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Fabrication and Testing Capabilities for 18650 Li/$(CF_x)_n$ Cells

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Sandia National Laboratories has world-class facilities for building and testing lithium and lithium-ion batteries. In this article we describe the in-house facilities for fabricating electrodes and cells in detail. Our in-house facility includes equipment for: 1) electrode coating, 2) electrode slitting, 3) electrode winding, 4) cell grooving, 5) electrolyte filling, 6) cell crimping and more. We also have a 48-channel Maccor tester and several impedance units for electrochemical characterization. These facilities provide flexibility for cell fabrication techniques which in turn allows us to continually improve cell performance. Under an internally funded program we are developing in-house capability to fabricate and evaluate 18650 Li/$(CF_x)_n$ cells using "Li-ion" electrode fabrication methodologies to prepare the thin film $(CF_x)_n$ electrodes. At a C/400 discharge rate cell delivered ~3.6 Ahrs capacity. We also evaluated cathodes of two different lengths for uniformity of loading. The loading along the electrode length was found to be extremely uniform, as the delivered capacity was proportional to cathode length. For example, a 0.91 meters long x 4.2 mil thick electrode gave 3.6 Ahrs capacity while a 0.72 meters long x 4.2 mil thick electrode (19.4% less length) gave 2.9 Ahr of capacity (19.4% less capacity). We also discharged the cells with 0.71 meters long electrodes at different temperatures. The cells delivered practically the same capacity over temperatures from 25 to 72°C. At -20°C the cells delivered 81% of the room temperature capacity at a C/200 rate; however, at -40°C the cells delivered close to 47% of the room temperature capacity under similar test conditions. The performance behavior of 18650 cells will be discussed in more detail in the paper.

Keywords: $(CF_x)_n$ = Carbon Monofluoride; capacity; self-discharge; PVDF; electrical testing; primary battery

1. INTRODUCTION

Sandia National Laboratories (SNL) has responsibility for the design and production of several power sources required to serve the national interest. SNL also maintains extensive research and development facilities in support of these activities. As a result, SNL has invested $10s of millions

over the past decade to develop infrastructure related to all aspects of power source development and production. This Section motivates the work performed on Li/$(CF_x)_n$ electrodes fabricated in-house, while Section 2 describes the resources available in-house that are specific to fabrication of Li-ion and Li/$(CF_x)_n$ chemistries. The single cell performance test results are provided in Section 3, and the paper is summarized in Section 4.

Interest in the Li/$(CF_x)_n$ chemistry is burgeoning lately for applications requiring long life, light weight and very low self-discharge because it yields the highest theoretical specific energy of any lithium primary chemistry (see Table 1). Self-discharge is on the order of <0.5 % per year near room temperature (1). These and other positive attributes such as its small voltage delay, cell safety, and lower weight* are expanding interest in this chemistry into new application areas. For example, the US Army is looking into the possibility of using Li/$(CF_x)_n$ cells to meet Land Warrior and Dismounted Soldier power requirements (2). Other US government organizations such as NASA and the CIA are considering this technology for celestial and terrestrial applications, respectively. In many of applications, battery safety is critical, as in confined areas such as in submarines. The US Navy evaluated the safety of the Li/$(CF_x)_n$ cells for the Navy use. According to US Navy 9310 Safety Testing, Li/$(CF_x)_n$ batteries under specified electrical abuse test conditions produced benign results (3).

Table 1. Comparison of theoretical and practical energy values for the four Li primary chemistries.

Chemistry	Voltage (V)	Specific Energy (Whr/kg)	
		Theoretical	Practical
$LiCF_x$	3.2	2.260	220
$LiMnO_2$	3.0	1.005	200-270
$LiSOCl_2$	3.6	1.470	430
$LiSO_2$	3.0	1.170	240

Even with all these favorable characteristics, however, this chemistry has been unsuccessful in challenging other primary chemistries in terms of commercial market penetration. For over 30 years Li/$(CF_x)_n$ has been resigned to low-current drain applications due to its poor performance at low temperatures and high discharge rates. For example, the practical capacity for this chemistry is only ~10% of the theoretical at moderate discharge rates (see Table 1). We hypothesized that these problems are aggravated partly by the use of thicker electrodes (> 40 mil thick) which contain Teflon as a binder material. The use of thick electrodes and larger amounts of electrically insulating binder materials increases the series resistance and concomitant IR drop inside the battery, which results in the precipitous drop in capacity at lower temperatures. Thinner electrodes are not currently commercially fabricated because there is no commercial need for cells with improved low temperature performance.

