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Abuse Testing Results From Symmetric Carbon/Carbon Acetonitrile Electrolyte Supercapacitors Using Over Voltage and Over Temperature Environments

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Abstract. Over-voltage and over-temperature testing was conducted on symmetrical electrochemical capacitor cells from NessCap employing acetonitrile-based electrolyte. The objective of this work was to identify the failure process and the chemical composition of the vented gasses from the supercapacitors. Over-voltage testing was done by charging the cell at a constant current of 80 amps until the cell vented. Over-temperature testing increased the cell temperature of fully charged cells at 5°C/min until the cell vented. In two over-voltage tests the cells vented at 3.60 volts at 65°C and 2.90 volts at 97°C. In three over-temperature tests the cells vented at 1.65 volts at 169°C, 2.10 volts at 131°C, and 2.20 volts at 106°C. Analysis of vented gasses using a Residual Gas Analyzer Mass Spectrometer (RGA-MS), Fourier Transform Infrared Spectrometer (FTIR), Drager diffusion tubes, and soda-lime tubes for hydrogen cyanide (HCN) measurements indicate that acetonitrile, carbon dioxide, and hydrogen were the dominate gases evolved. Trace amounts of hydrogen cyanide was observed by the soda-lime tubes during the test, however, neither the RGA-MS or Drager diffusion tubes indicated the presence of this compound. In one of the over-voltage and over-temperature tests a spark gap ignition source was used. The ignition source initiated a fireball followed by continued flames from the capacitor at the vent site.

Introduction

This work was done as part of the U.S. Department of Energy (DOE) Energy Storage Program. The DOE Energy Storage Program provides support to develop and evaluate integrated energy storage systems involving batteries, superconducting magnetic energy storage (SMES), flywheels, super capacitors and other advanced energy storage devices. In addition to energy storage devices, the DOE program supports improvements in multi-use power electronics, controls, and communications components. An important part of this work includes analyzing and comparing technologies and application requirements with participation from industry, academia, research organizations and regulatory agencies.

Many supercapacitors now available use acetonitrile (CH_3CN) as the solvent for a number of mixed salts in the tetraalkylammonium group with PF_6^- or BF_4^- anions.[1] The acetonitrile (AN) solvent is highly flammable, easily absorbed into the body, and can decompose into hydrogen cyanide (HCN) under the right conditions. The added salts in the AN may also pose some risks because of the fluorine additions. The work reported in this paper is part of our effort to

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characterize the hazards associated with the use of AN-based electrolyte in symmetric carbon/carbon supercapacitors for utility applications.

A review of the available literature reported in the European Union Risk Assessment Report [2] identified a number of ways that AN can be hazardous. By all accounts AN is a highly flammable solvent that can easily be absorbed into the body through the skin and lungs. Once in the body, the solvent metabolizes such that the most toxic component is HCN. The NFPA hazard ratings identify acetonitrile at a hazard level #2 for health and #3 for fire on a scale of 0 to 4. The OSHA TWA exposure limit is 40 ppm and the NIOSH recommended TWA is 20 ppm.[3] Human exposure studies indicated that health effects in some volunteers began at 160 ppm for a 4-hour exposure. In all low level exposure studies there was no indication of any long term effects.

An Oak Ridge National Laboratory report, “Pyrolysis and Combustion of Acetonitrile (CH3CN),” [4] measures the products of pyrolysis under various conditions. The results of this work identified a number of conditions that would result in elevated levels of HCN. The worst case scenario is one in which there is no or very little oxygen at temperatures near 1,000°C. According to this report, the HCN yield can be as high as 90% in an oxygen starved high temperature environment. As the oxygen and reaction times increase, the percent of HCN yield is decreased to 0%. Because of this dependence on temperature, oxygen level and reaction time, the HCN yield in a supercapacitor would be difficult to predict. Previous abuse testing [5] measured only trace amounts of HCN from supercapacitors in over-temperature and over-charge conditions. The work reported here supports previous results but also indicates that the generation of HCN may be affected by internal capacitor temperature before and after venting. There is also no evidence of any hazardous gasses released by the tetraalkylammonium based salts.

