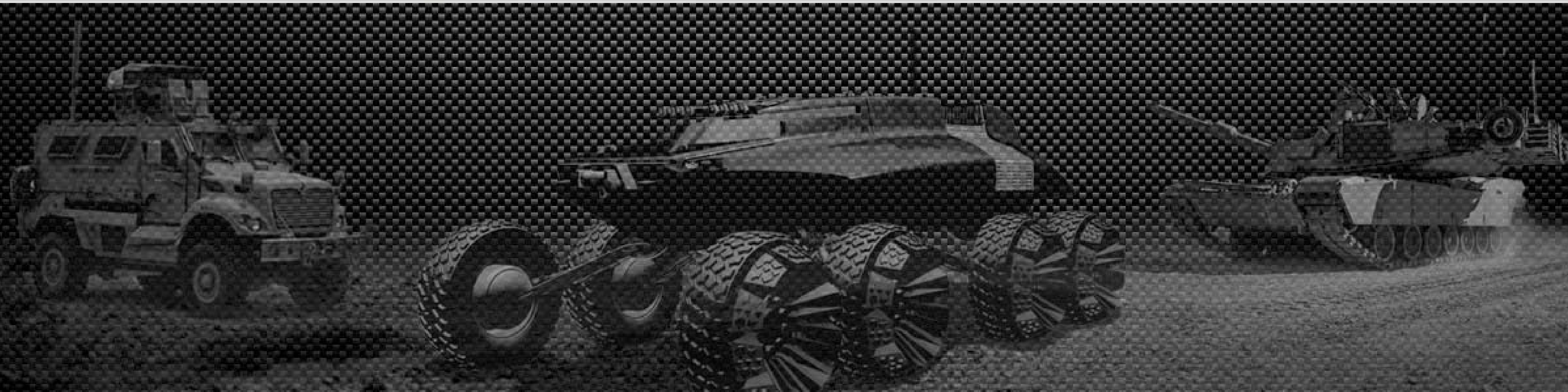
U.S. ARMY TANK AUTOMOTIVE RESEARCH, DEVELOPMENT AND ENGINEERING CENTER

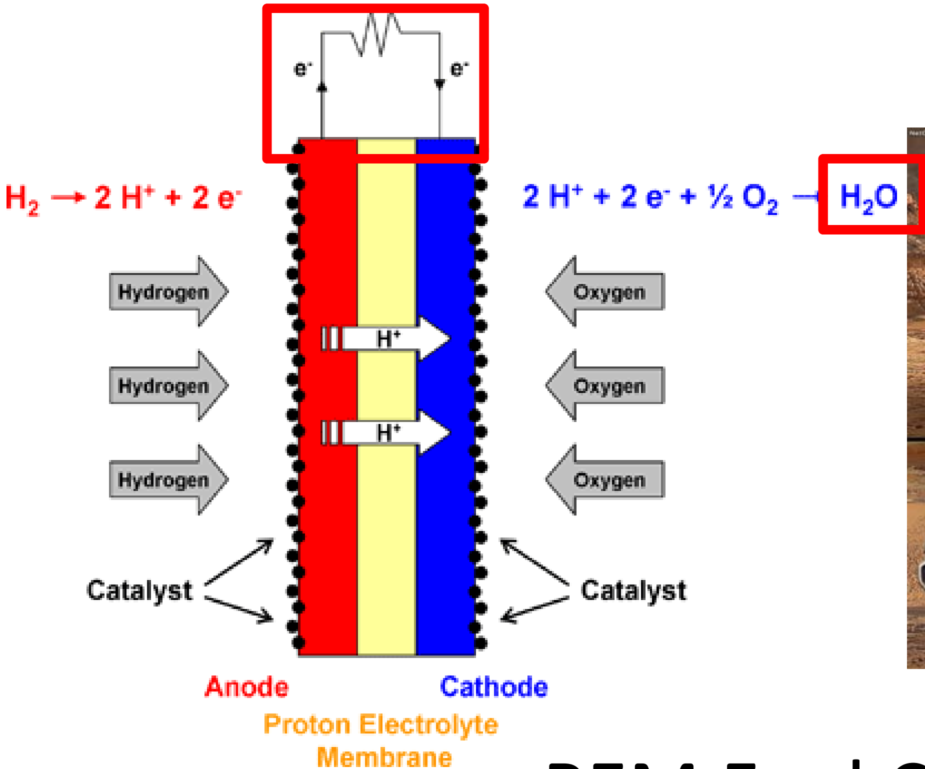
Fuel Cell All-Terrain Transport (FCATT) Proton Exchange Membrane (PEM) Fuel Cell Stack Failure Analysis

