Investigation of the Anomalous Low Voltage Condition of the Oxygen Generation Assembly

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Hydrogen orbital replacement unit serial number 00002 of the Oxygen Generation Assembly was exhibiting an increasingly anomalous low voltage condition in cell #1 of electrolysis cell stack serial number 00005. The hydrogen orbital replacement unit was removed on November 16, 2016, and the on-board spare hydrogen orbital replacement unit serial number 00003 installed to continue oxygen generation system operation. The removed orbital replacement unit was returned from the International Space Station to Collins Aerospace for test, teardown, and evaluation, and failure analysis.

Nomenclature

ACTEX	=	Activated Carbon/Ion Exchange
AOGA	=	Advanced Oxygen Generation Assembly
ECS	=	Electrolysis Cell Stack
EDS	=	Energy Dispersive X-ray Spectroscopy
FA	=	Failure Analysis
FOD	=	Foreign Object Debris
H2 ORU	=	Hydrogen Orbital Replacement Unit
ICP	=	Inductively Coupled Plasma Spectroscopy
IEC	=	Ion Exchange Capacity
ISS	=	International Space Station
MEA	=	Membrane Electrode Assembly
OGA	=	Oxygen Generation Assembly
OGS	=	Oxygen Generation System
ORU	=	Orbital Replacement Unit
PEM	=	Proton Exchange Membrane
RSA	=	Rotary Separator Accumulator
SEM	=	Scanning Electron Microscopy
SN	=	Serial Number
TT&E	=	Test, Teardown, and Evaluation
WRS	=	Water Recovery System

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I. Introduction

The Oxygen Generation System (OGS) provides oxygen for life support to the crew cabin of the International Space Station (ISS). Potable water is delivered from the Water Recovery System (WRS) and electrolyzed into hydrogen and oxygen. The hydrogen can be vented to space or delivered to the Sabatier carbon dioxide reduction system to recover additional oxygen from water production. The OGS was designed to generate oxygen at a maximum rate of 5.4 kg/day (12 lb_m/day) when operated by day/night orbital cycles. The OGS has more recently been operating continuously with a selectable oxygen generation rate between 2.3 and 9.2 kg/day (5.1 and 20.4 lb_m/day, respectively). The Oxygen Generation Assembly (OGA) is part of the OGS and contains the Hydrogen Orbital Replacement Unit (H2 ORU) which is an evacuated dome that houses the Electrolysis Cell Stack (ECS) and the Rotary Separator Accumulator (RSA). Figure 1 shows a simplified schematic of the OGA.

