

Diagnostic Techniques: Gas/Electrolyte/Cell Component Analysis

Rudolph G. Jungst, Ganesan Nagasubramanian, Chris C. Crafts, and Theodore T. Borek
MS 0613 Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185
Contact: R. G. Jungst, 505/844-1103, fax: 505/844-6972; email: rgjungs@sandia.gov

Objective:

- Understand the mechanisms of performance degradation and interactions of cell components under a variety of conditions.

Approach:

- Develop a suite of analytical techniques and postmortem analysis methods aimed at identifying the generated gas products and measuring gas leak rates, electrolyte breakdown products, electrode delamination, binder breakdown products, etc. The following analytical techniques are either being used or will be evaluated for analysis of the reaction products or breakdown of cell components:
 - 1) For gas analyses: GC, GC/MS, helium leak detection, etc.
 - 2) For electrolyte decomposition: IC, GC, GC/MS, LC/MS
 - 3) For cathode or current collector dissolution: ICP-MS
 - 4) Electrode delamination: visual inspection
 - 5) Separator breakdown: flow porometry
 - 6) Binder breakdown: GPC

Accomplishments:

- A procedure for measuring leak rates of 18650 Li-ion cells was evaluated on both Sony and Gen1 product as part of a general seal analysis. The method was refined and then applied to estimate actual leak rates for the Gen1 cells at both ambient and elevated temperatures. Laser welded seals were recommended for Gen2 cells.
- Electrolyte samples were collected from 10 Gen1 ATD baseline cells and analyses of both the salt and organic solvent were carried out. High LiPF_6 concentrations and indications of solvent reaction were found.
- Inductively coupled plasma-mass spectroscopy (ICP-MS) was applied to both electrolyte and electrode samples from Gen1 cells to look for evidence of cathode dissolution and migration of current collector materials. Initial results show little dissolution after short aging times.
- ICP-MS measurements of lithium content were also made on Gen1 anodes and cathodes to confirm that the SOC range for cycling had not changed significantly after aging.

- A postmortem procedure for 18650 lithium-ion cells has been successfully applied to Gen1 samples for observation of the condition of cell components and recovery of electrode and separator samples for analyses.
- Delamination of cathodes from the aluminum current collector and also anodes from the copper current collector was observed in some thermally aged Gen1 cells.

Future Activity:

- Leak rate measurements on Gen2 trial cells will be carried out to confirm seal quality.
 - The properties of the binder materials in the Gen1 cell and possible interactions with the electrolyte or its breakdown products (swelling, specific absorption, etc.) must be investigated.
 - Measurements of cathode dissolution and migration will be extended to more highly aged Gen1 cells.
 - Analysis of separator samples for porosity changes after aging will be completed.
 - Gel permeation chromatography method development for detection of binder breakdown will be concluded and Gen1 samples analyzed.
 - Analytical methods will be implemented on the Gen2 cells, as diagnostic samples become available.
 - Studies focused on the SEI layers are being initiated.
-

Cell Leak Testing and Seal Analysis

Early in the life test experiments, evidence began to accumulate that ATD Gen1 cells were not hermetic, especially after being exposed to high temperatures. Observations such as discoloration and salt deposits on the cell end caps, solvent odor after cell storage in a closed container, visible accumulation of liquid solvent, and weight loss after high temperature storage were all made at one time or another. However, these manifestations of leakage were seldom observed consistently. Sandia was requested to analyze the seals to see if a cause for the apparent leakage could be determined.

Gen1 and Sony cells were studied for leak behavior by analysis of disassembled parts and by He ingress tests on whole units. Both Gen1 and Sony seals are of similar crimp construction. The bulk seal material in both is polypropylene, but the sealing film found by IR differs: Gen1 uses poly(isobutylene) only while Sony uses a polyamide/rubber mix. Both seal types are affected by temperature.

Earlier oven testing on Sony cells showed a slight change in He ingress within hours, and significant change over several weeks at 70°C. In the later He ingress testing done on new condition Gen1 cells, cells were exposed to He and directly evaluated at that same temperature. The leak rate of Gen1 cells changed significantly from 25°C to 50°C, but less so from 50°C to 70°C, in a matter of hours (see Figure 1). Cells exposed at 70°C did not return to the same 25°C rate, but rather a new higher rate. From this work, using a Varian Leak Detector Turbo 959-50, and referring to related He bombing charts, we

believe that the actual He leak rate through the Gen1 seals increases from 1.0×10^{-6} std cc/sec to 1.0×10^{-5} std cc/sec when the cell goes from 25°C to 70°C .