Test Procedure

In Figure 1 is a photograph of the test setup for both the over-voltage and over-temperature testing of the Nesscap symmetric carbon/carbon AN-based electrolyte supercapacitors. The maximum operational voltage of the capacitor is 2.7 volts with a capacitance of 3,500 Farads. Voltage, current, and temperature were measured with National Instruments components during the test. The test was recorded with two Sony video cameras. Qualitative real-time gas analysis was accomplished with a Residual Gas Analyzer (RGA-MS) and a Fourier Transform Infrared Spectrometer (FTIR). Drager diffusion tubes were utilized to indicate the presence of HCN gas (20 – 200 ppm) through color changes in the tube both inside and directly outside of the enclosed 45.7 cm square (18” square) clear plastic test chamber. An additional video camera was trained on the Drager diffusion tubes for remote indication of HCN. The placement of the diffusion tube was inside the plastic test enclosure at the back of the box away from the venting gases. The enclosure air was drawn through the soda-lime tubes to measure the presence of HCN near the point of venting.[6] The soda-lime tubes had a pump rate of 0.2 l/min. of gas during the acetonitrile venting interval. In addition, a spark ignition source was provided near the vent on one of the over-voltage and over-temperature tests.

Figure 1: Supercap Test Setup

The capacitor was charged from 0 to 2.7 volts (100% SOC) just prior to all tests. In over-voltage tests the charge rate was 80 amps. Voltage was allowed to rise as needed to maintain the charge rate. In the over-temperature tests, a brass block was fitted with four cartridge heaters, one in each side that runs length-wise. A thermocouple was inserted into the front face of the top brass block that enables a Labview program to control the heating rate during the test. The heat block/Labview system was programmed to raise the capacitor temperature approx. 5°C/min in a continuous fashion to the point of venting, or in the last over-temperature test the capacitor was heated to a maximum temperature of 250°C. Capacitor temperatures were measured with three thermocouples. Thermocouples were placed on the terminal end, on the side in the middle, and on the bottom, i.e., the non-terminal end.

Test Results

Over-voltage Tests

After the capacitor was charged to 2.7 volts, an 80 amp charge was initiated. Two over-voltage tests were performed: (#1) charged with a compliance voltage of 5V and no ignition source; (#2) charged with a compliance voltage of 10V and an ignition source. The cell voltage rose quickly to 3.6 volts where it briefly plateaued for a number of seconds after which it began to rise again to a maximum value of 3.70 and 3.78 volts for test #1 and #2 respectively. After reaching peak voltage, the capacitor voltage begins to fall to a minimum value of 3.60 (#1) and 2.90 (#2) volts just before venting. After venting, the voltage rose to the compliance voltage of 5 or 10 volts. In Figure 2 and 3 are the results plotted showing the cell voltage, and temperature.