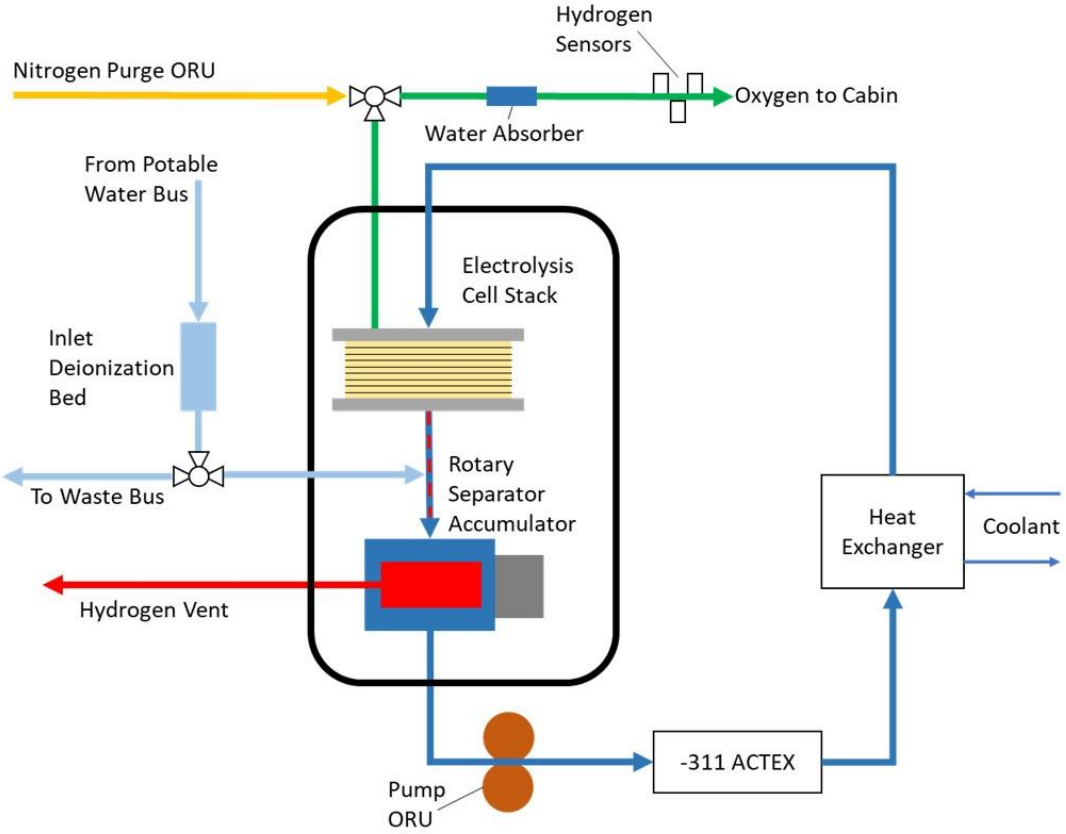

Figure 1. Simplified schematic of the OGA.

The ECS is a Proton Exchange Membrane (PEM) water electrolysis cell stack. The ECS consists of a repeating unit of cells where each cell is isolated from the next by a separator plate that prevents fluid mixing. The cells are contained between the base plate and compression plate by compressive hardware which maintains proper compressive loading to ensure sealing of the fluids within the cell stack assembly and electrical conductance through the active area of the cells. The core component of each cell is a Nafion® membrane, a perfluorosulfonic acid polymer, which has low permeabilities for hydrogen and oxygen allowing for effective separation of the product gases. Nafion also exhibits a high proton conductivity which allows for efficient charge transfer across the membrane to facilitate the electrolysis reaction. The proton conductivity is a strong function of the membrane water content. The cation coordinated with the sulfonic acid group (H^+ for virgin Nafion) and membrane pre-treatment affect the membrane water content. The affinity for monovalent and multivalent cations is higher than H^+ which makes Nafion susceptible to cation contamination from corrosion products or impurities introduced through contaminated water sources. Cation contamination affects the bulk membrane properties; specifically, proton conduction and water content are reduced. When electrodes are applied to the membrane it is referred to as a Membrane Electrode Assembly (MEA).

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The OGS operates as a liquid cathode feed electrolysis system. A drawing of a single cell and the electrochemical reactions occurring for this operating mode are shown in Figure 2. In this operating configuration water is recirculated on the cathode (hydrogen side) of the cell stack. Water permeates to the anode (oxygen side) due to hydraulic and chemical potential gradients across the membrane. Some of the permeated water is lost as vapor with the oxygen product stream to the crew cabin, another portion is consumed in the electrolysis process, and some is carried back to the cathode due to electro-osmotic drag caused as protons conduct across the membrane. The water through electrolysis is dissociated into oxygen, protons, and electrons. The protons and electrons recombine on the cathode and hydrogen is evolved and carried out of the cell stack with the excess water flow through the cathode. The excess water flow carries heat away from the cell stack to be rejected to an external source. The net result of the water balance leaves the anode drier than the cathode preventing liquid water from leaving with the product oxygen and slightly increasing the cell voltage due to increased membrane resistance. This effect limits the maximum current that can be achieved for a liquid cathode feed configuration, but OGA operates at a conservative point within this range.