Standard He Bomb Tests at Temperature

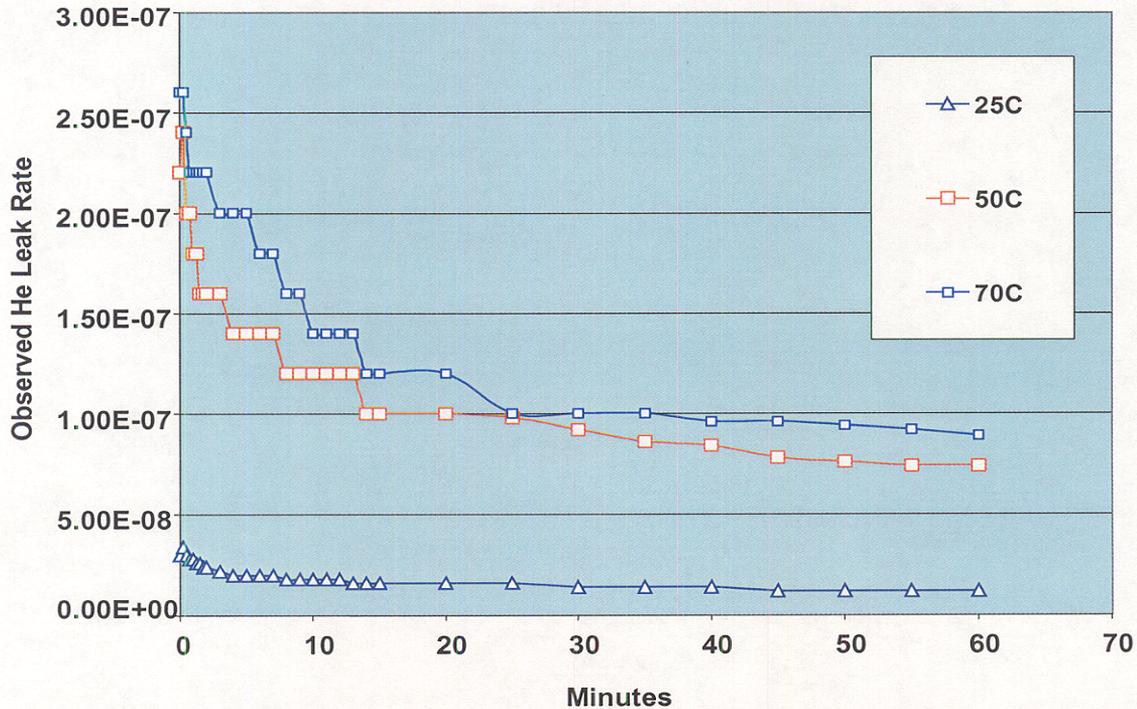


Figure 1. Observed He Leak Rate of a Gen1 Li-Ion Cell at Different Temperatures

Electrolyte Decomposition

Decomposition of the electrolyte in lithium-ion cells is measured by two primary analytical methods: ion chromatography (IC) for the salt, and gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) for the organic solvent. PF_6^- and F^- are quantified using a specialized IC method developed at Sandia for the ATD program, while Li^+ is measured by a standard IC technique. This allows the $\text{Li}^+/\text{PF}_6^-$ ratio to be checked. The instrumental response for PF_6^- is shown to be linear over a wide range of concentrations. Sensitivity for F^- by this method is also good with a detection limit of as little as 6.6 mM in the undiluted electrolyte.

Electrolyte samples were recovered from a number of Gen1 life test cells by centrifuging. Cells stored at 40, 50, and 70°C , cycled and uncycled, were sampled, as well as two control cells that had not been heated or cycled. Figure 2 shows the IC results.