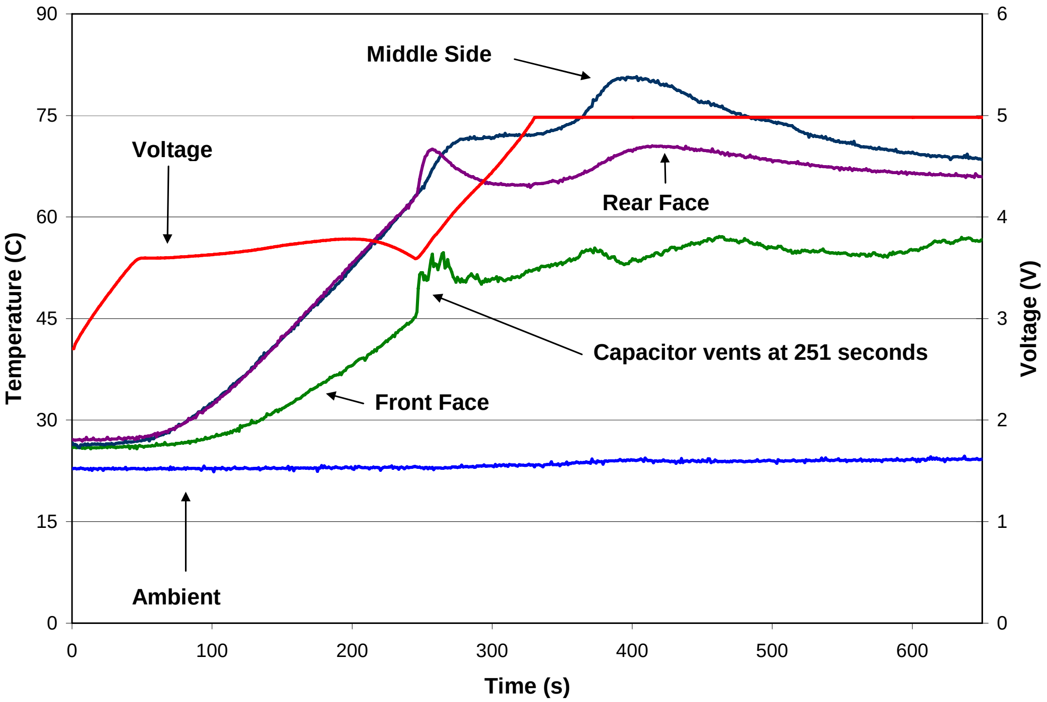

Figure 2: Over-voltage Test #1 at 80 amps, Cell V, Cell T

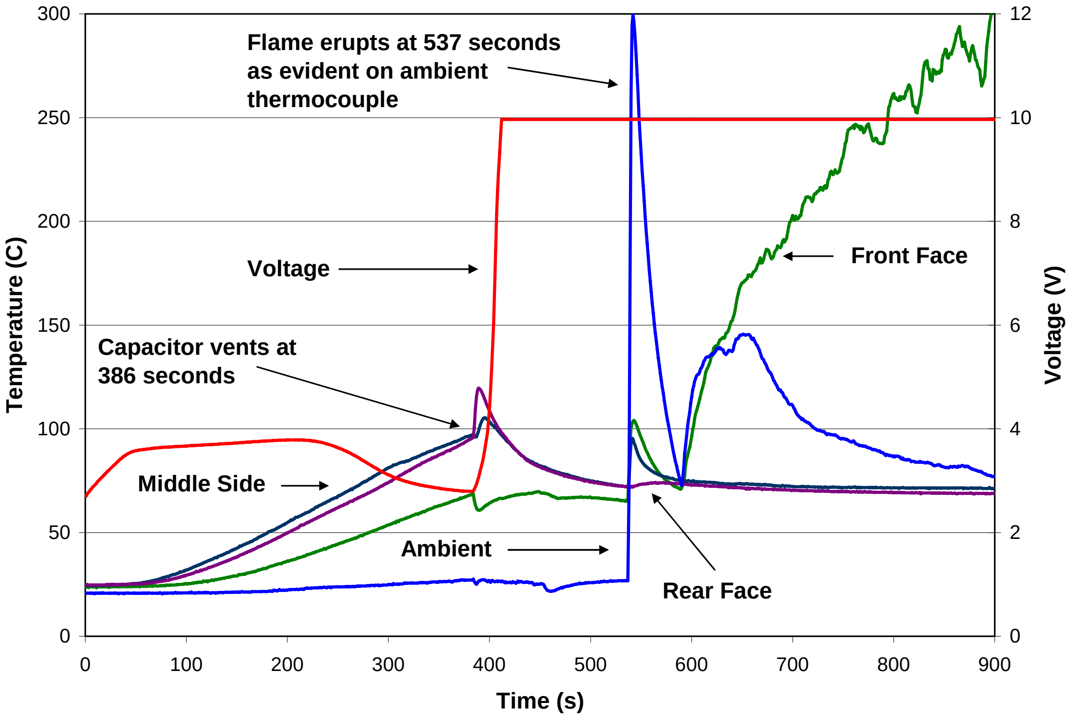

Figure 3: Over-voltage Test #2 at 80 amps, Cell V, Cell T.

Figure 3 shows the effect of the flame initiation. At 537 seconds into the test, the AN ignites into a fire ball and produces a sharp spike in the ambient temperature up to 300°C. The front face of the capacitor heats up to over 300°C after the fire goes out. The middle side area of the capacitor remains at a relatively constant temperature of about 75°C.

In Figure 4 and 5 are the vented gas profiles monitored using the RGA-MS which was set to continuously measure certain expected gas species. Initially, AN was monitored using fractional products (mass 27 and mass 13). Subsequently, AN was measured directly (mass 41) to increase sensitivity. The over-voltage test #1 results in Figure 3 show a large spike in hydrogen, AN fractional products (mass 27, mass 13), and carbon dioxide at about 351 seconds. Venting occurred at 251 seconds and the difference between venting and RGA-MS results at 351 seconds reflects the time lag between venting and gas analysis. Figure 5 shows the gas analysis for over-voltage test #2 with ignition source. In this case the RGA-MS was programmed to register the AN (mass 41) directly instead of using the fractional products (mass 13 and mass 27) as proxy indicators. At about 500 seconds into the test the AN and hydrogen spike, but only the AN continues to rise until about 655 seconds where the AN ignites and produces a fire ball and burns for about 5 seconds. At 680 and 730 seconds the carbon dioxide spikes. After the fire ball the hydrogen and carbon dioxide spike and the AN concentration drops to a very low level.