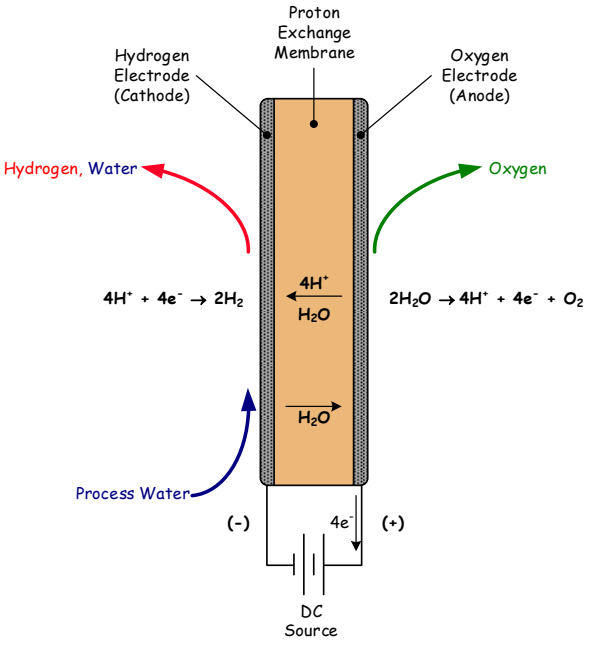

Figure 2. Drawing of a liquid cathode feed electrolysis cell.

The OGS was launched in 2006 and made operational in 2007, with H2 ORU Serial Number (SN) 00001 installed. H2 ORU SN 00001 experienced a fast shutdown due to a high cell voltage in 2010 and was removed and replaced with H2 ORU SN 00002. H2 ORU SN 00001 was returned to ground for Test, Teardown, and Evaluation (TT&E), and Failure Analysis (FA). The cause of the high voltage condition was cationic contamination resulting from corrosion products in the recirculation loop due to low pH[1]. H2 ORU SN 00002 was assembled with ECS SN 00005 in 2009 and installed in 2010 after the failure of H2 ORU SN 00001. However, this ORU saw limited operation until the permanent installation of the Activated Carbon/Ion Exchange (ACTEX) bed in 2011 as corrective action for the high voltage failure. The OGS continued normal on-orbit operation with H2 ORU SN 00002 installed for 5.3 years. In 2016 an anomalous low voltage condition started to exhibit in cell #1 while the OGS was in standby mode. The low voltage condition continued to deteriorate over a two-month period and the decision was made to remove H2 ORU SN 00002 from service and replace with the on-board spare H2 ORU SN 00003 in November of 2016. H2 ORU SN 00002 was returned from the International Space Station (ISS) and delivered to Collins Aerospace's Windsor Locks, CT facility in July of 2017 for TT&E and Failure Analysis. The results of these investigations are presented in this paper.

II. On-Orbit Operating History

H2 ORU SN 00002 was in operation for 46,373 hours (5.3 years) and produced 4,535 kg (9,997 lb_m) of oxygen. A timeline of on-orbit events leading up to the low voltage anomaly through the removal of the ORU is shown in Figure 3.

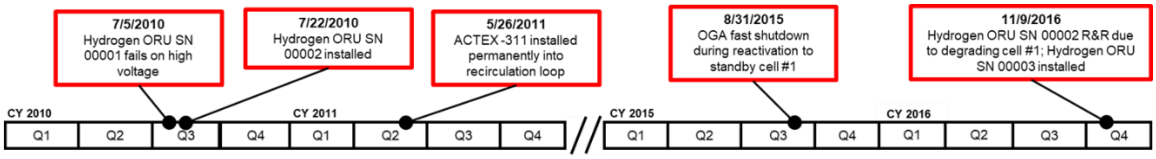

Figure 3. Timeline of on-orbit OGS events before and after the low voltage anomaly.

III. Hydrogen ORU Teardown, Failure Investigation, and Results

Prior to the TT&E a fault tree was derived that focused on the cell stack and, specifically, on conditions within cell #1 that would manifest the anomaly. The branch of the fault tree for the cell stack is shown in Figure 4.