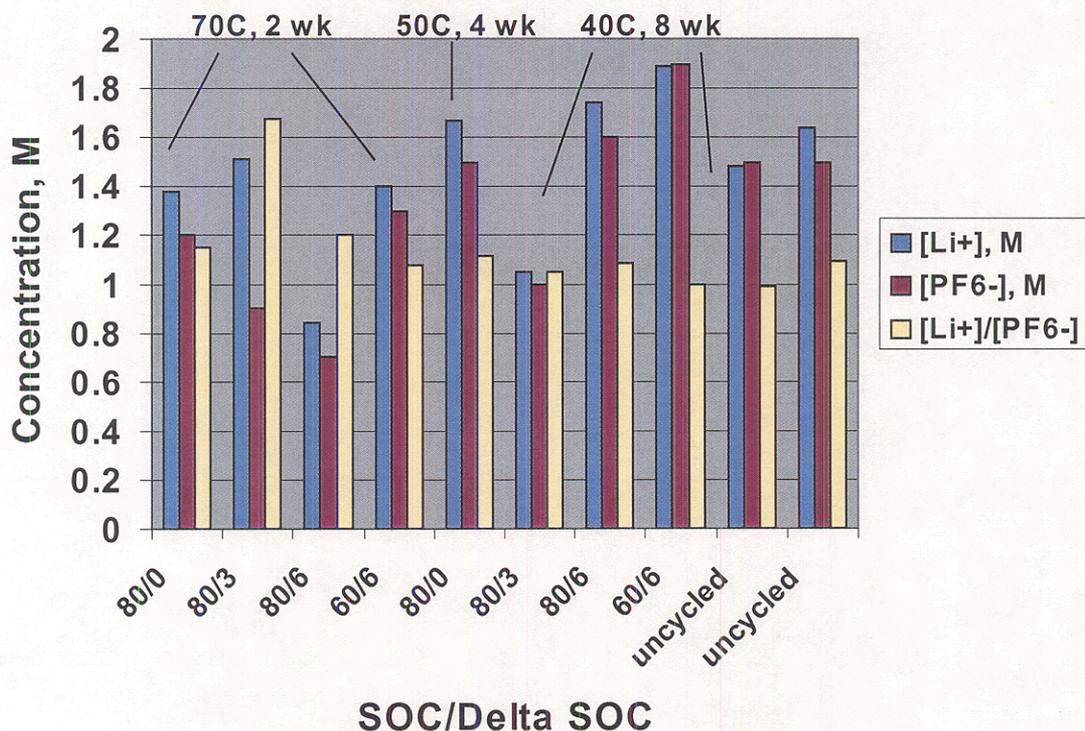


Figure 2. Electrolyte Salt Analysis Results for Gen1 Li-Ion Cells

The Li^+ and PF_6^- concentrations are nearly the same, as expected, but in most cases the salt concentration is considerably above the nominal 1M at which the cell was built. The only significant discrepancy between the Li^+ and PF_6^- results is for one of the 70°C samples, while the highest overall salt concentrations occurred in 40°C samples. If the increased salt concentrations were due to loss of volatile solvent through leaks, this would be expected to be more noticeable at 70°C than at 40°C. Further evidence that leaks are not responsible for the higher LiPF_6 levels is found in the lack of correlation between salt concentration and weight loss, as shown in Figure 3. Small amounts of fluoride (17-89 ppm) were detected in most samples, but there was no consistent trend with the aging conditions.

Companion organic solvent analyses were performed on the same electrolyte samples by GC/FID. This allowed a quantitative analysis of both EC and DEC as well as some of their possible decomposition products. The results of the GC measurements are shown in Figure 4. While the EC/DEC ratio was elevated above 1, especially in the 70°C samples, the DEC response was essentially constant, not what would be expected from a loss through leaks at higher temperatures. Again, there was no correlation with weight change. Both EC and DEC peak area responses on the GC were significantly below what is observed for a bulk sample of electrolyte.