* Typically a 4-Ahr 18650 Li/$(CF_x)_n$ cell weighs ~28 grams which is ~ 14 grams lower than the weight of a 2.5-Ahr same size Li-ion cell.

In order to test this hypothesis, we have leveraged Sandia's capabilities in fabricating Li-ion cells with thinner coatings to address this problem by fabricating thinner electrodes. We fabricated $(CF_x)_n$ electrodes 4.2 mil (0.1 millimeters) thick (10x thinner than current standard commercial technology) and measured the discharge performance at low temperatures, which will be described in Section 3. The extensive facilities described in Section 2 below have allowed us to adapt and fine-tune Li-ion methodologies to prepare and tailor the properties of thin film $(CF_x)_n$ electrodes as desired. Without these facilities we would have been forced to depend on commercial battery manufacturers where the freedom of doing basic research and development on this important chemistry would have been severely restricted.

2. FABRICATION OF $(CF_x)_n$ 18650 CELLS USING SNL's IN-HOUSE FACILITIES

In previous Li-ion cell work, two different PVDF binders had been used. Kureha W#1300 was used to bind the cathode material, while Kureha W#9200 was used for the anode. In the case of Li/$(CF_x)_n$ cells, the anode is metallic lithium, and does not require a binder. Since $(CF_x)_n$ is a cathode material, the first thought for choice of binder would be the Kureha W#1300. On the other hand, Kureha W#9200 might also be a good choice, since one of the discharge products of this chemistry is carbon. It was not clear initially which one of the binders was likely to work better for the $(CF_x)_n$ based on the Li-ion work. Therefore electrodes were prepared using each binder and tested in a single cell configuration. The electrical data suggested that the Kureha W#9200 binder may be more suitable, and thus was used in the experiments described below. The inferior performance of cells with W#1300 binder might have come from the poor adhesion of the active material to the electrode. Electrodes were coated on both sides of an aluminum current collector (12 microns thick) with a 3 micron carbon coating on each side (InteliCoat, South Hadley, MA, USA). We found that a thin coating of carbon is necessary to promote adhesion of the $(CF_x)_n$ onto the Al current collector.

2.1. Recipe for making slurry for the $(CF_x)_n$ cathode

The properties of the slurry, particularly the viscosity and particle size, greatly impacted the quality of the electrode and subsequent electrochemical performance. Slurries were made with extreme care to achieve the properties necessary for making reproducible electrodes. The slurry was prepared on a BYK AE High Speed Dissolver Dispermat AE1-M. Typically, 7.5 gm of PVDF was dissolved in 200 ml of N-Methyl-2- Pyrrolidinone (NMP). To this solution were added 7.5 gm of acetylene black and 50 ml additional NMP, and the mixture was stirred for 20 minutes. Finally, 135 gm of $(CF_x)_n$ were added and the mixture was stirred at 3200 RPM for 1hour. The viscosity of the slurry was measured to be between 230-240 cP using a BYK-Gardner USA Cap Viscometer, Model# Cap 2000+. The aggregate particle size of the slurry was measured using a Hegman-Fitness-of-Grind gage. The optimum aggregate particle size of the slurry was typically around 3-5 microns, which we found to be ideal for fabrication of reproducible electrodes. Typical optimized slurry composition was 90 w% $(CF_x)_n$, 5w% PVDF, and 5 w% acetylene black.

2.2. $(CF_x)_n$ Electrode Coating

A Hohsen (Osaka, Japan) Electrode Coater, shown on the right, was used to apply and heat-treat coatings. The oven was preheated to 130°C to evaporate off the NMP solvent. The as-coated cathodes were ~130 mm wide and several meters long. Typically the active material coatings were 2.1 mils thick on each side of the current collector. The average total electrode thickness of the dry electrode was around 4.9 mils (including the current collector). Prior to rolling, the electrode was cut to length by hand and then slit the 130 mm to 50 mm wide in a Hohsen slitter (not shown). The electrode was baked at 100°C overnight and kept in a dry room (dew point -40°C or better).