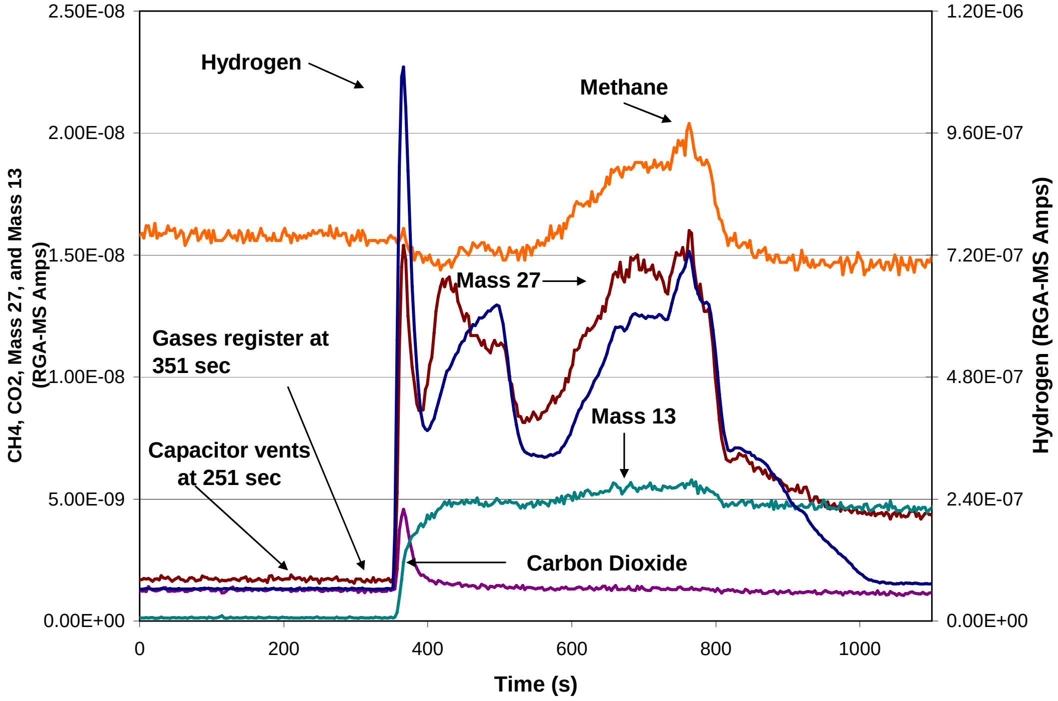

Figure 4: RGA-MS Gas Analysis For Over-voltage Test #1

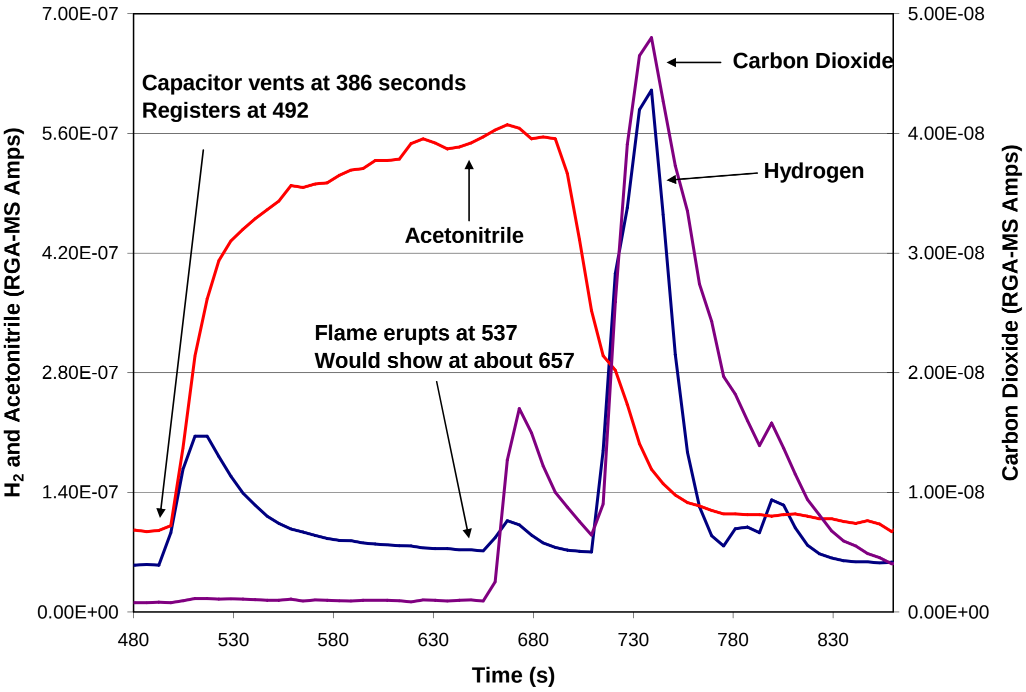

Figure 5: RGA-MS Gas Analysis For Over-voltage Test #2

In both over-voltage tests the FTIR spectra confirm the results obtained with the RGA-MS measurements.