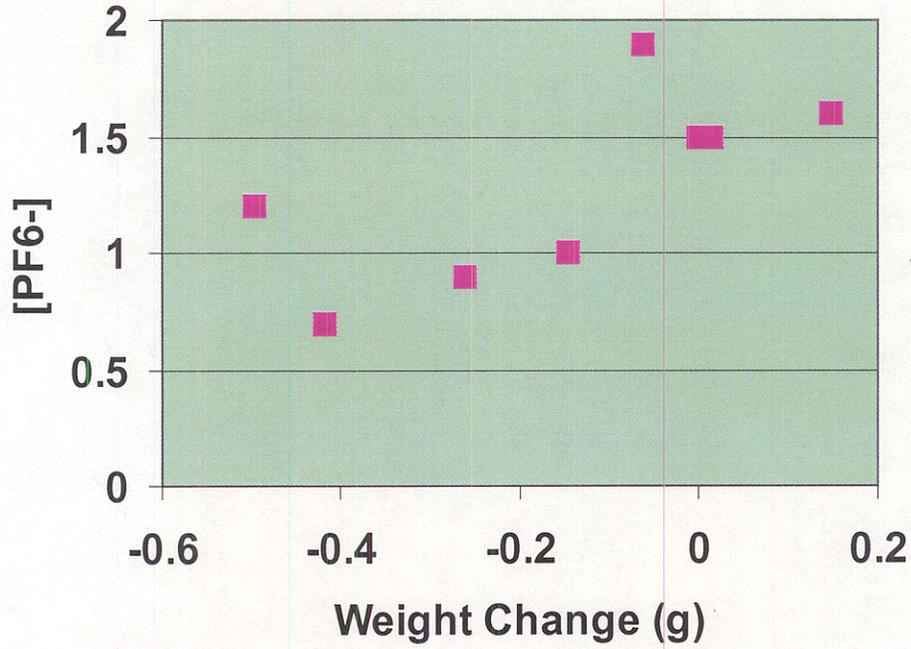


Figure 3. Comparison of PF₆⁻ Concentration with Cell Weight Change

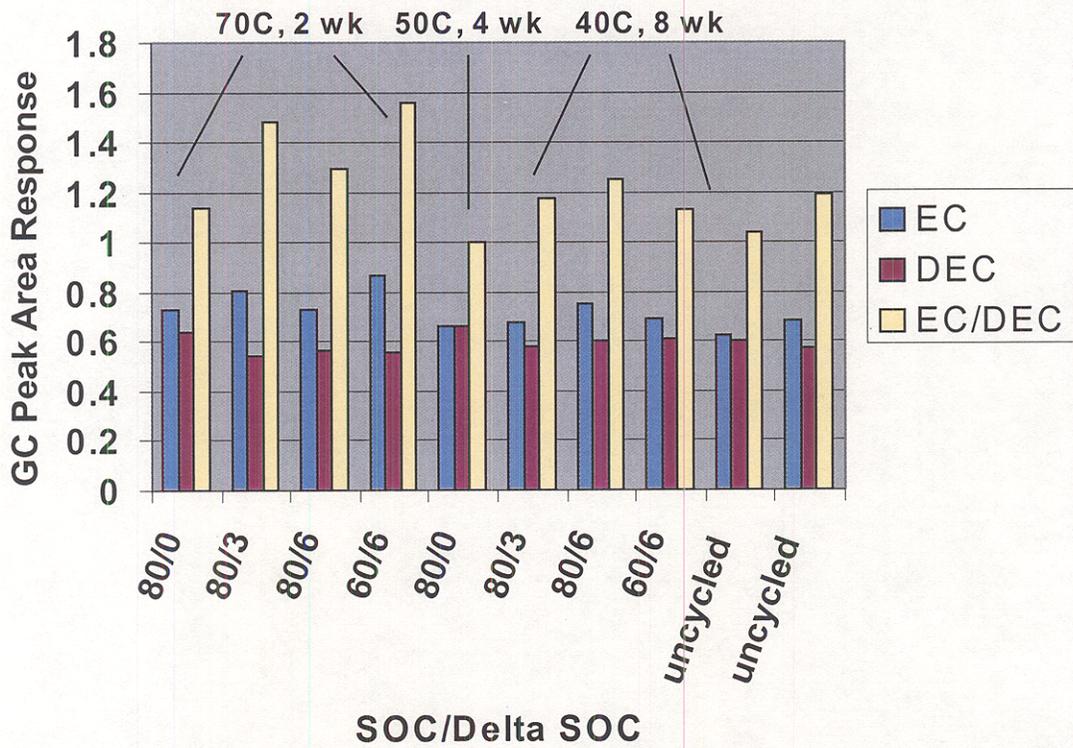


Figure 4. GC Analysis of Organic Solvents in Gen1 Cell Electrolyte

One possible reason for the observed results could be reaction of the solvents with other materials within the cell. This is supported by the observation of one significant new peak (as yet unidentified) in the gas chromatogram. However, this peak appears under all conditions, even in the control cells. Another explanation could be the selective retention of solvents within the electrode binder. PVDF is known to swell in the presence of battery electrolyte, but this behavior has not yet been studied in the context of the ATD program.

Cathode or Current Collector Dissolution

Analysis of the electrode materials and electrolyte by inductively coupled plasma/mass spectrometry (ICP/MS) enables the composition of these cell components to be tracked after various thermal treatments. The primary species of interest relate to the migration of metals from the cathode active material or from the current collectors to other parts of the cell. It is also possible to determine the lithium content of the cathode and anode materials by using this method.