Photo 1. Hohsen Electrode Coater

2.3. Anode

For 18650 cells, thin lithium electrodes specially made with copper cladding are employed as the anode (Furukawa, Japan). The copper is 8-10 microns thick with a 20-micron Li film vapor deposited on each side (see Photo 2). The Cu cladding was necessary to withstand the tension applied while winding the cell. A nickel tab was normally cold-welded to the anode before winding.

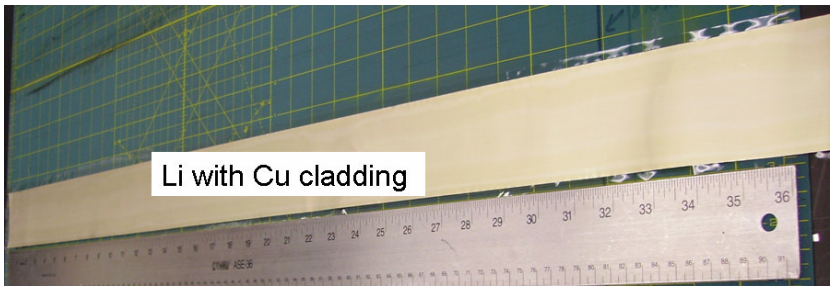

Photo 2. Li electrode with Cu cladding

2.4. Cathode

The photo on the right (Photo 3) shows the $(CF_x)_n$ electrode coated at Sandia. This electrode has been cut to length, slit to width and baked at 100°C overnight. After baking the electrodes remain in a dry room (dew point -40°C or better).

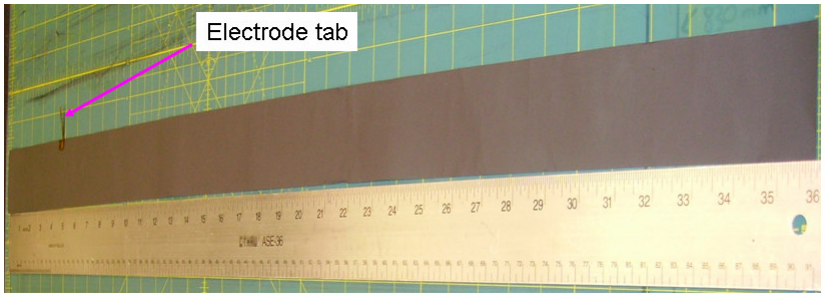

Photo 3. SNL $(CF_x)_n$ electrode with tab welded ultrasonically

2.5. Ultrasonic Welding

Before attaching the current collector tab to the cathode, a small area (2mm x 5mm) of the coating was dissolved using NMP as the solvent approximately 10 cm from one end of the electrode. The area was wiped clean of any residue before baking again in vacuum at 100°C overnight in a National Appliance Company Vacuum Oven (Model #5861). Finally, the tab was attached for electrical contact (see photo 4) using an Ametek Ultrasonic Welder.

Photo 4. Amtech Ultrasonic Welder

2.6. Cell Winding

The photo 5 on the right shows a semi-automatic Hohsen winder that we used for winding cell rolls. For the 18650 cells 54-mm wide anodes, 50-mm wide cathodes, and 58-mm wide Celgard (North Carolina, USA) 2325 separators were used. Since the anode is on the outside of the roll it is longer

than the cathode by about 4-5 cm. Initially we were building cells that have typically 0.91 meters long cathode electrodes.

Recently we started using a new semi-automatic winder from Hohsen (photo 6). This machine can take a maximum electrode length of only 0.81 meters which is 10 cm shy of the other machine described above. The capacity of 18650 cells made with this winder is somewhat less (around 3 Ahr).