Dr. Theodore Burye

21-May-2018



PEM Fuel Cell Overview

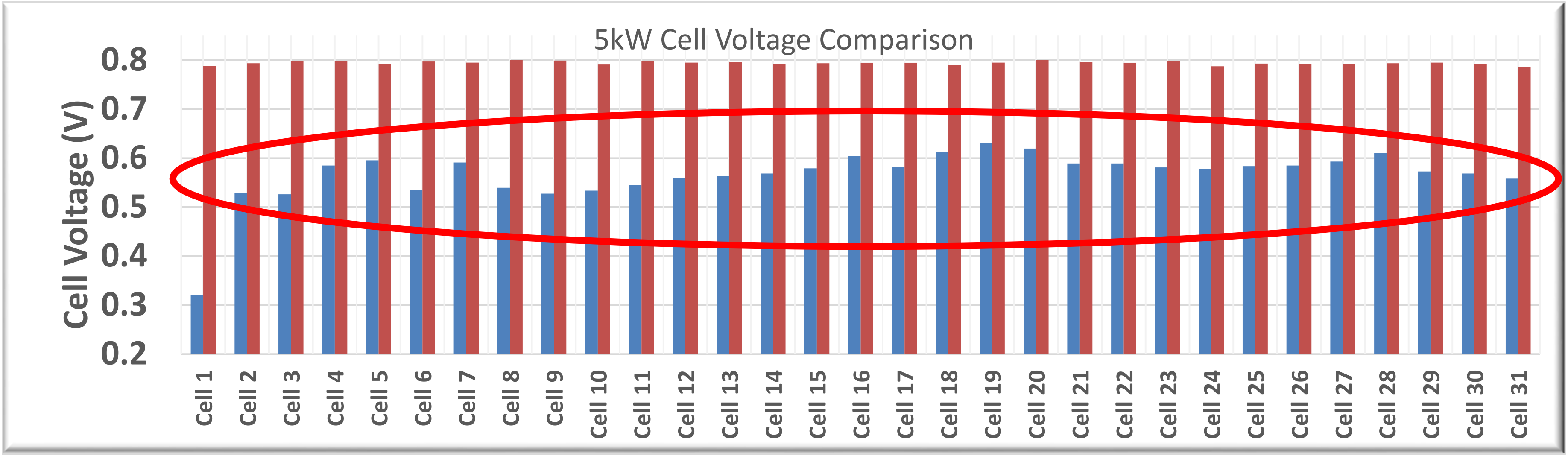


PEM Fuel Cell Key Facts:

- Generates Electricity from Hydrogen Fuel
- Used to Power Vehicle Auxiliary or External Devices
- Generates Water that can be Consumed by the Warfighter
- Quieter than an Internal Combustion Engine

https://www.sigmaaldrich.com/materials-science/renewable-alternative-energy/pem-fuel-cells.html https://www.NetCarShow.com

FCATT PEM Fuel Cell Not Performing Well



Cell = (Catalyst + Anode + Cathode + PEM Material)

FCATT Vehicle Observations:

- Poor Vehicle Performance
- Pungent Odor from Water Exiting the Tailpipe

Characterization Technique Analysis

Gas Chromatography (GC) & Mass Spectroscopy (MS)

Mass Spectrometer

Gas Chromatograph

Characterization Technique Analysis

Scanning Electron Microscopy (SEM) & Energy Dispersive Spectroscopy (EDS)

