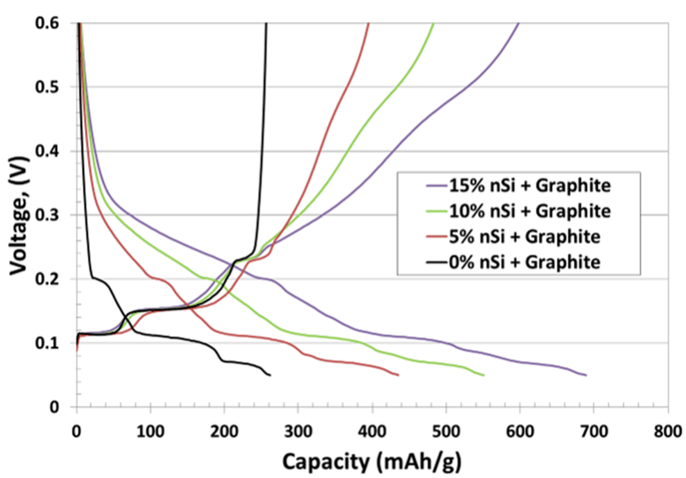

Figure I-1: Example cycling data for electrodes used to evaluate abuse response. Varying silicon amounts are shown, allusing gen 2 electrolyte with 10% FEC by weight. The materials used and cells fabricated were evaluated to ensure that all program data generated was comparable through the multi laboratory collaboration.

Materials level evaluations were conducted to understand the effect of several different materials properties on the overall energy output during a runaway or abuse event. DSC experiments were conducted to investigate the effect of silicon active material particle size and silicon loading in the electrode ARC bomb evaluations were conducted in a step wise fashion to understand the contribution of each electrode component to gas generation for the materials only. The ARC evaluations do not immediately show the effect of these interactions in a full cell, since they exclude the lithium silicon alloying reactions and any catalytic effects from those reaction products. Figure I-2 shows a summary of experimentation performed on the silicon electrodes for this program.

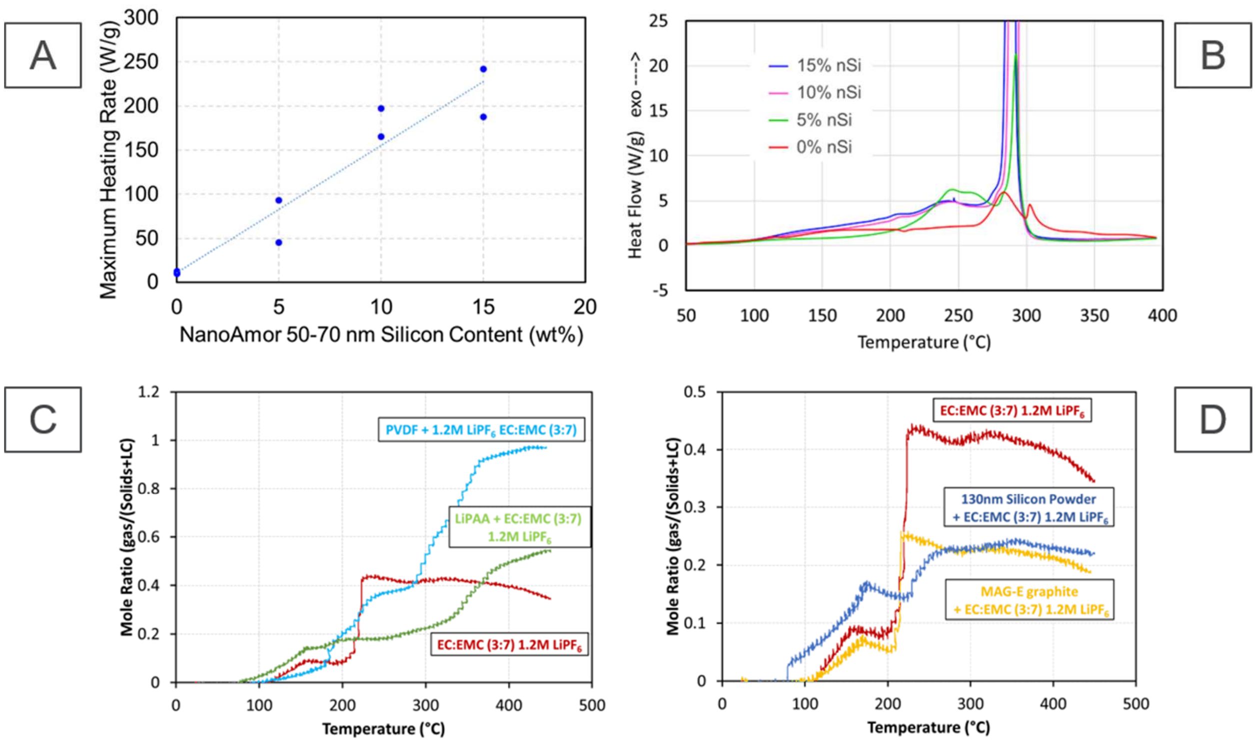

Figure I-2: Selected material level evaluations for next generation anodes. Panels show the effect of silicon content on heating rate (A) and material decomposition (B), and gas generation based on electrolytes and binder (C) and with the addition of active electrode materials (D).

Panel A of Figure I-2 shows that there is a dependence in energy output that varies with silicon content, which is indicative of the silicon material being a prime participant in the energetic decomposition of these materials. Panel B shows that this increase in energy during decomposition is primarily in the high rate output between 250 and 300 °C, using electrolyte containing 10 wt% FEC. Panel C shows the ARC response to the stepwise addition of binder materials to electrolytes to show that there is only minimal overall effect on abuse response. Panel D indicates that the addition of silicon or graphite powder to baseline electrolyte does not dramatically increase the gas generation. Panels C and D indicate that any increased response from silicon based anodes cannot be directly contributed to interactions of the materials only. Any response clearly requires the interactions that only occur once lithium silicon alloy reactions are present within the cell.

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. Starting with the anticipated highest overall enthalpy output, the 15 and 10 % silicon content cells were formed and put on ARC testing at 100% SOC (4.1V vs. NCM523). Pictures of the result are showing in Figure I-3.

Figure I-3: ARC conditions from attempted evaluation of 18650 cells using NCM523 vs. 10 and 15 wt% nanosilicon.

The overall cell response was sufficient to cause several failures within the ARC experimental setup, which is normally able to handle both research and commercial grade 18650 cells. The exact failure mechanism is not obvious and more testing is underway to identify the issue that was observed. It is evident that there was a good amount of gas and heat generated during this experiment. The immediate priority for this research is to understand and quantify exactly what is occurring within the nanoscale lithium silicon electrode system

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 (particle size, electrolyte ratios, electrode composition) can have impact on safety and thermal response characteristics. We have reported on the 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

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