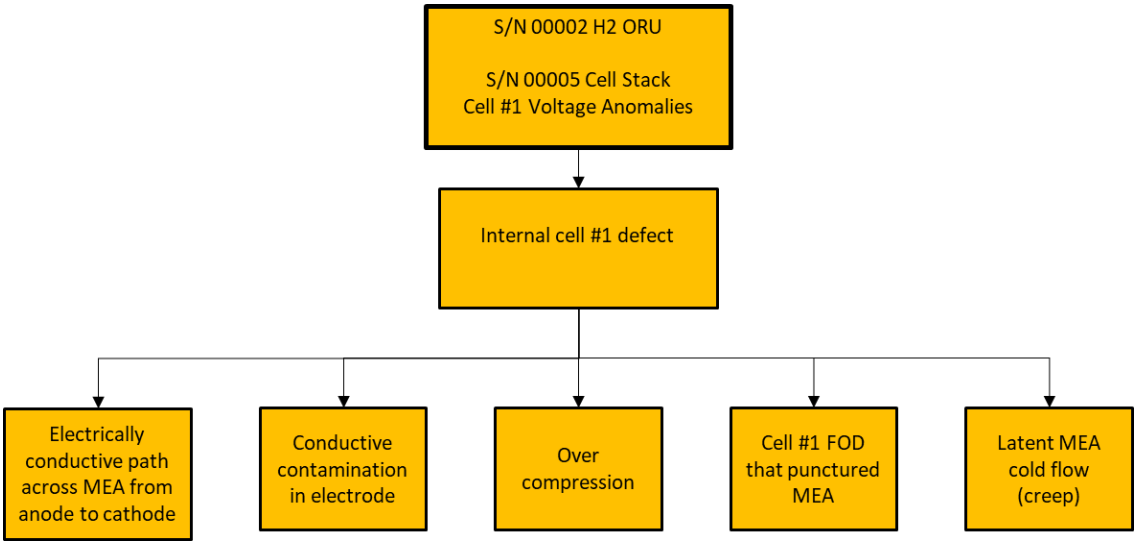

Figure 4. Cell stack fault tree prior to TT&E activities.

The H2 ORU was systematically inspected throughout the teardown process. Electrical connections and harnessing were inspected for proper connection and measured to ensure continuity, insulation resistance, and dielectric properties all met specifications. The dome internal and external components were inspected for Foreign Object Debris (FOD) and damage. No observations were made during this process. Water samples and swabs were collected at eight fluid connections throughout the ORU to analyze for any chemical, microbial or particulate contaminant. No abnormal contaminant was discovered in these samples.

The next step in the teardown process was to remove the cell stack from the dome enclosure for evaluation. Leakage checks performed on the cell stack indicated there was no loss of seal integrity and the membranes of each cell were still acting as separators of the anode and cathode compartments. Cross cell measurements of the membranes also showed that gas permeabilities remained within the cell stack specification. Electrical checks on the individual cells showed nominal membrane resistance. A test for electrical short was performed on the cells with cell #1 exhibiting a short which was not present in the other cells. Shorting of this nature can be due to loss of membrane dielectric properties from membrane degradation, membrane thinning or partial penetration of the membrane with an electrically conductive object. Electrical shorts within the membrane provide an alternate pathway for current and, depending on the severity of the short, can prohibit electrolysis potential from being reached.

Compressive load on the stack was measured to ensure no loss of loading had occurred since the cell stack was assembled and was found to be within specification. Visual examination of the fluid passages was conducted with a borescope and no obstructions or FOD were observed. The cell stack was then disassembled and split to remove cells #1 and #2 for non-destructive and destructive analysis. The remaining cells (#3-28) were placed into an engineering fixture to maintain a light compression on the cell hardware to ensure the cells remained hydrated. The cell stack was later reassembled with a new cell # 1 and 2; and the remaining cells #3-28. During the course of this assembly, cell #28 exhibited similar phenomena to the cell #1 failure. Cell #28 was removed from the remaining cells for non-

destructive and destructive analysis as was conducted for cells #1 and #2. A new cell #28 was added to the stack reassembly and the stack was returned to flight spares after completing protoflight testing.