The Drager diffusion tubes inside the back end of the containment box and outside the containment box indicated no HCN from 20 to 200 ppm. The soda-lime tubes near the front corner of the containment box and the point of venting did measure HCN on both over-voltage tests at a concentration of 0.22 mg/m^3 for test #1 and 10.68 mg/m^3 for test #2. These results were obtained by pumping gases through the soda-lime tubes for the entire length of the test at a flow rate of 0.2 l/min. The total time that the gas collection system was exposed to AN vapors is in Table 1. For test #1 the AN exposure time was 460 sec and the total collection time was 3,180 sec. The collection point for test #1 was near the edge of the front corner of the 45.7 cm (18”) square enclosure. For test #2 the AN exposure time was 336 seconds and the total collection time was 2,460 sec directly in front of the capacitor vent. The collection position, cell temperature, compliance voltage, and/or fire may have a significant effect on HCN levels between the two over-voltage tests.

Over-temperature Tests

Three over-temperature tests were performed at a constant heating rate of 5°C/min up to venting temperature or 250°C. Over-temperature data from test #1 was lost due to a computer glitch and only the data in Table 1 remains. Over-temperature test (#2) also included an ignition source to evaluate the effect of fire. The over-temperature test results #2 and #3 are in Figure 6 and 7 and show the cell voltage and temperature as the cell temperature increased to the point of venting and beyond. In Figure 6 venting occurs at 1,519 seconds at a temperature of 131°C. The spark source ignites the acetonitrile gas at 1,530 sec producing a fire ball that burns for about 30 sec. The fire results in about a 130°C temperature spike at the front face (cell terminal). After the electrolyte burns, the heaters are turned off and the bulk cell temperature slowly drops to around 110°C at 3,000 sec.

In Figure 7 (over-temperature test #3) a leak develops in the vent plug at 1,331 sec. This shows up as a small drop in temperature. At 1,851 sec and 106°C the capacitor vents with little effect on the capacitor temperature. In this case temperature continues to rise until the maximum block temperature of 250°C is reached. At a cell temperature of 205°C, the cell voltage begins to fall off rapidly as the electrolyte is lost.

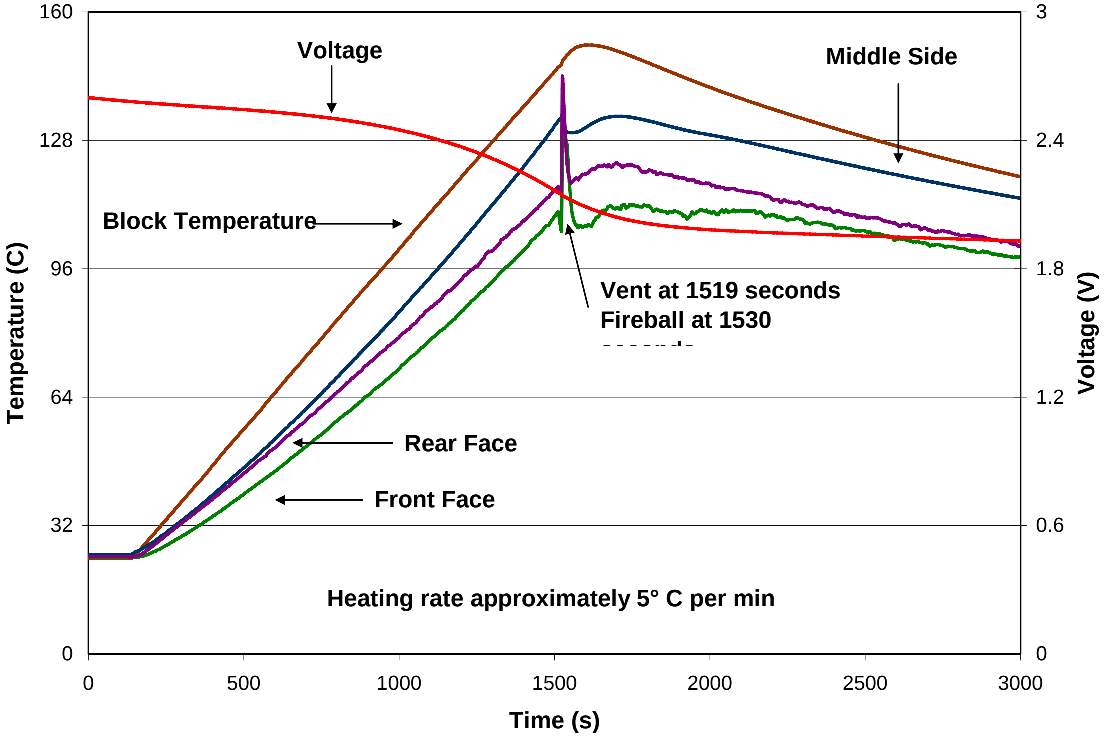

Figure 6: Over-temperature Test #2 With Voltage, and Temperature.