Figure 5 shows the trace metals analysis of typical samples of anode and cathode material. The arrows indicate species of particular interest, namely Cu in the cathode and Al, Ni, and Co in the anode. The 250 ppm Cu concentration in the cathode is the largest of these. However, the largest impurity overall in the cathode is Fe (nearly 1300 ppm), which is an impurity in the lithium. All other metals present are at very low levels. Our initial conclusion is that metal migration is not significant after short storage times at elevated temperature.

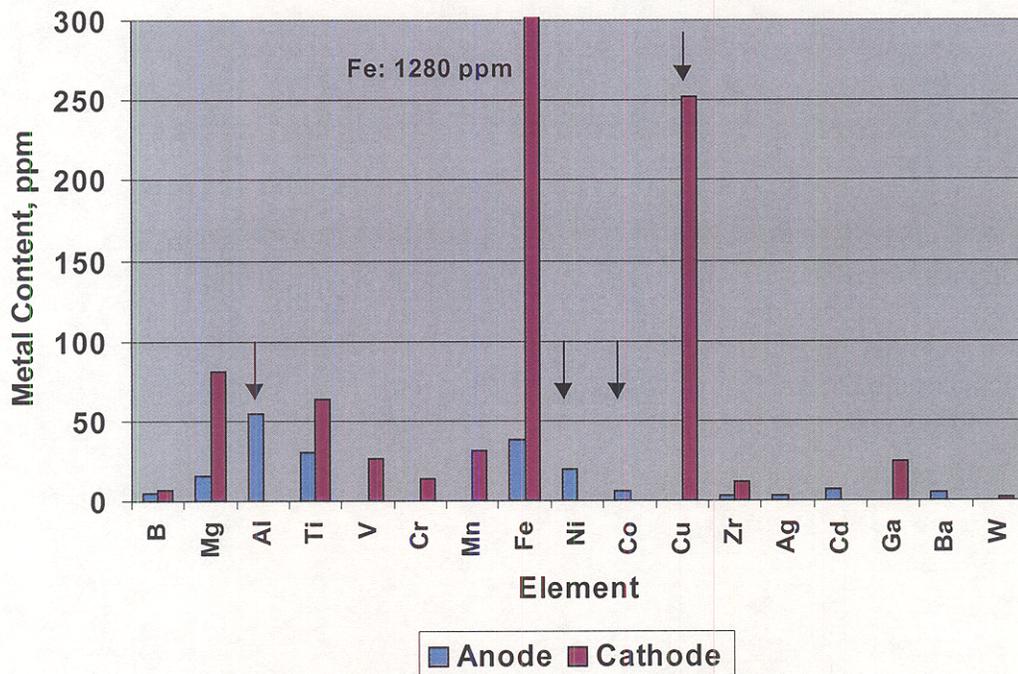


Figure 5. Metals Analysis of Gen1 Cell Electrodes after Life Test at 70°C for 2 Weeks

A similar analysis was done on the 10 electrolyte samples collected from Gen1 cells and the results again showed very low levels of Al, Cu, Ni, and Co. The current collector metals were all less than 2 ppm except for one sample that had an upper limit for aluminum of 3.4 ppm. Nickel ranged from 0.4 to 8.3 ppm and cobalt was less than 0.1 ppm in most samples. These results are consistent with the low values found for the electrodes.

The lithium content of the anodes and cathodes was also determined in the same ICP-MS measurements. A sample of the Sumitomo mixed metal oxide powder was analyzed as a reference point and was found to have a Ni/Co ratio of 85/15 rather than the nominal 80/20 that was expected. The Ni/Co ratio in Gen1 cell cathode material was virtually the same as the powder. Figure 6 shows a comparison of the measured lithium content of the cathode with the amount expected for three cells opened at slightly different states-of-charge. The values agree closely for the three cells that were analyzed, although this test cannot distinguish whether all the lithium is capable of being cycled. X-ray diffraction measurements are being made to confirm whether any new phases are present in the positive active material. Preliminary indications are that the lithium content of the cathode has not shifted noticeably after aging.

