Thermal Battery Degradation Mechanisms

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Abstract

Diffuse reflectance IR spectroscopy (DRIFTS) was used to investigate the effect of accelerated aging on LiSi based anodes in simulated MC3816 batteries. DRIFTS spectra showed that the oxygen, carbonate, hydroxide and sulfur content of the anodes changes with aging times and temperatures, but not in a monotonic fashion that could be correlated to phase evolution. Bands associated with sulfur species were only observed in anodes taken from batteries aged in wet environments, providing further evidence for a reaction pathway facilitated by H_2S transport from the cathode, through the separator, to the anode. Loss of battery capacity with accelerated aging in wet environments was correlated to loss of FeS_2 in the catholyte pellets, suggesting that the major contribution to battery performance degradation results from loss of active cathode material.

Introduction

Recent lifetime assessments of thermal batteries have revealed clear evidence for materials aging, although the extent, rate and correlation with performance are still not well understood. Characterization (chemical and electrochemical) of LiSi/FeS_2 batteries shows changes in the cathode material (FeS_2) consistent with the growth of a sulfate impurity phase, while anode materials show evidence for the discharged Li_7Si_3 phase. A better understanding of changes in cathode and anode materials and the correlation with battery performance is needed in order to accurately predict the future performance and to provide guidelines for accurate design margins for batteries destined for life extension program needs.

Approach

Our approach to understand these changes is to use high sensitivity analytical tools, such as diffuse reflectance infrared spectroscopy (DRIFTS), to evaluate impurity phases observed in batteries pulled from the stockpile, and compare these phases to those seen when pristine battery materials are exposed to accelerated aging conditions. Infrared absorption provides a powerful technique for detecting impurity phases in thermal battery materials [1-8]. This approach should ultimately allow aging mechanisms to be determined. Combining this information with measures of performance, such as discharge behavior, will allow the impact of materials aging to be determined.

In FY14 we began a study of materials changes that occurred as a result of accelerated aging of LiSi/FeS_2-based thermal battery materials. Simulated MC3816 batteries were exposed to temperatures up to 180°C for times up to two years, in the presence and absence of water vapor. DRIFTS showed a clear degradation of the FeS_2 cathode only in the presence of water vapor as the temperature and exposure time increased. Preliminary micro-analytical and x-ray diffraction measurements on LiSi anodes exposed to high temperatures in the presence of water vapor clearly showed that sulfur had migrated across the separator and reacted with Li. This year we used DRIFTS to investigate the reaction products in the anode as a function of temperature, time, and the presence/absence of water. Aged anode spectra were compared with spectra from standards corresponding to intermediate products. Discharge curves for batteries aged in the presence of water vapor showed a significant decrease in capacity that can be explained by a loss of active material in the cathode. Changes in the DRIFTS spectra, combined with capacity loss estimates from the discharge curves, were used to provide further evidence for the

reaction pathway proposed in Wesolowski's FY14 annual report [9] and to quantify the sensitivity of DRIFTS spectra to the loss of active cathode material.

Results and Impacts

The aging study is described in more detail in Wesolowski et. al. [9]. Briefly, simulated MC3816 batteries were built, sealed and stored at temperatures of 75°C, 130°C, and 180°C for times up to two years. One set of batteries aged under these conditions was wrapped in Fiberfrax insulation that had been exposed to moist air (Wet) in order to determine whether the presence of water vapor influenced aging. An anode pellet stored in dry air in a sealed container and several batteries built with dry Fiberfrax and stored at ambient temperature were used as controls. Figure 1a-d shows the DRIFTS spectra from batteries wrapped in dry Fiberfrax (Dry) and aged at the indicated times and temperatures.