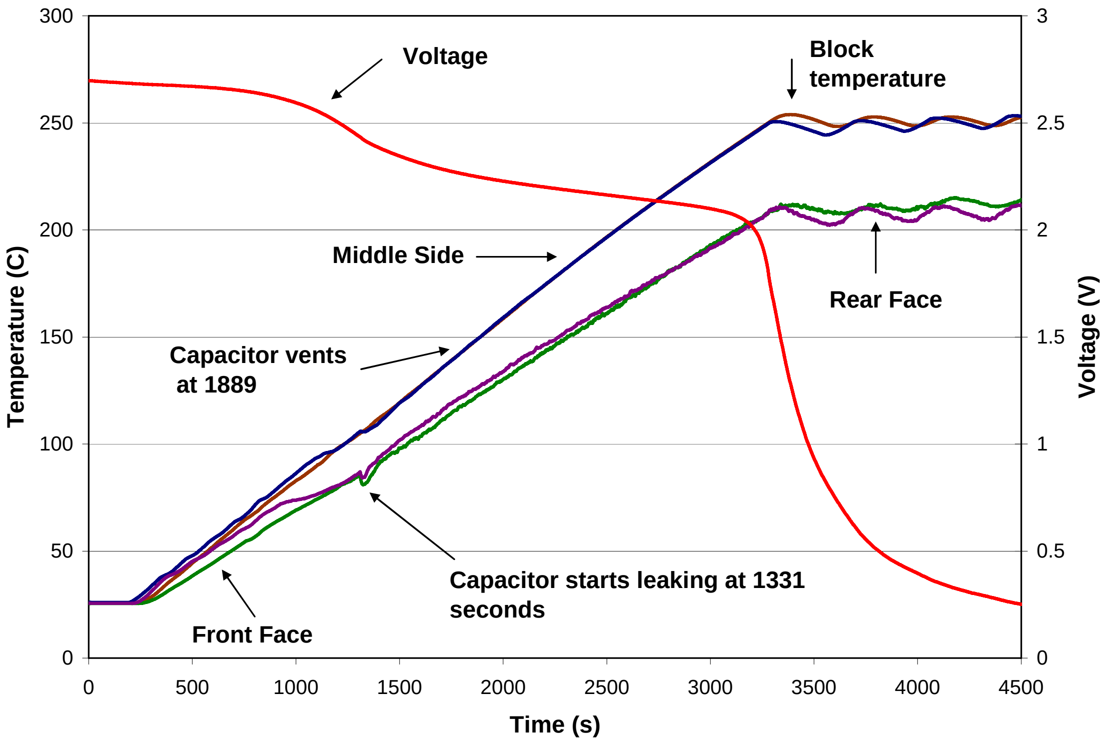

Figure 7: Over-temperature Test #3 With Voltage and Temperature.