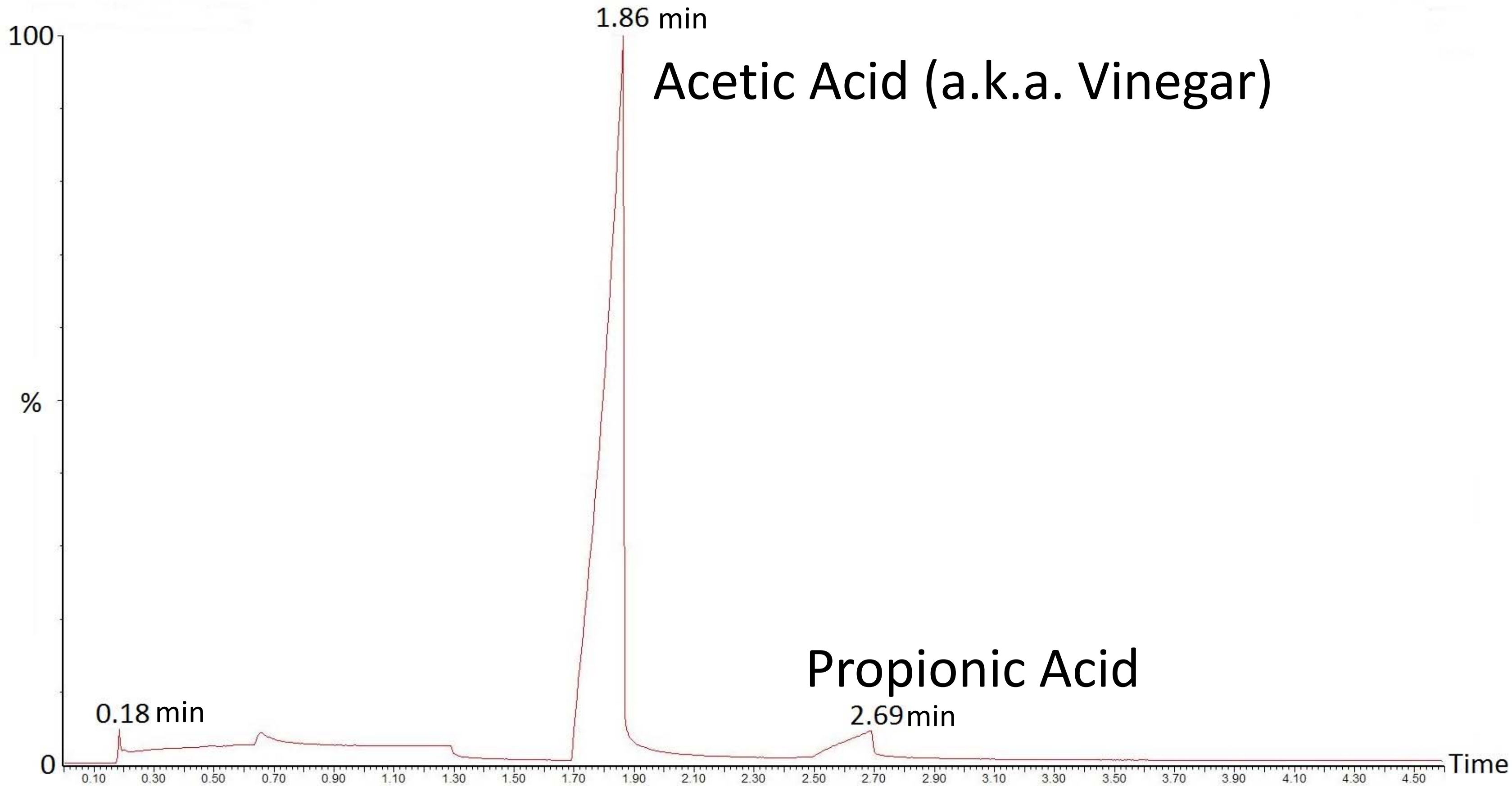
Characterization Technique Analysis

X-Ray Diffraction (XRD)