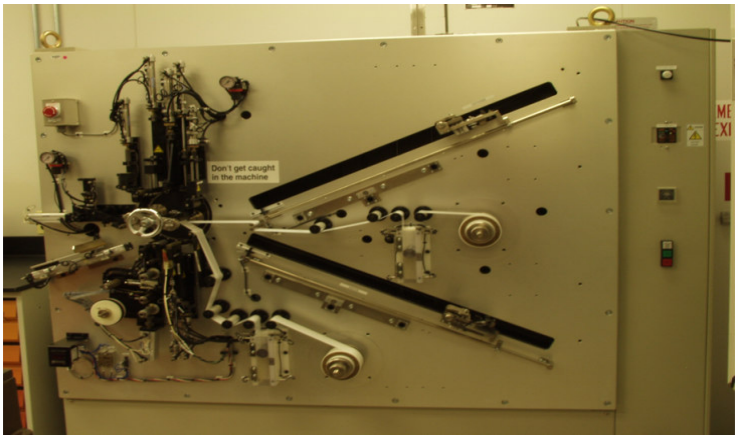

Photo 5. Cell Winder for winding cell rolls for 18650 cells

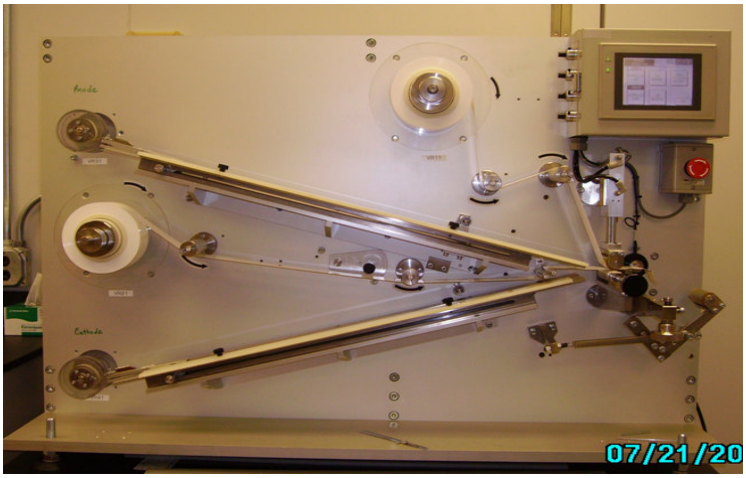

Photo 6. Hohsen manual winder

2.7. Cell Grooving

The anode tab was spot-welded to the bottom of the 18650-can through the central mandrel hole and the can was grooved just above the roll to prevent the roll from sliding out of the can. The cell grooving was accomplished using the machine shown in photo 7. After grooving, the header (consisting of a burst disc, polypropylene-type cup, Ni washer as replacement for the PTC current

controlling device) was attached to the cathode tab using the Amtech ultrasonic welder described above.

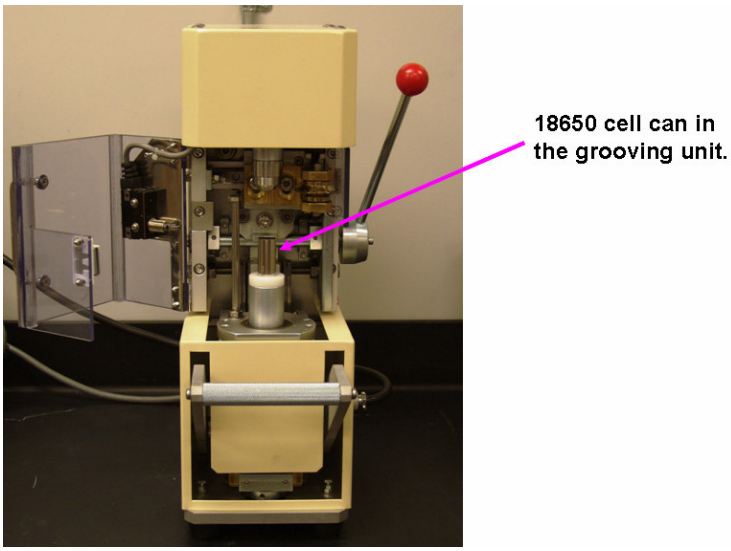

Photo 7. Cell Groover

2.8. Cell Filling and Crimping

After attaching the header, the cells were moved into an Argon atmosphere glove box for electrolyte filling and crimping. Cells took approximately 3.2 ml of electrolyte. After filling, the cells were crimped and the open circuit voltage was measured to insure against shorting. Before testing for capacity or impedance, the cells were kept at 40°C overnight to allow for soaking of the electrolyte into the cathode bulk. A finished cell is shown below in photo 8.