Cells #1 and #2 were retested for shorting behavior individually within a set of engineering end plates with increasing load applied to the hardware. Cell #2 continued to show no signs of shorting throughout the test up to nominal compression values, whereas cell #1 exhibited a short with just the weight of the engineering end plates which was exacerbated as the compressive load was increased. Further analysis was conducted on cells #1 and #2 by placing the MEA and MEA support structure into a conductive compression fixture. Cell #1 in this configuration continued to show signs of shorting. The anode MEA support was removed, and the remaining components recompressed and cell #1 showed improved performance with no significant shorting. The cathode MEA support was removed, the anode MEA support replaced and cell #1 was recompressed and showed improved performance with no significant shorting. Both the anode and cathode MEA supports were removed so that just the MEA was compressed. Again cell #1 exhibited no significant shorting. The results of this testing showed that the MEA support structure when in a compressed state was causing cell #1 to exhibit shorting. The magnitude of the shorting was highest with both MEA supports in place, followed by just the cathode MEA support in place and then the anode MEA support.

The MEAs from cells #1, #2, and #28 were removed from their support structures for further analysis and maintained in sealed bags with water to prevent drying. Optical microscope and lightbox inspections were conducted to locate and map out areas of interest and any FOD on the electrode surfaces. The electrode surface maps were used to determine the best areas for further observation. The MEAs were wrapped around a mandrel for analysis by X-ray computed tomography. One piece of FOD that was located on the anode of cell #1 during visual observation was investigated during this analysis and showed a high-density particle with a penetration of approximately 50% of the MEA thickness. Subsequent attempts to relocate the FOD particles for additional characterization were unsuccessful, and it is believed the particle was loosened during the analysis and lost into the water. Other non-destructive testing techniques were performed but were not able to image the thin film membranes with enough definition to be functional.

The electrode surface maps were then used to determine the best sample locations for destructive analysis. Samples were taken from the same regions in the cell for comparison: the water inlet, two-phase outlet, and the oxygen outlet. Two additional samples were taken from cell #1 and one from cell #28 where FOD was identified. A portion of the samples from cell #1 and cell #2 were put aside for chemical and elemental analysis. The remaining samples were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) on the MEA surface and cross sections.

Chemical and elemental analysis of the MEA samples was conducted by digesting the MEA in aqua regia and analyzing the resulting solution with Inductively Coupled Plasma Spectroscopy (ICP). These results can then be correlated to the respective cations and the amount of cation contamination in the MEA can be elucidated. The results of this analysis were 4x to 6x lower than what was discovered during the FA of ECS SN 00003. These values are in line with expected cation species that are present in the ISS water chemistry and the amount of cation exchange that would occur over the cell stack's operating lifetime. This level of cation contamination throughout the stack would only minimally impact cell voltages and MEA properties and is not considered a root cause of this failure.

Surface imaging of the MEAs with SEM/EDS allowed for a closer inspection of areas where delamination of the electrodes, tears, and FOD were located. The tears and delamination observed are consistent with the manufacturing process and the required process to remove the MEA support structure from the electrodes. Imprints of the MEA support on the anode were consistent with the higher surface area of that support and showed only minor amounts of membrane creep in the anode direction. The imprints on the cathode from the MEA support were highly pronounced showing MEA creep in the cathode direction as expected due to the lower surface area of this support compared to the anode support. No signs of puncturing or penetration from FOD were observed.