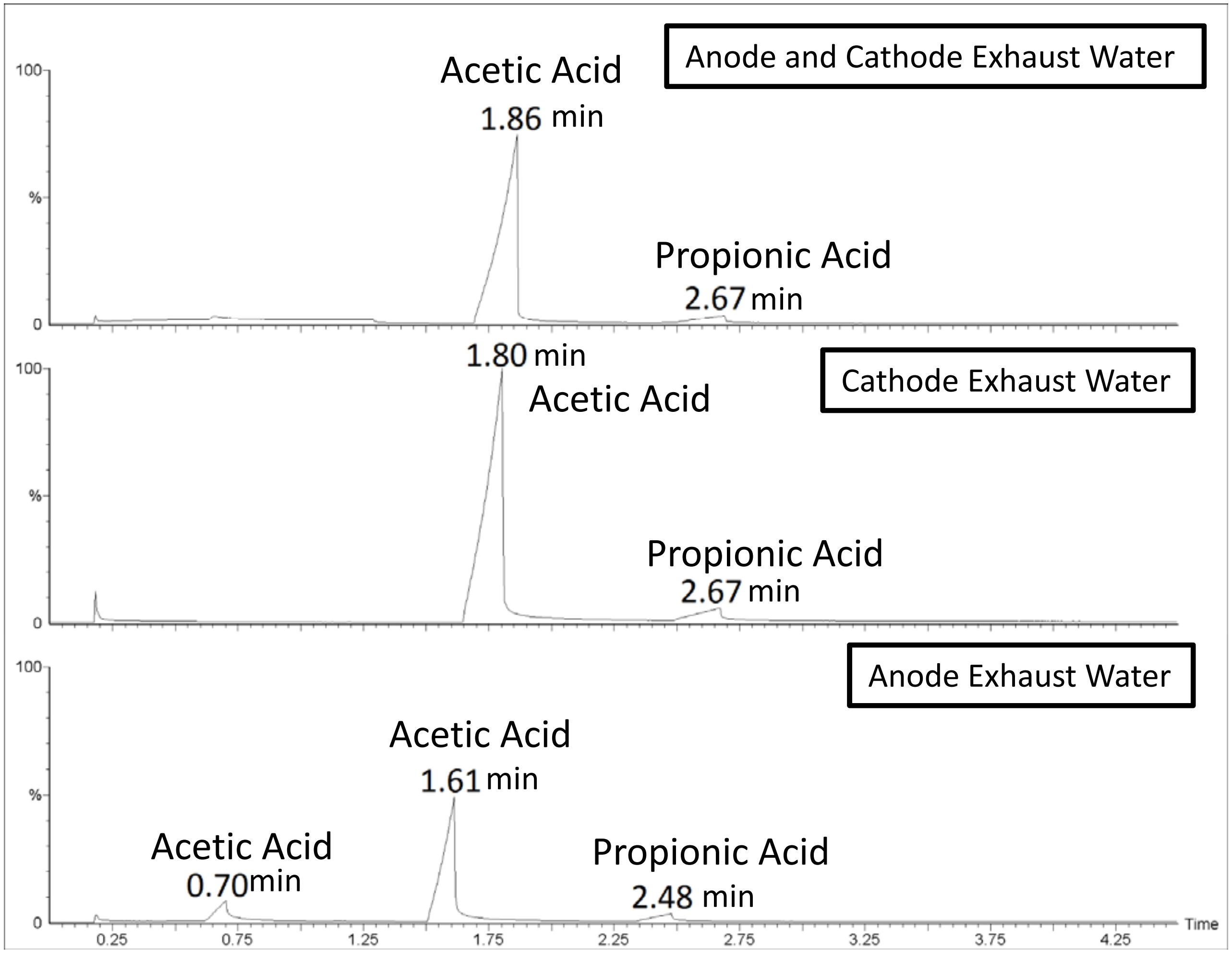
Characterization Technique Analysis

Thermo-Gravimetric Analysis (TGA)

