Thermal and overcharge abuse analysis of a redox shuttle for overcharge protection of $LiFePO_4$

Joshua Lamb[1], Christopher J. Orendorff[1], Khalil Amine[2], Gregory Krumdick[2], Zhengcheng Zhang[2], Lu Zhang[2] and Antoni S. Gozdz[3]
[1]Sandia National Laboratories
Albuquerque, NM
[2]Argonne National Laboratory
Argonne, IL
[3]A123 Systems LLC
Waltham, MA

$LiFePO_4$ based li-ion battery chemistries are becoming increasingly popular because of their increased safety and low heat output. However, they can be susceptible to failure due to overcharging of the cell. While commercial cells typically are protected from overcharge by circuitry in a battery pack, it is desirable to develop inherent overcharge protection within cells. Redox shuttles have been previously used to provide overcharge protection[1], however there are concerns about the heat generation during overcharge protection of a full cell, especially as cells become larger.[2] This is of particular interest for overcharge caused by imbalance of cells within a battery pack.

This work investigated the performance and abuse tolerance of cells protected using a redox shuttle in collaboration with Argonne National Laboratories. 18650-type cells were constructed at prototyping facilities at Sandia National Laboratories (SNL) as well as by A123 Systems. These cells were then evaluated at the Battery Abuse Testing Laboratory at SNL.

The thermal efficiencies were evaluated using isothermal battery calorimetry. Cells containing the overcharge shuttle were observed to reach a steady state value of approximately 3.8 volts, with a small variance in direct proportion to the applied current. In all cases the heat output from the cells was measured to reach ~90% of the total input power. The heat output was also measured using isothermal calorimetry over 50 cycles and the effect of cycling on the heat output and shuttle equilibrium voltage was observed.

The cells were also tested at higher rates of overcharge. Some of these results at an overcharge current of 1A can be seen in Figure 1. This data shows that under these conditions the cell containing the shuttle rapidly reaches a steady state voltage, while the temperature increases until a moderately high steady state temperature is reached. The control cell meanwhile rapidly increases in both applied voltage and cell temperature until cell failure. The heat output of the cell was measured as well, with results similar to that observed using isothermal calorimetry.

The ability of the shuttle to rebalance cells in series was also evaluated. Two cells in series were taken deliberately out of balance individually then charged as a single pack to observe the time needed to bring the cells into balance with one another. This was done for cells moderately out of balance (Cell 1 100%, Cell 2 80%) as well as cells severely out of balance (Cell 1 100%, Cell 2 50%). Additional detail will be provided in the presentation.

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.

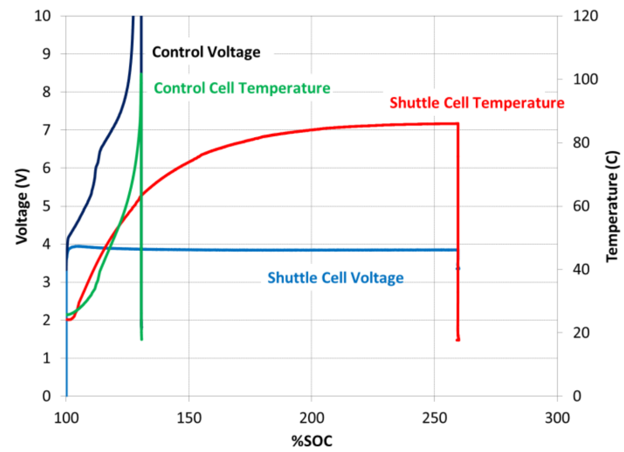

Figure 1. Performance of 1 amp-hour 18650 cells with and without overcharge protection. The control cell rapidly increases in voltage and temperature under overcharge conditions, while the protected cell quickly reaches a steady state voltage. The rise in temperature is also observed to be mitigated somewhat.

1. Chen, Z.H., Y. Qin, and K. Amine, *Redox shuttles for safer lithium-ion batteries.* Electrochimica Acta, 2009. **54**(24): p. 5605-5613.
2. Dahn, J.R., et al., *High-rate overcharge protection of LiFePO4-based Li-ion cells using the redox shuttle additive 2,5-ditertbutyl-1,4-dimethoxybenzene.* Journal of The Electrochemical Society, 2005. **152**(6): p. A1283-A1289.