National Aeronautics and Space Administration

Zero-volt tolerant lithium-ion batteries for surviving spacecraft dead bus scenarios

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Objectives

The task had three primary objectives, based on the main challenges to be overcome to enable Li-ion batteries (LIB) that can survive deep-discharge (zero-volt) events.

1. Investigate novel anode substrates, and novel protective coatings for copper, to be selected based on: a) minimal oxidation during voltammetry testing, b) ability to support active anode material coatings, and c) retention of performance during deep-discharge vs. copper.
2. Investigate modified electrolytes with the goal of forming an electrochemically stable SEI compared to baseline electrolytes.
3. Incorporate these elements into a high energy LiNi0.8Mn0.1Co0.1O2 (“NMC811”)/graphite cell chemistry, in laboratory cells.

Background

Lithium-ion batteries (LIB) have become ubiquitous as an essential energy storage technology. Anomalous scenarios including spacecraft dead bus, power failures and Lazarus mode operation can result in these batteries being drained beyond zero state-of-charge and eventually reaching 0V. Current Li-ion cells have a 2.5 V minimum: deep discharge causes irreversible damage and permanent partial or complete loss of capacity. This was observed when the MSL ATLO Testbed battery sustained both decreased capacity and increased impedance due to inadvertent deep discharge from harness insulation failure. Current power subsystem designs adopt switches or other mitigation controls (e.g., Array Battery Interface Slice on Europa Clipper) which add complexity, cost, and points of failure. Batteries with innate tolerance to deep discharge with no loss in performance after extended durations near 0V would be preferred. In spite of these benefits, this is considered a niche technology with little commercialization, limited to Enersys/Quallion's Zero-Volt™ cells, in which copper is replaced by titanium; these cells possess much lower energy than state-of-art high-energy Li-ion in the same format.

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Approach

- Screen alternative materials from commercially available options: nickel, tantalum, molybdenum, nitinol, titanium and grafoil.
- protect copper foils with coatings deposited via magnetron sputtering, including titanium nitride (Fig. 1), titanium, nickel, and gold.
- Incorporate electrodes (without any active anode coating) into corrosion cells with a Li metal counter electrode. Cyclic voltammetry was used to measure the potentials of oxidation vs. Li/Li+, as well as current densities at relevant potential values (Table 1). At 3.5 V, near the anode potential range expected during a deep-discharge event, the nickel and tantalum substrates measured oxidation currents 4-5 orders of magnitude lower than copper, on par with titanium.
- Li-ion anodes were coated onto substrates that showed promise in corrosion testing for assembly into coin cells. These cells used a commercial cathode with a high energy active material, LiNi0.8Mn0.1Co0.1O2 (NMC811), to eliminate any variations due to the cathode and demonstrate functionality with a state-of-art positive electrode material.

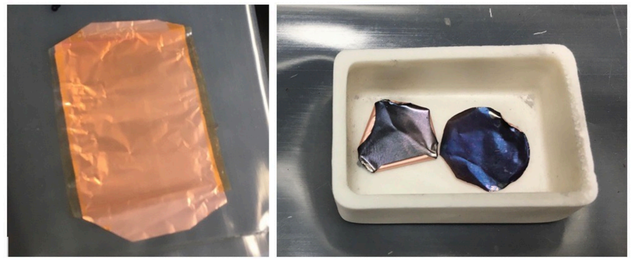

Figure 1. Titanium nitride coating deposited on copper substrate before (left) and after (right) annealing.

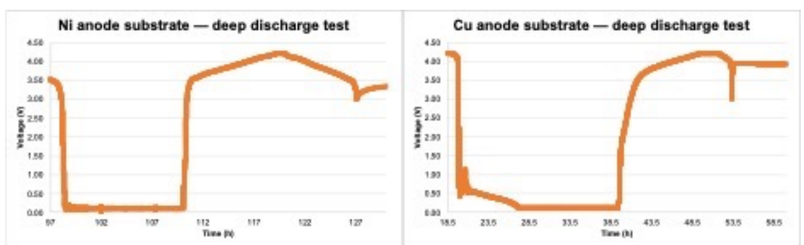

Figure 3. Cycling performance of Li-ion cells with Ni (left) and Cu (right) anodes subjected to 12 hours at 0.10 V vs. Li/Li+. The Ni anode had little faradaic reactivity during deep discharge and was able to support a healthy cycle afterward; the Cu anode had more reactivity at low voltages and was not able to discharge any significant capacity following recharge.