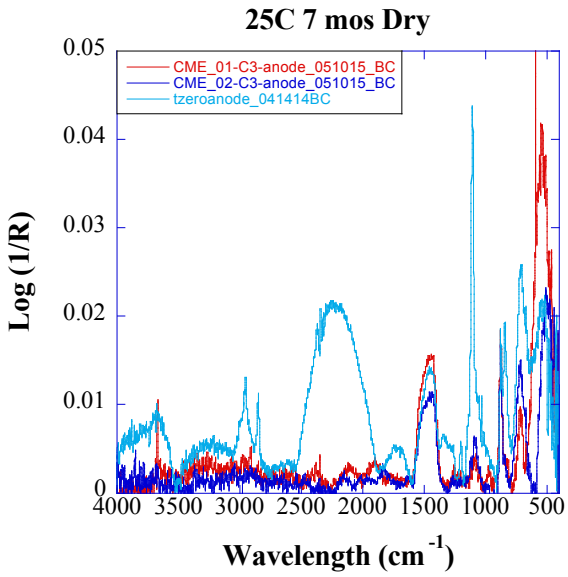

Figure 1a: DRIFTS spectra from anode pellets; tzero light blue not mounted in battery, red and blue aged at 25°C for 7 months.

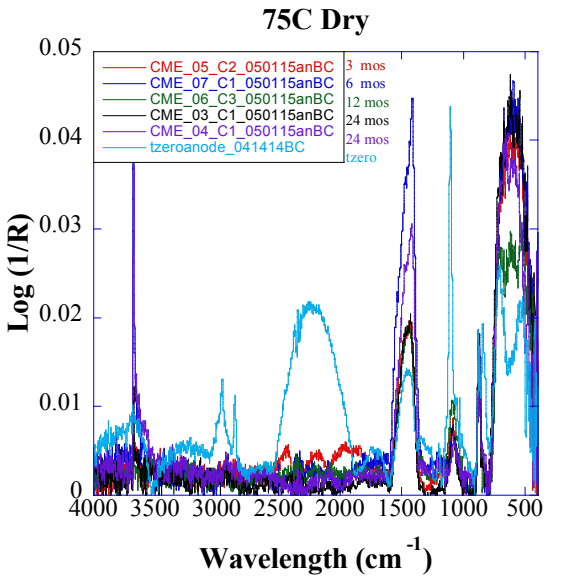

Figure 1b: DRIFTS spectra from anode pellets; tzero light blue not mounted in battery, red 3mos, blue 6 mos, green 12 mos, black and purple 24 mos aged at 75°C.

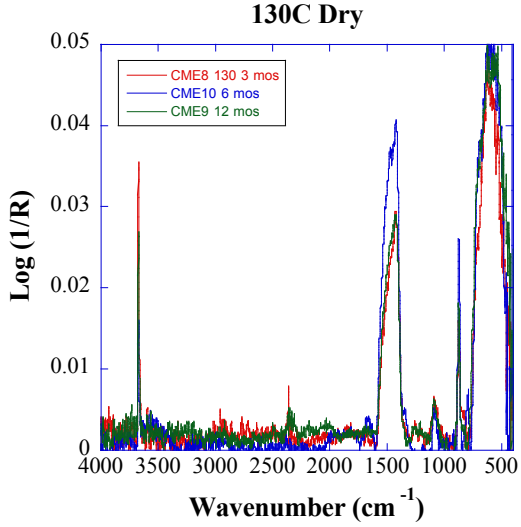

Figure 1c: DRIFTS spreactra from anode pellets; red 3 mos, blue 6 mos, green 12 mos, aged at 130°C.

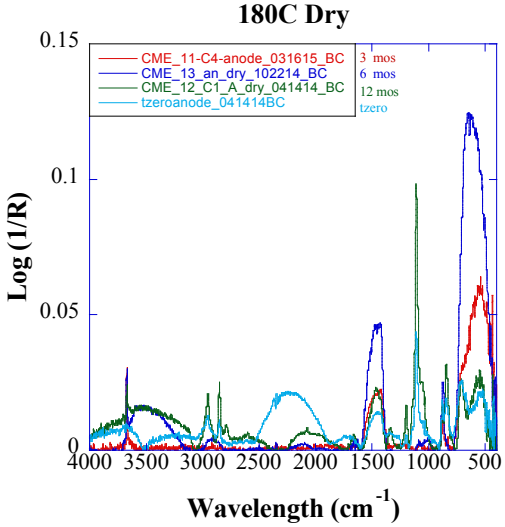

Figure 1d: DRIFTS spectra from anode pellets; tzero light blue not mounted in battery, red 3mos, blue 6 mos, green 12 mos, aged at 180°C.