Photo 8. SNL-Built 18650 Li/$(CF_x)_n$ Cell

3. RESULTS AND DISCUSSION

The 18650 cells were evaluated for capacity at different temperatures in EC:PC:EMC (1:1:3 w%)- 1 M $LiBF_4$ (Sandia Electrolyte, "SNL-E"). The ionic conductivity of SNL-E is ~4-5 mS/cm at and near room temperature.

3.1. Improvement in Delivered Capacity in 18650 cells

Figure 1 shows the evolution of delivered capacity in 18650 cells. The cells compared in Figure 1 all have 0.91 meters long cathodes. Although the initial capacity was around 1.5 Ahrs, the delivered capacity increased to 3.6 Ahrs by optimizing the electrode quality, thickness etc. The key to improving the discharge capacity of the cell was found to be related to the rheology of the cathode slurry. The process of optimization of properties of the slurry, such as the viscosity, aggregate particle size, etc. took several iterations to obtain the optimum mix of properties. The slurry that repeatedly gave the best performance had a viscosity of ~230 cP and an aggregate particle size of <5 μm.

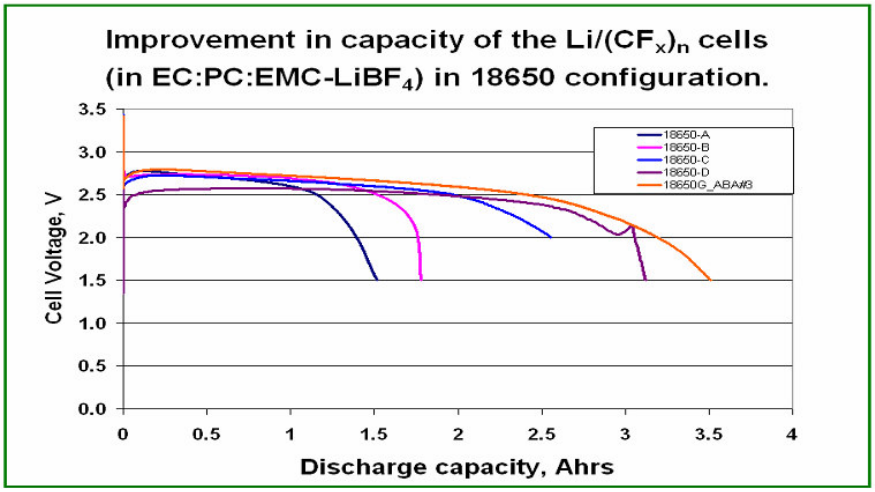

Figure 1. Improvement in 18650 cell capacity obtained at 25°C in SNL-E

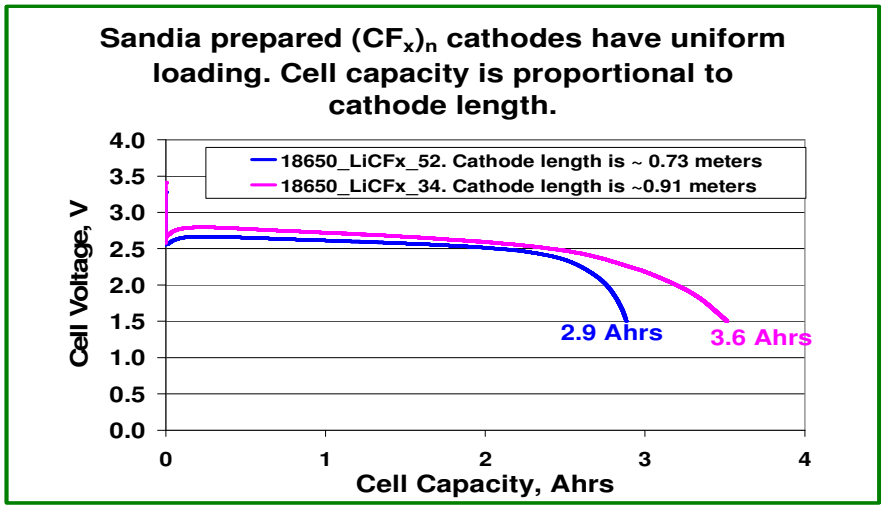

Figure 2. compares the discharge capacity of these cells discharged at 10 mA.

We also checked for uniformity of electrode loading across the length of the electrode. We made 18650 cells with cathodes of different lengths (0.91 and 0.81 meters).