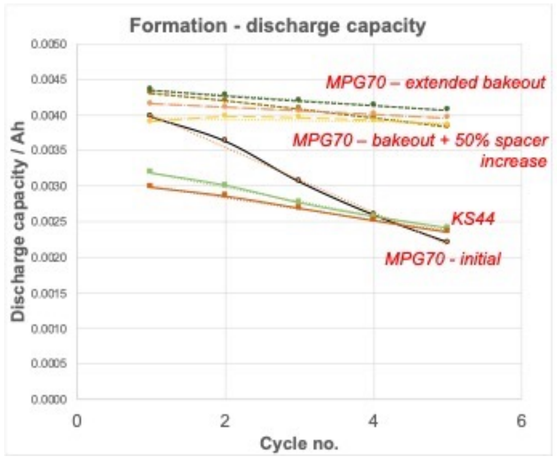

Figure 2. Results of optimization study formation cycling. A combination of additional drying steps, additional spacer disks for increased stack pressure, and the MPG-70 active graphite material yielded the most stable performance. KS44 graphite yielded poor results even with the other optimization factors in place.

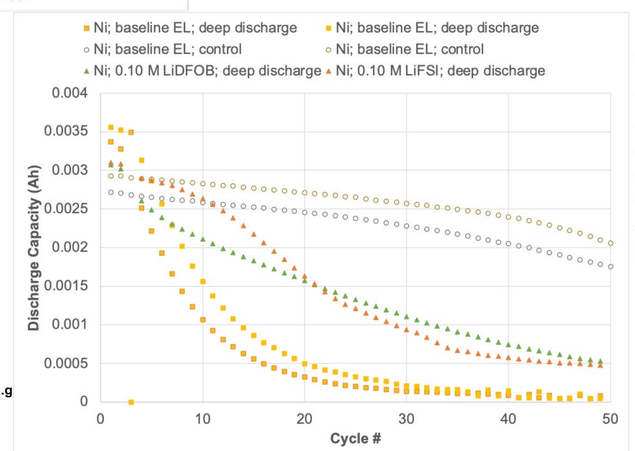

Figure 4. Cycle life testing at C/5 rate, 3.00 – 4.10 V, following 12 hours at 0.10 V vs. Li/Li+ (control cells were not subjected to deep discharge). The modification of the electrolytes with additives offered some improvement in capacity fade.

Results

- At 3.5 V, near the anode potential range expected during a deep-discharge event, the nickel and tantalum substrates measured oxidation currents 4-5 orders of magnitude lower than copper, on par with titanium.
- An optimization study was carried out on anode coating processes. As a result, a graphite active material was selected (Mitsubishi MPG-70 over Timcal KS44), additional drying steps were added, and more stack pressure was introduced into the cells via spacer disks (Fig. 2).
- Cells were assembled with copper or nickel anodes and were subjected to deep discharge testing. Initial screening of full Li-ion cells indicated superior performance of the Ni anode as compared to the Cu anode after a deep-discharge test (Fig. 3): the Ni anode showed a healthy cycle following deep discharge, while the Cu anode cell was unable to deliver any discharge capacity.
- Figure 4 shows cycle life of Ni-based anodes with the baseline electrolyte and electrolytes with additives deep discharge, compared to control cells with Ni-based anodes and no deep discharge event. Capacity retention was heavily impacted by the deep discharge, and none of those cells show comparable performance to the control cells. However, the cells with the modified electrolytes did have less rapid degradation and more capacity retained after 50 cycles than those with the baseline, suggesting that a combination of approaches may be additive.

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