The tzero pellet, which was not aged inside a sealed battery, displays similar bands to the controls aged at 25°C, although the intensities vary among all the controls. Aging at higher temperatures does not produce additional bands, but again the intensities of the prominent peaks vary with aging time and temperature in a non-monotonic fashion, with the most prominent intensity increases occurring for 180°C (note the scale difference). These random variations in band intensity in the anode pellets are in contrast to the uniform band intensities observed among the catholyte pellets for Dry builds [10]. The random variation observed among the bands in the anode pellets likely occurs because these bands do not belong to the majority anode constituent Li-Si (which does not have active IR modes), but rather to adsorbed species such as H_2O, OH, CO_3^{2-} and C-H.

The DRIFTS spectra obtained from batteries wrapped in Fiberfrax exposed to a moist environment (Wet) and aged at the indicated times and temperatures are shown in Figure 2 a-c.

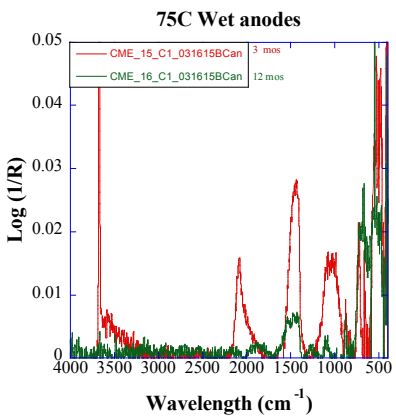

Figure 2a: DRIFTS spectra from anodes aged at 75°C.

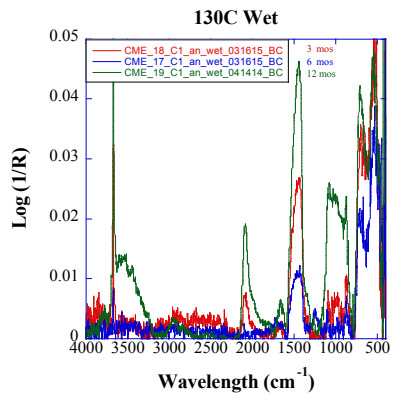

Figure 2b: DRIFTS spectra from anodes aged at 130°C.

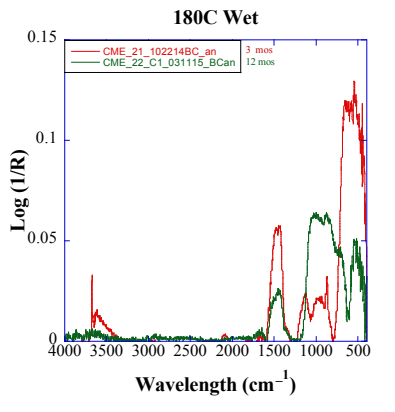

Figure 2c: DRIFTS spectra from anodes aged at 180°C.

The “Wet” anodes aged in batteries with Fiberfrax exposed to a moist environment show similar bands seen in the control and “Dry” aged anodes except for the additional prominent broad peak associated with S-O vibrations observed at 1100 cm^{-1}. In order to discern changes that may have occurred as a result of aging, plots of peak intensity for the dominant bands are shown in Figure 3 a-e.

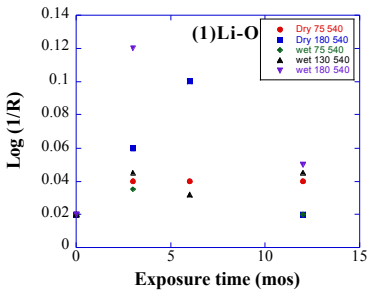

Figure 3a: Peak intensity for Li-O band at 540 cm^{-1}.

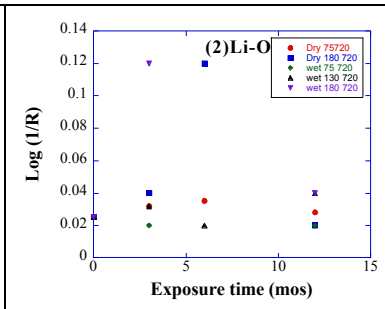

Figure 3b: Peak intensity for Li-O band at 720 cm^{-1}.

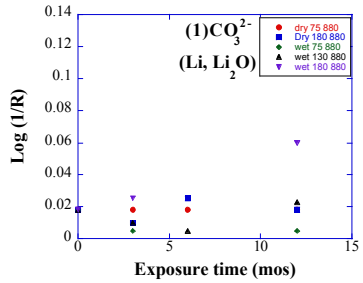

Figure 3c: Peak intensity for CO_3^{2-} band at 880 cm^{-1}.