The discharge capacity was found to be proportional to the cathode length. The longer electrode (0.91 meters gave 3.6 Ahrs and the shorter (0.81 meters long) 2.9 Ahrs. The 19.4% reduction in length resulted in a 19.4% reduction in capacity indicating that the full electrode length was active in the cell. In addition, the operating voltage for the cell with shorter electrode is slightly lower than that with the longer electrode. This is expected since for the same discharge current (10 mA), the current density is higher for shorter electrode (13.6 $\mu A/cm^2$) than for the longer electrode (10.9 $\mu A/cm^2$).

3.2. Temperature Performance

We also evaluated the discharge capacity of cells at different temperatures. The cells were discharged at a 15 mA current. No change in delivered capacity was observed in the temperature regime from 25 to 72°C. At -20°C, however, the cells only delivered 81% of the room temperature capacity, while at -40°C the cells delivered close to 47% of the room temperature capacity. These results are significant in comparison to the performance of the commercial cells at low temperatures. Recall that at low temperatures commercial $(CF_x)_n$ cells deliver <10% of the room temperature capacity.

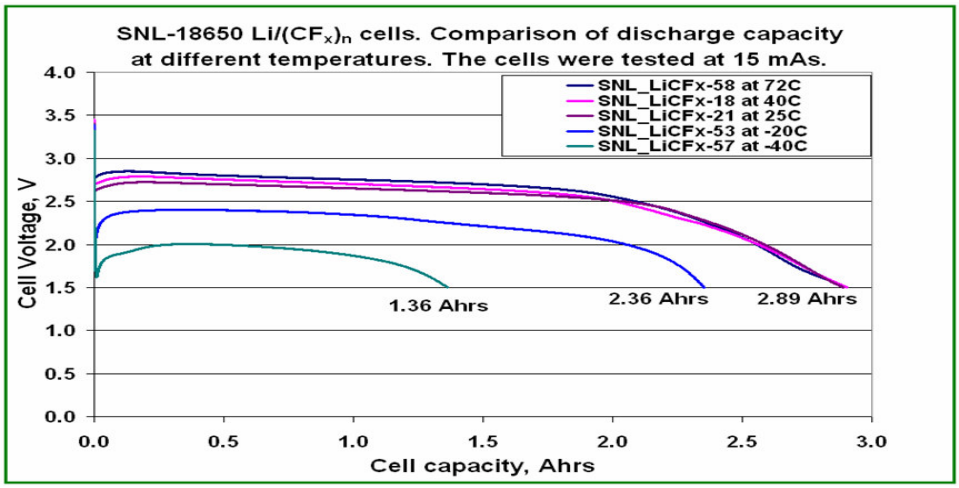

Figure 3. Discharge capacity at different temperatures

4. SUMMARY

The goal of this work is to produce a robust Li/$(CF_x)_n$ battery for Sandia internal applications. Sandia National Laboratories has invested in developing a large infrastructure to address power source R&D problems for niche applications. We have successfully demonstrated the adaptation of Li-ion electrode preparation methodologies to $(CF_x)_n$ electrode fabrication. A suitable binder material (Kureha W#3200) was identified for use as a cathode binder material. 18650 cells were fabricated in-house using SNL-prepared electrodes. Several different combinations of electrode compositions, thicknesses, binder materials, etc. were evaluated to develop electrodes with reproducible behavior. We showed that the electrodes have uniform loading across the electrode length. We obtained as high

as 3.6 Ahr capacity in 18650 cells. We also measured cell capacity at different temperatures. Between 72 and 25°C the discharge capacity was essentially the same. At -20°C, the capacity dropped to 81% of the room temperature value, and at -40°C it decreased to 47%, which represents about a five-fold improvement over current state-of-the-art of commercial cells. We will continue our efforts to improve the low temperature performance by minimizing the impedance, improving the thermal stability, etc by fine-tuning the chemistry.

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References

1. Handbook of Batteries 2nd Edition, David Linden, Editor: McGraw Hill, New York, p14.68, 1998.
2. Arek Suszko, RDECOM, CERDEC, Army Power Division, Fort Monmouth, NJ personal communication.
3. US Navy Technical Manual , S9310-AQ-SAF-010 issued on August 19, 2004