Cross sections of the samples were optically captured to document the indents from the membrane supports and the degree of membrane creep over the operating lifetime. These images highlighted the indenting of the anode and cathode MEA supports showing areas of membrane thinning where the support had pushed into the MEA and the MEA had crept around the support. In addition to the support media there were signs of additional membrane thinning from another unrelated process. The severity of this additional thinning was two-phase outlet > oxygen outlet > water inlet where in the water inlet cross section images the pattern of the MEA support is easily observed. The samples were mounted for cross section analysis in the SEM. MEA thickness between the sealing and support area exhibited thicknesses consistent with the MEA following manufacture. As the thickness was measured going into the support area bulk thickness showed some slight thickness reduction consistent with compression and creep of the MEA. Areas where the support interfaced with the MEA were the thinnest points. The thinnest points observed in cells #1 and #28 showed a 90% reduction in thickness at the two-phase outlet sample. The severity of this thinning followed the same pattern as the general thinning observed optically where at the water inlet the thinnest region represented only a 50%

reduction in original thickness. General membrane thinning was also observed in the samples following the same trend: at the two-phase outlet the loss of membrane thickness was 70% of the original thickness, and at the water inlet the general membrane thickness showed minimal loss. The measurements and severity of thinning were observed in all three cells. This thinning is consistent with chemical degradation of the MEA which will be discussed in the next section. An additional observation was made for cell #28 where a piece of support material was found embedded in the MEA surface and another piece penetrated through 30% of the MEA thickness. In the cell #28 case the cell was uncompressed during initial cell stack disassembly and then recompressed in the engineering fixture. Cells #3-28 were used to assess the feasibility of rebuilding a cell stack and following the repair attempt cell #28 exhibited shorting behavior similar to the original cell #1 signature. The cause of the embedded support material is believed to be due to hydrogen embrittled support pieces realigning when compression was released on the cell stack and reorienting during the subsequent compressions allowing some pieces to embed and penetrate the MEA. These findings along with the observed thinning would have contributed to compromise the cell.

The thinning observed in cells #1, #2, and #28 is consistent with chemical degradation of Nafion. This process occurs due to hydroxyl and peroxyl radicals attacking the -COOH end group of the Nafion. This reaction, which has been termed the "unzipping" reaction, continues along the main chain of the Nafion and leads to mass loss both from the main chain and side chain along with hydrofluoric acid. An illustration of the chemical degradation mechanisms is shown in Figure 5. The release of hydrofluoric acid is what caused the low pH conditions that led to the failure of ECS SN 00003. In the case of ECS SN 00005 the chemical degradation mechanism is responsible for the thinning observed both locally at extreme points and the bulk thinning across the MEA. The severity of the thinning across the MEA surface is believed to be affected by the hydration state of the MEA. As water moves across the cathode cavity the gas/liquid ratio slowly increases as water is consumed and hydrogen is evolved and pulled out into the bulk flow. At the far end of the cathode cavity the bubbles being removed from the cell start to affect the amount of water contacting the MEA and lead to reduced water content at the two-phase outlet port. As the MEA starts to lose water content it becomes more susceptible to the chemical degradation reactions. To a limited extent cathode feed electrolysis cells are at increased risk of this chemical degradation process when operated at higher currents due to the water balance that exists on the anode. OGA operates at a conservative current to minimize this effect. The extreme thin points revealed in this investigation can be correlated to the MEA support interface which, as the membrane thins from chemical degradation, the dielectric properties are reduced leading to apparent electrical shorting across the MEA at nominal electrolysis voltages. This is in agreement with the earlier testing where the support was removed from the failed MEAs and the shorting behavior disappeared when the support materials were removed.