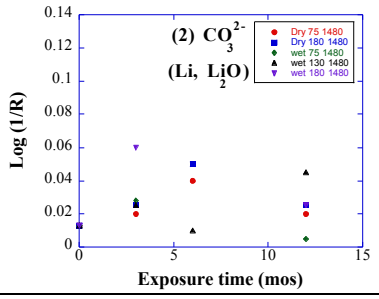

Figure 3d: Peak intensity for CO_3^{2-} band at 1480 cm^{-1}.

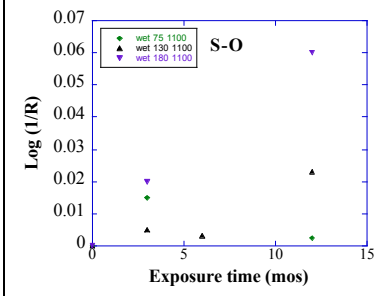

Figure 3e: Peak intensity for S-O band at 1100 cm^{-1}.

The peak intensity plots in Figure 3, which correspond to concentrations of these constituents in the anode, more clearly show that phase evolution does not evolve monotonically as a function of aging time and temperature. Both “Wet” and “Dry” anode builds show high Li-O band intensities for aging at short times at 180°C. The appearance of a broad S-O band at 1100 cm-1 for the wet builds is consistent with the previously reported [9] observation of S in the anode by SEM/EDS and Li_2S in the anode by XRD. These results are consistent with the reaction pathway proposed in [9] which produces Li_2O and Li_2S in the anode as a result of the reaction of Li with H_2O and H_2S respectively. However, similar peak intensities for the Li-O bands are observed in both wet and dry builds, where the availability of water for reaction is expected to be significantly different. The appearance of the S-O band only in wet builds provides further evidence for the H_2S mediated reaction pathway.

Correlation of changes in peak intensity in DRIFTS spectra as a result of aging with loss in discharge capacity enables a more quantitative understanding of aging mechanisms in thermal battery materials. Figure 4 shows correlated a) discharge curves and b) DRIFTS spectra from catholyte pellets, for batteries aged in the presence of water vapor (Wet Fiberfrax) for 6 months at different temperatures. The loss of capacity observed in the discharge curves can be clearly correlated with the loss of active FeS_2 observed in the DRIFTS spectra. For batteries aged at 75°C, although a 5% reduction in capacity is observed in the discharge curve, no reduction in FeS_2 is seen by DRIFTS. This puts a lower limit on changes in active FeS_2 concentration that can be detected by DRIFTS. Batteries aged at 130°C show a good correlation between a 10% loss in capacity observed in the discharge curve and a 12% loss in FeS_2 observed by DRIFTS. Aging

at 180°C results in a 43% loss in capacity according to the discharge curves and a 70% loss of FeS_2 seen in the DRIFTS spectra. The discrepancy here could arise if the FeS_2 particles are reacting on the surface while still maintaining a FeS_2 core that may not be fully penetrated by the IR probe. High-resolution electron microscopy studies of the reaction front would be needed to confirm this hypothesis.

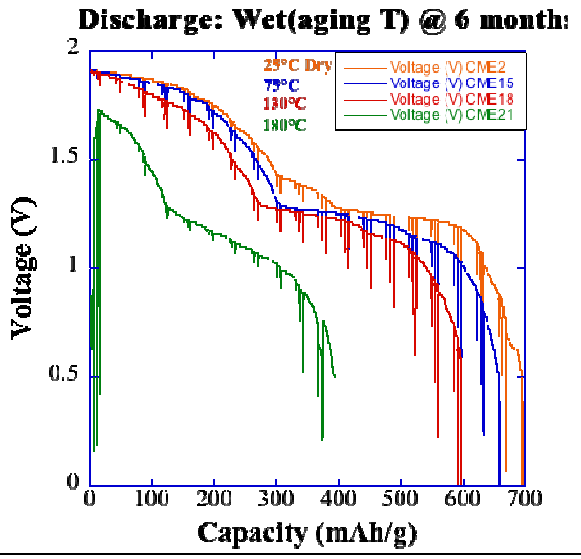

Figure 4a: Discharge spectra from batteries aged with Wet Fiberfrax at different temperatures for 6 months.