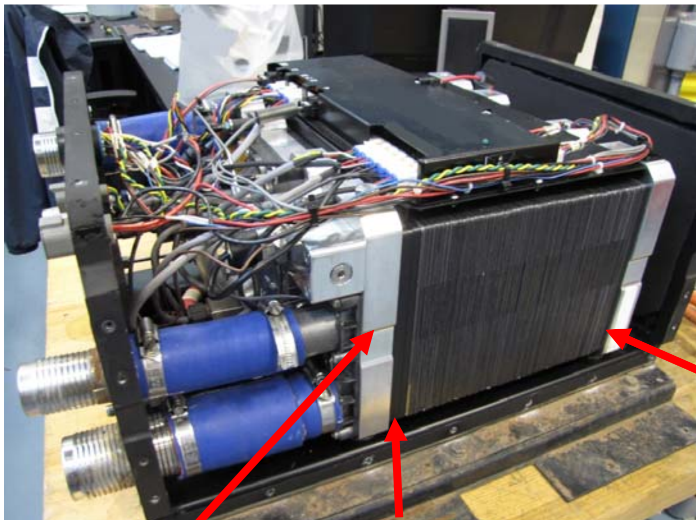
FCATT Tailpipe Exhaust Water Analysis Shows a Problem with the Vehicle System

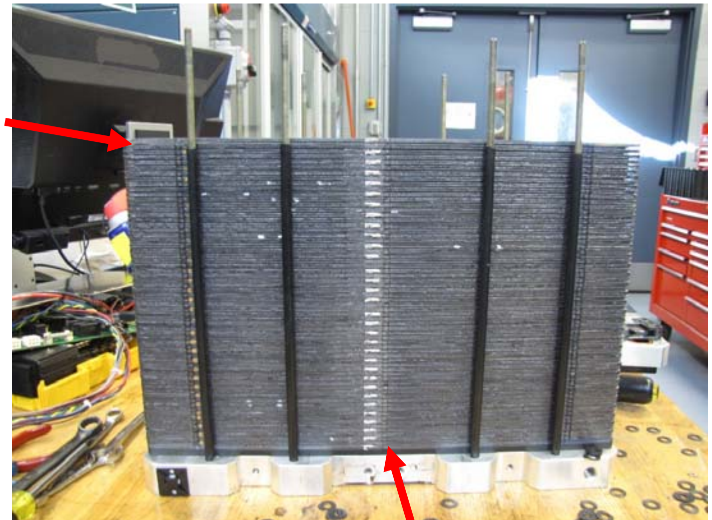


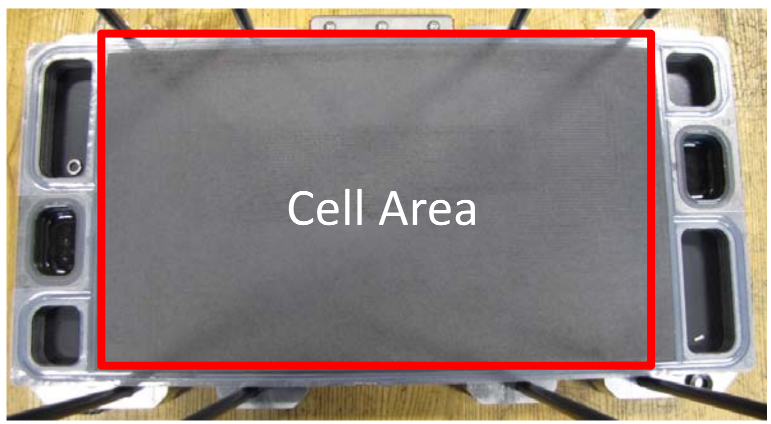
FCATT Cathode and Anode Exhaust Water Show Acetic Acid from Fuel Cell Stack



FCATT PEM Fuel Cell Stack Deconstructed to Determine Failure Mode







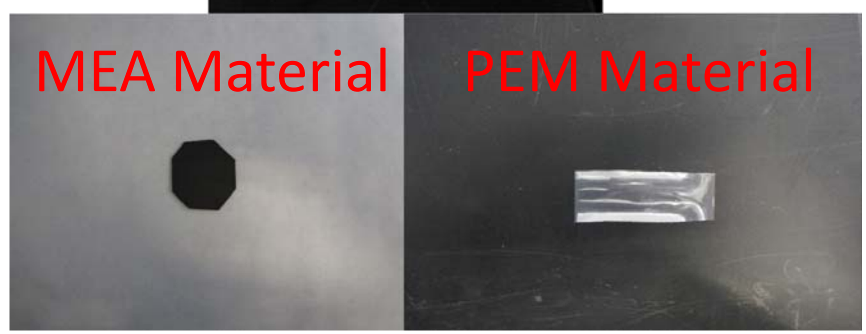
Cell and PEM Material Samples Analyzed to Determine Source of Acetic Acid