Opened Cell Voltage	Aging Conditions	Cathode Lithium Content, Li_x	Estimated Li_x of Unaged Cell at Same SOC
3.48	60°C, 56 day	0.73	0.75
3.28	60°C, 4 weeks	0.82	0.81
3.42	70°C, 2 weeks	0.78	0.77

Figure 6. Lithium Content of Aged Gen1 Cell Cathodes

Electrode Delamination

Visual observations of electrode delamination made during cell postmortems have been recorded. The database is still relatively small at this point, since complete disassembly

has only been done on 12 cells. Instances of major delamination have been observed for both the anode and the cathode. Cells not showing delamination were mostly either unaged or stored at 50°C in the life test. Most of the opened cells that were stored at 70°C show major amounts of delamination. Therefore, the preliminary conclusion is that a positive relation exists between delamination and storage temperature. Information on observations of delamination is being collected from the other laboratories working on the ATD program to put together a more comprehensive picture of its occurrence.

Separator and Binder Breakdown

Separator porosity is influenced by elevated temperature and complete shutdown should occur in the vicinity of 120 – 130°C. Characterization of the pore size of the separator can be done by using flow porometry and a trial measurement has been carried out on a sample of the virgin material to demonstrate this capability. Results are shown in Figure 7. The bubble point pore diameter indicates the largest detected pore and was 0.028 microns for this sample. Separator samples have been obtained from some of the life test cells and porosity measurements for these are in progress.

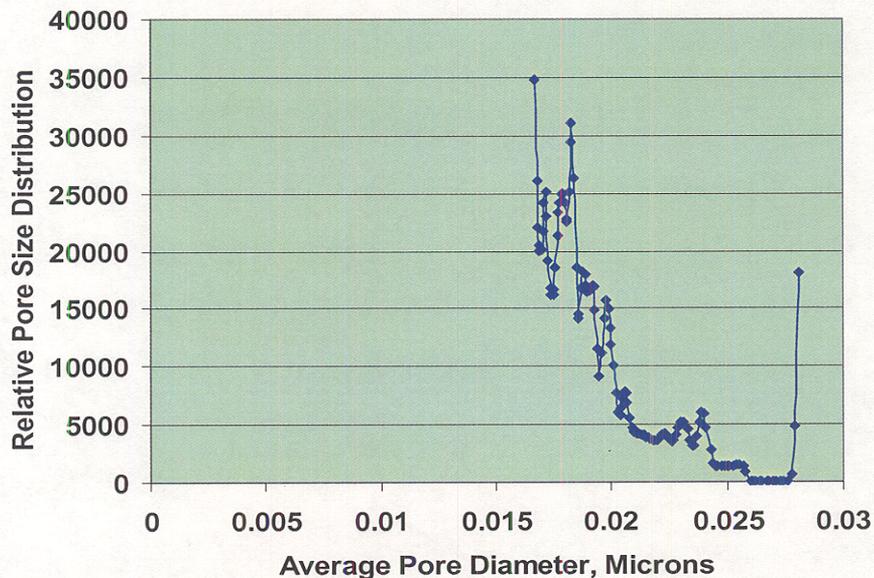


Figure 7. Capillary Flow Analysis of a Virgin Sample of the Gen1 Separator

Breakdown of the polymeric structure of the binder should be detectable by dissolving the PVDF from an electrode and analyzing the material by gel permeation chromatography (GPC). Feasibility trials are still in progress for the GPC technique.

Future Work

Diagnostic measurements remain to be completed on the Gen1 cells. This includes an investigation of the reasons for the high concentration of electrolyte salt found in both Sony and Gen1 cells. Possible interactions or selective absorption of electrolyte constituents by the binder or other cell components will be studied. Measurements of the migration of current collector or cathode materials within the cell will be extended to samples that have been stored at elevated temperature for longer periods of time. Tests of separator porosity and binder breakdown must also be completed. Leak rate evaluations will be performed on Gen2 trial cells as requested in order to confirm that the seals are indeed leak tight. The major diagnostics effort in the latter part of the next year will be to apply the developed techniques to analysis of the Gen2 cells after they have been subjected to life tests.

Acknowledgements

The Sandia Analytical Laboratory supports the ATD program by performing headspace gas sampling and analysis, electrolyte analysis for organic and inorganic constituents, and inorganic analysis of cathode and anode materials. Specialized methods for determining the electrolyte salt concentration were developed by members of the Explosive Materials/Subsystems Department. Postmortems of lithium-ion cells and collection of component samples were done by the Sandia Lithium Battery R&D Department. We are grateful to the following individuals for performing the indicated analyses: T. T. Borek (GC/MS), S. E. Klassen and E. P. Boespflug (IC), J. E. Reich (ICP-MS), M. J. Russell (cell postmortem and leak rate measurements), and H. L. Case (postmortem sample collection and distribution).

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.