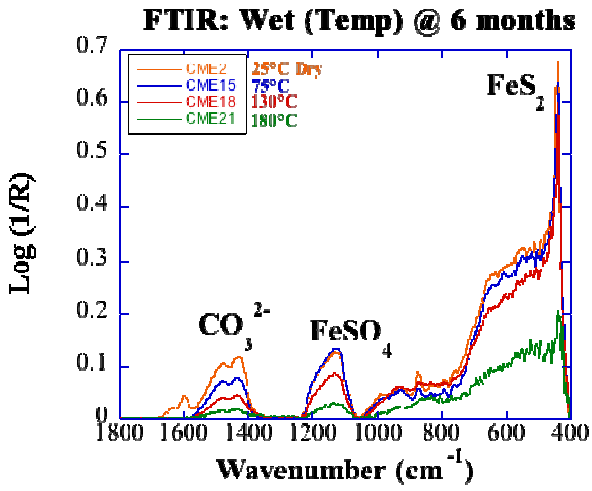

Figure 4b: DRIFTS spectra from catholyte pellets in batteries aged with Wet Fiberfrax at different temperatures for 6 months.

Conclusions and Future Work

Diffuse reflectance IR spectroscopy provides the sensitivity needed to investigate phase content and degradation due to aging in both LiSi anode and FeS_2 cathode materials. Accelerated aging of LiSi/FeS_2-based, simulated MC3816 batteries, show that although significant changes in oxide and sulfur content occur in the anode upon aging, a quantitative measure of the degradation of the active LiSi material could not be assessed by DRIFTS. Observation of sulfur related peaks in the anode after aging in wet environments provide further evidence of the reaction pathway proposed in FY14 [9]. Correlation of the loss of capacity measured by the discharge curves with the loss of active FeS_2 material in the cathode suggest that the main contribution to performance degradation results from loss of active cathode material.

Summary of Findings and Capabilities Related to Aging

Accelerated aging studies of simulated MC3816 batteries show that the presence of water can lead to significant degradation of the active FeS_2 cathode material and degradation of battery performance.

References

[1] J. G. Dunn, W. Gong, D. Shi, Thermochimica Acta, 208, 293 (1992).

[2] J. G. Dunn, W. Gong, D. Shi, Thermochimica Acta, 215, 247 (1993).

[3] M. J. Borda, D. R. Strongin, M. A. Schoonen, Geochimica et Cosmochimica Acta, 68, 1807 (2004).

[4] C. R. Usher, K. W. Paul, J. Narayansamy, J. D. Kubicki, D. L. Sparks, M. A. Schoonen, D. R. Strongin, Environ. Sci. Technol., 39, 7576 (2005).

[5] R. Murphy, D. R. Strongin, Surface Science Reports, 64, 1, (2009).

[6] T. Bajada, Sci. Tot. Environ., 336, 269 (2005).
[7] L. Xin, R. McCreery, J. Electrochem. Soc. 145, 3083, (1998).
[8] R. A. Guidotti, F. M. Reinhardt, SAND83-2271, (1985).
[9] D. Wesolowski, A. Allen, SAND2015-1890; *Thermal Battery Accelerated Aging Study*, in FY2014 SNL Enhanced Surveillance Annual Report: Part 2 – Non-Nuclear Materials R. Stinnett, (2014).
[10] N. Missert, R. Garcia, SAND2015-1890; *Thermal Battery Materials Degradation*, in FY2014 SNL Enhanced Surveillance Annual Report: Part 2 – Non-Nuclear Materials R. Stinnett, (2014).

Administrative Addendum

- **Milestone Status:**

Listing and status of milestones for FY15 subtask plan:

1) Complete IR analysis of anodes in aged simulated MC3816 batteries. COMPLETED
2) Determine IR signatures for LiSi standards. COMPLETED
3) Establish baseline for IR signatures in MC2238A $CaCrO_4$ cathodes. Deferred to FY16
4) Determine reaction pathways in aged simulated MC3815 batteries. COMPLETED

- **Financial Leveraging:**

The work represented was paid for by:

Source	**Dollar Amount ($k)**
Enhanced Surveillance	$110K
Surveillance	
Systems	