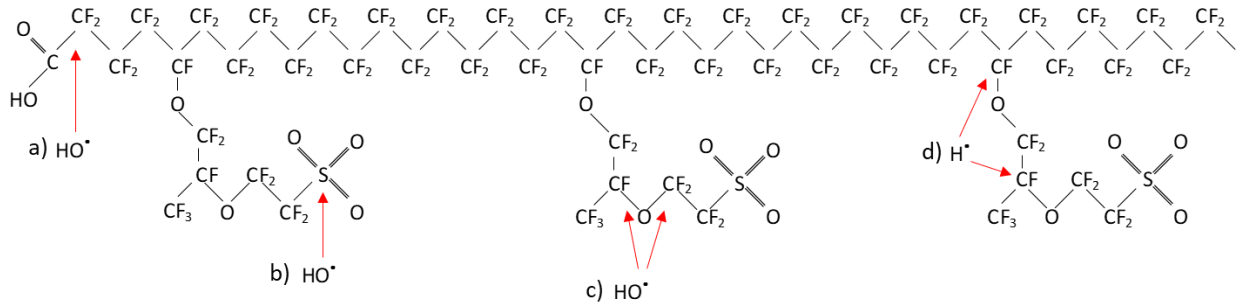

Figure 5. Illustration of the chemical degradation mechanisms of Nafion a) radical attack on the -COOH end group, b) radical attack on the C-S bond of the sulfonic acid, c) radical attack on the ether groups of the side chain, and d) radical attack on the tertiary carbons of the side chain.

The Ion Exchange Capacity (IEC) of cells #1, #2, and #28 was measured to determine the contribution to thinning based on chemical degradation compared to creep. The IEC is determined via an acid-base titration and measures the number of available functional groups responsible for ion exchange in the MEA. If creep solely was the cause of the failure the equivalent weight of the sample would be the same as was originally reported for the material. With chemical degradation the functional groups measured in the titration would be reduced compared to the material originally reported value. Three samples each from cells #1, #2, and #28 were collected across the MEA surface. All samples showed a significant loss of mass and loss of functional groups consistent with prolonged chemical degradation. While creep or MEA relaxation under compression may play a part in the thinning process it is believed that the majority of the MEA relaxation occurs during the initial stack compression process and that the creep over the cell stack's lifetime plays a minimal part in additional thinning.

IV. Cell Stack Redesign

The materials for the OGA cell stacks were procured between 1999 to 2000. The chemical degradation mechanism of Nafion membrane was known but not fully understood. By 2005 research had developed an improved understanding of the chemical degradation mechanism and the manufacturer changed the polymer process to include a post fluorination step that replaced the carboxylic acid end groups (-COOH) with a completely fluorinated end group. The fluorinated end group has improved resistance to the chemical degradation mechanism and the polymer unzipping reaction. There are other chemical degradation mechanisms of Nafion from hydroxyl and peroxyl attack; however, the hydration state of the MEA along with the slower kinetics of these reactions help to minimize their effects. The legacy Nafion is no longer commercially available and has been replaced with the chemically stabilized version. An updated OGA cell stack along with spare cell hardware have been procured to ensure the OGA can operate through the extended life of the ISS. The updated OGA cell stack incorporates the addition of this chemically stabilized Nafion. As an additional safeguard against chemical degradation the addition of a chemical degradation mitigator has been incorporated into the MEA. These modifications are expected to minimize the degree of chemical degradation and ensure the updated cell stacks meet their design life of five years. As a risk mitigation to the Advanced Oxygen Generation Assembly (AOGA) program the modified OGA cell stack is expected to be assembled into the next H2 ORU and delivered to ISS for future operations.

The AOGA cell stack incorporates the MEA changes made for chemical degradation mitigation and includes an improved MEA support structure to minimize membrane thinning during compression and creep over the cell stack's lifetime. These modifications are being made to ensure that AOGA cell stacks continue to meet the operating design life of five years and a storage requirement of two years.

V. Conclusions

The TT&E and FA of the low voltage anomaly of H2 ORU SN 00002 revealed the root cause to be prolonged chemical degradation of the MEA over the cell stack operating life. The chemical degradation was responsible for significant mass loss which led to thinning and breakdown of the Nafion dielectric properties resulting in a high resistance short at nominal electrolysis potentials. Chemical degradation is not physically observable for an operational cell stack, but the release of fluoride can be monitored through analysis of the recirculation loop ACTEX bed. Additionally, observation of trending data, specifically low voltage during standby operation, remains the best indicator for membrane thinning and early detection of failure to allow for ORU replacement. Creep was shown not to be a major contributor to the overall thinning, but compression set at the cell stack assembly causes initial thinning as the MEAs conform to the compressive load. Design changes have been made to future ECS builds for the OGA and AOGA programs to mitigate the effects of chemical degradation and minimize compression set and creep.

Acknowledgments

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