Cell Sample Size

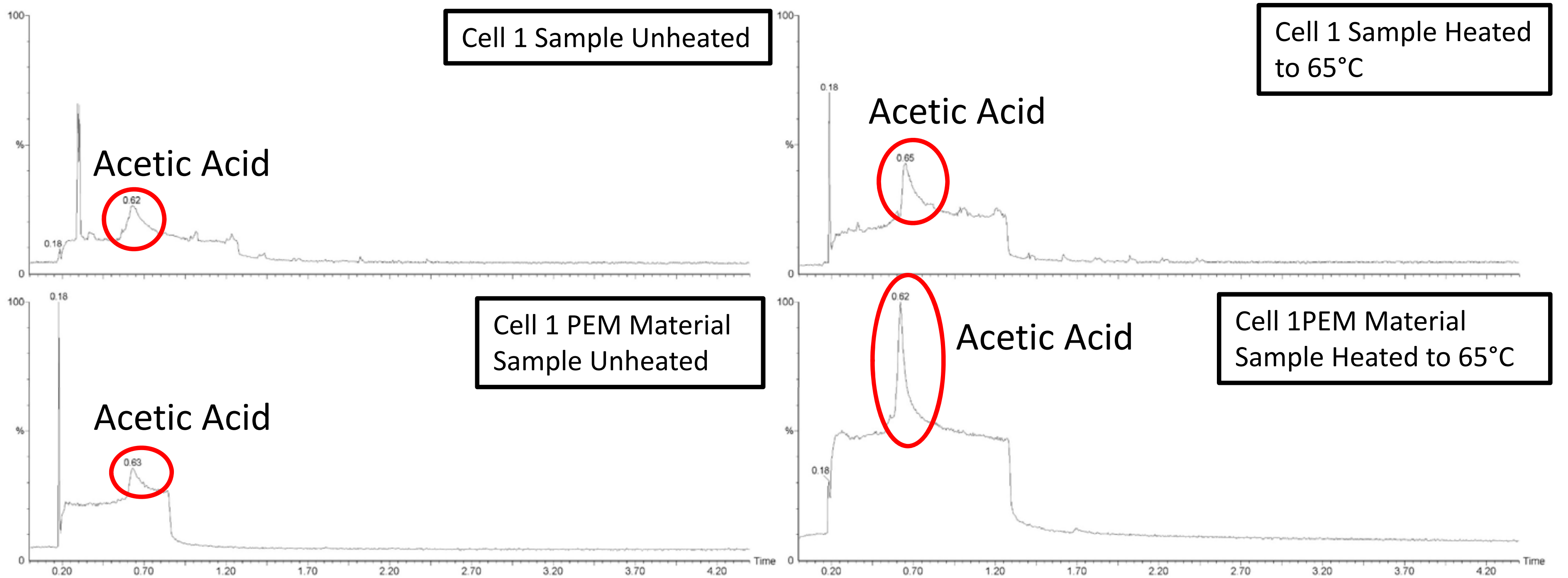
PEM Material Sample Size

Heated to Room Temperature and 65°C in Deionized Water for 24-hrs each.