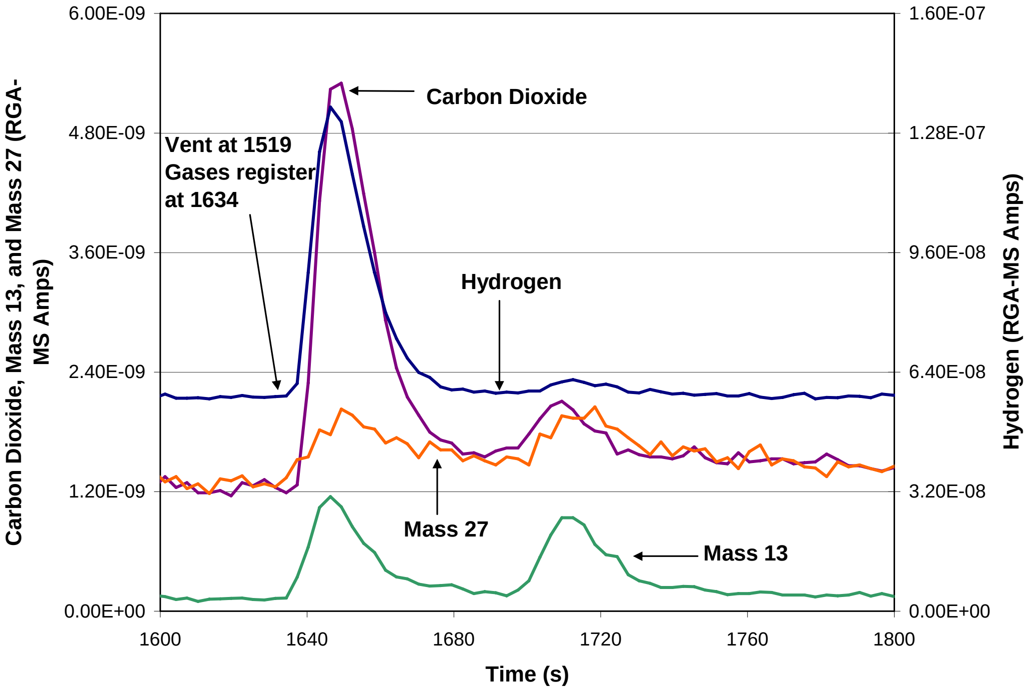

Figure 8: RGA-MS Gas Analysis For Over-temperature Test #2

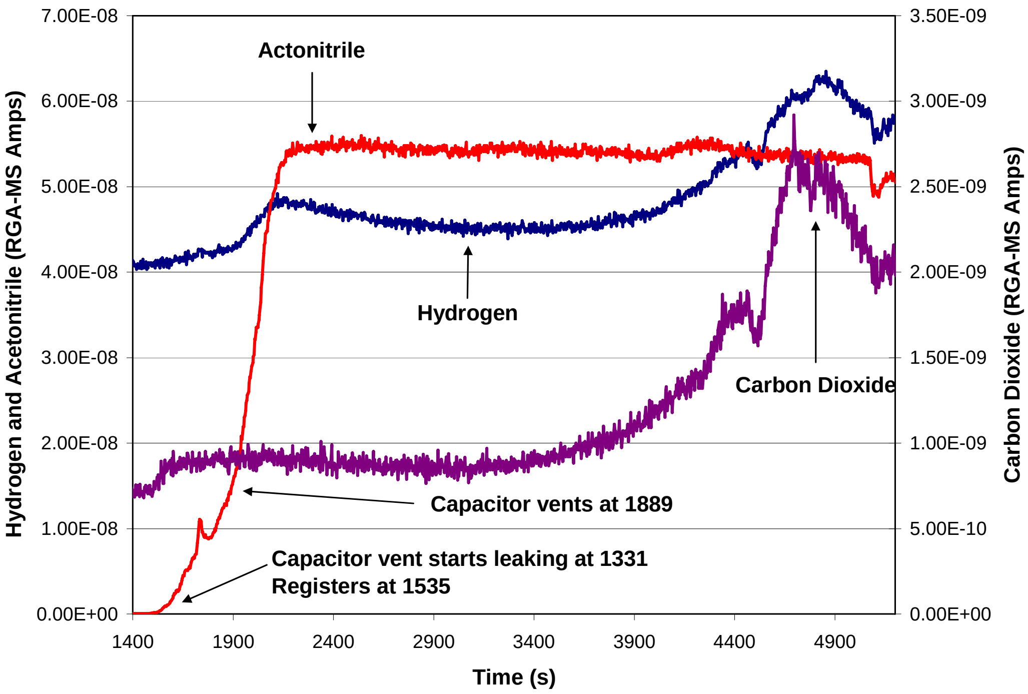

Figure 9: RGA-MS Gas Analysis For Over-temperature Test #3

In Figure 8 and 9 are the RGA-MS results showing the vented gases. In Figure 8 (over-temp test #2) at about 1,635 sec the vented gases H_2, CO_2, and the AN fractional products (mass 27 and 13) show up on the RGA-MS. These gases then decrease after the fire ball which burns for about 30 seconds. The max Cell temperature of about 140°C immediately decreases as the heater is turned off after the fire.

In Figure 9 the AN, H_2, and CO_2 show up early at 1,535 sec. due to the leaky vent plug. Actual venting occurred at 1,889 sec. Gas concentrations remained stable until about 4,000 sec when the CO_2 and H_2 levels increased dramatically, while the AN levels remained relatively constant. At 4,000 sec the cell temperature had been sitting at 250°C for at least 600 sec. This most likely contributed to the increased CO_2 and H_2 levels.

In both over-voltage tests the FTIR spectra confirm the results obtained with the RGA-MS measurements.

The Drager diffusion indicator tube in the back side of the containment box and outside the containment box indicated no HCN from 20 to 200 ppm. The soda-lime tube sample did measure HCN on all over-temperature tests at 3.10 mg/m^3 for test #1, 2.86 mg/m^3 for test #2 and 94.17 mg/m^3 for test #3. Since there was no dramatic increase in measured HCN after the spark initiated fire, the quantity of HCN, if any, from the fire cannot be determined. Also, HCN measurement tests with soda-lime tubes using only acetonitrile vapor produced no measurable HCN. Thus, the dominate source of HCN was most likely the internal gases vented from the capacitor and the high internal capacitor temperature as seen in over-temperature test #3.

