SAND2018-0319R

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

Kyle Fenton, Eric Allcorn, and Ganesan Nagasubramanian

Background

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.

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 aim to understand the fundamental reactions and quantify response from silicon based anodes under abusive conditions. This included evaluation of anodes containing between 0 and 15 wt% silicon from a variety of sources. 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 impacting runaway response and gas generation including solvent selection, electrode processing, silicon content, and the effect of water. Previous efforts to evaluate these parameters in 18650 cell form factors using accelerating rate calorimetry (ARC) proved difficult due to the gas generation and temperatures involved during runaway. In order to try and quantify

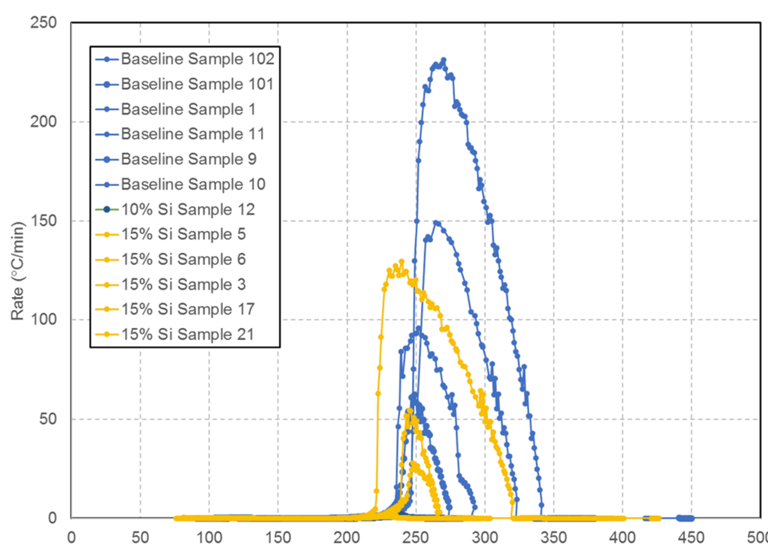

Figure 1 - Accelerating rate calorimetry (ARC) response for 18650 cells with graphite anodes (blue), 10 wt% silicon (green), and 15 wt% silicon (yellow). Heating rate is not normalized to active material content, so peak heating rates and overall runaway enthalpy is shown for qualitative purposes only.

these effect, 18650 cells were made with electrodes cut to a much smaller overall cell capacity of roughly 600 mAh nominal capacity. The excess space within the cell was minimized using a copper insert to keep the ratio of electrolyte to electrode material constant. The comparison between graphite anodes and those containing up to 15% silicon can be seen in Figure 1.

Figure 1 shows ARC response for 18650 cells with graphite anodes (blue), 10 wt% silicon (green), and 15 wt% silicon (yellow). Heating rate is not normalized to active material content, so peak heating rates and overall runaway enthalpy is shown for qualitative purposes only. The overall response of the cells are very similar between graphite and silicon based composite electrodes. This result contradicts many of the observations seen in previous evaluation of silicon anode materials. Gas samples were taken during testing and analyzed to evaluate species evolved during runaway. Gas analysis showed that the silicon containing electrodes generated higher levels of short chain hydrocarbons (ethane and propane), had less short chain organics (ethanol and propene), and similar concentrations of carbon dioxide and carbon monoxide. The overall gas generated in silicon based cells was about twice that generated in graphite containing cells.

In an effort to fully understand silicon contribution to abuse response, electrodes were made with newly acquired Paraclete Energy 100 nm silicon materials. Silicon, Hitachi Mag-E graphite, Timcal C45 carbon, and lithium polyacrylic acid (LiPAA) were used in weight percentage ratios of 15/73/2/10 respectively. Electrodes parameters were 55 µm thickness, 45 % porosity, and areal capacity of 3.3 mAh/cm^-2. This was then coated and put on formation cycling in half cell configuration as seen in Figure 2. Overall, this material exhibits a high first cycle coulombic efficiency of 89 % and stable cycling for the first 5 cycles at approximately 600 mAh/g. Evaluations are ongoing to evaluate the response of this material to abuse conditions and understand the mechanisms observed during runaway.

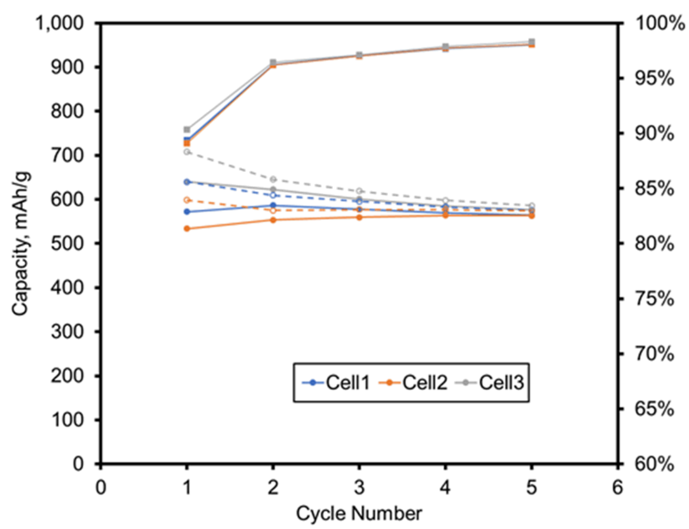

Figure 2 - Half cell electrochemical cycling performance of 15% Paraclete nSi anodes cycled at C/10 from 1.5V – 0.05V vs. metallic lithium.

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. Additionally, the fundamental reactivity and gassing behavior that has been observed in silicon offers opportunities for better understand the safety of these materials.

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.