In Table 1 are the supercapacitor over-voltage and over-temperature summary results. The results indicate that all over-voltage tests vent at voltages near 3.7 volts and all over-temp tests vent at temperatures of 106°C or greater. The venting process produced a great deal of AN liquid and gas with trace amounts of hydrogen and carbon dioxide. The measurement results were somewhat mixed with HCN. No HCN indication was seen in the Dragger diffusion tubes and RGA-MS measurements even though the HCN levels measured with the soda-lime tubes were high enough for the Drager diffusion tube to show an indication. Since the soda-lime tube continuously collected gas samples over the entire test period, this makes the timing of HCN exposure and level difficult to quantify. The soda-lime pump times in Table 1 ranged from 2,400 to 4,140 sec with acetonitrile exposure times between 336 and 3,659 sec. Some of the HCN measurement variability can be normalized out by assuming that HCN is only collected while exposed to AN, but in the case of over-voltage test #1, a much lower HCN value is measured. This low HCN value for over-voltage test #1 may be attributed to the position of the collection tube near the front corner of the box, and/or a lower maximum cell temperature near 82°C, and/or a lower compliance voltage. The higher HCN levels measured in over-temperature test #3 may also be due to high cell temperatures near 250°C and an extended exposure to the vented gases. This explanation is supported by the rise in decomposition gas products (CO_2 and H_2) seen in Figure 9 after the capacitor reaches 250°C. In the first two over-temperature tests the cell heater was turned off immediately after venting, thus, maximum temperature was much lower.

Table 1: Summary Results From Over-voltage and Over-temperature Tests

Test	Max Voltage	Vent Voltage	Vent Temp C	Time at Venting (sec)	Total Soda-lime Pump Time (sec)	Length of Acetonitrile Exposure (sec)	Soda-lime Measured HCN (mg/m^3)	Spark Source
Over-voltage #1	3.70	3.60	65	251	3180	460	0.22	N
Over-voltage #2	3.78	2.90	97	385	2460	336	10.68	Y
Over-temperature #1*	2.46	1.65	169	934	NA	1232	3.10	N
Over-temperature #2	2.59	2.10	131	1519	2400	124	2.86	Y
Over-temperature #3**	2.69	2.20	106	1889	4140	3659	94.17	N

* Lost Voltage and Temp Data
** Vent Leaked

Summary

As expected all of the capacitors vented after over voltage or temperature. In over-voltage tests the maximum voltage was near 3.7 volts and venting occurred at 3.6 and 2.9 volts. In over-temperature tests the vent temperature was 169°, 131°, and

106°C. The low venting temperature value at 106°C was most likely due to the leaky vent. The venting voltage and time is only valid for the above conditions. At lower charge rates or lower heating rates, the venting voltage or temperature may change.

The vented gases are predominately acetonitrile, and trace amounts of carbon dioxide, hydrogen, and other organic gases. Hydrogen cyanide was only measured with the soda-lime tube, and when soda-lime tubes were only exposed to AN vapors, no measurable HCN was identified. With the present test results, it is not known if any HCN was produced from the burning AN vapors, but based on the low HCN measurement in over-voltage test #1 and the high HCN measurement in over-temperature test #3, there are data to indicate that sensor location and cell temperature may significantly impact the HCN measurement. It is not clear why the Drager diffusion tubes did not indicate any HCN.

After watching the video of all of the over-voltage and over-temperature tests, the most impressive visual effect is the quantity of electrolyte that is sprayed from the capacitor. The acetonitrile spray and/or vapor can last as long as an hour after the initial venting and is the most obvious hazard.

References

1. B.E. Conway, Electrochemical Supercapacitors, Scientific Fundamentals and Technological Applications, ©1999 Kluwer Academic/Plenum Publishers, ISBN 0-306-45736-9.
2. “European Union Risk Assessment Report, Acetonitrile,” Institute for Health and Consumer Protection, European Chemicals Bureau, Volume:18, CAS No:75-05-8, EINECS No: 200-835-2.
3. Material Safety Data Sheet, Acetonitrile.
4. Phillip F. Britt, “Pyrolysis and Combustion of Acetonitrile (CH3CN),” Oak Ridge National Laboratory, ORNL/TM-2002/113.
5. H.M. DeJarnette, et al., “Preliminary Abuse Tolerance Assessment of Acetonitrile Based Super-Capacitors for Navy Power Applications,” 42nd Power Sources Conference, June 12-14, 2006, pp. 91-94.
6. Hydrogen Cyanide, Method 6010, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 8/15/94.