(Stack Operating Temperature is 65°C)



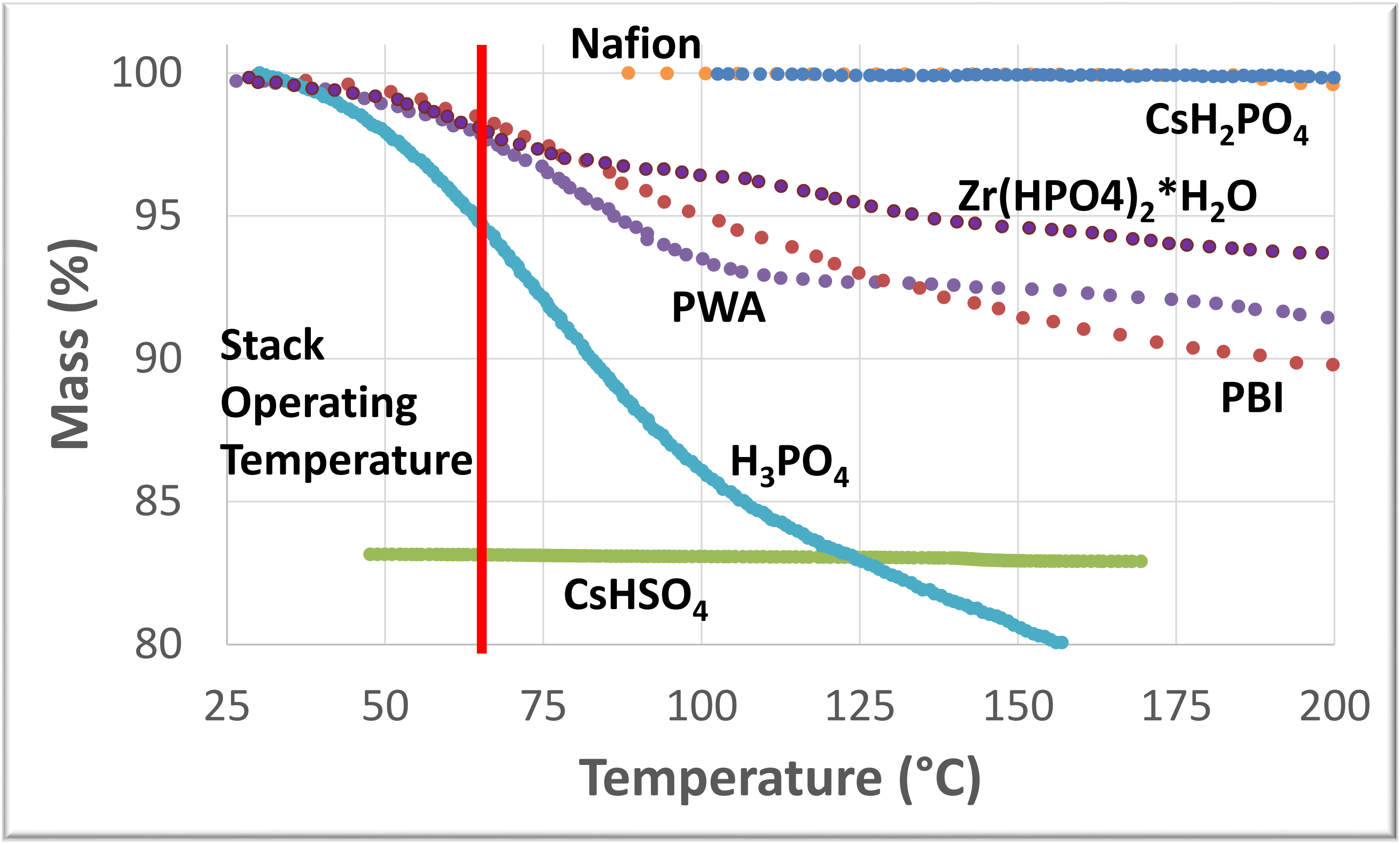
PEM Material Produced Additional Acetic Acid under Increased Heating



Understanding what PEM Material Choices are Available is Important for Cell Performance Purposes

1. Sulfonated Perfluorinated Polymers (a.k.a. Nafion)
2. CsH_2PO_4
3. Phosphotungstic Acid (PWA)
4. Polybenzimidazole (PBI)
5. $CsHSO_4$
6. H_3PO_4
7. $Zr(HPO_4)_2H_2O$

Material Choice and Operating Temperature are Important



1. At Stack Operating Temperature PEM Mass Degradation Could be Between 1.5 wt.% and 17 wt.%
2. PEM Mass Degradation could be Much Worse if Temperatures are Greater

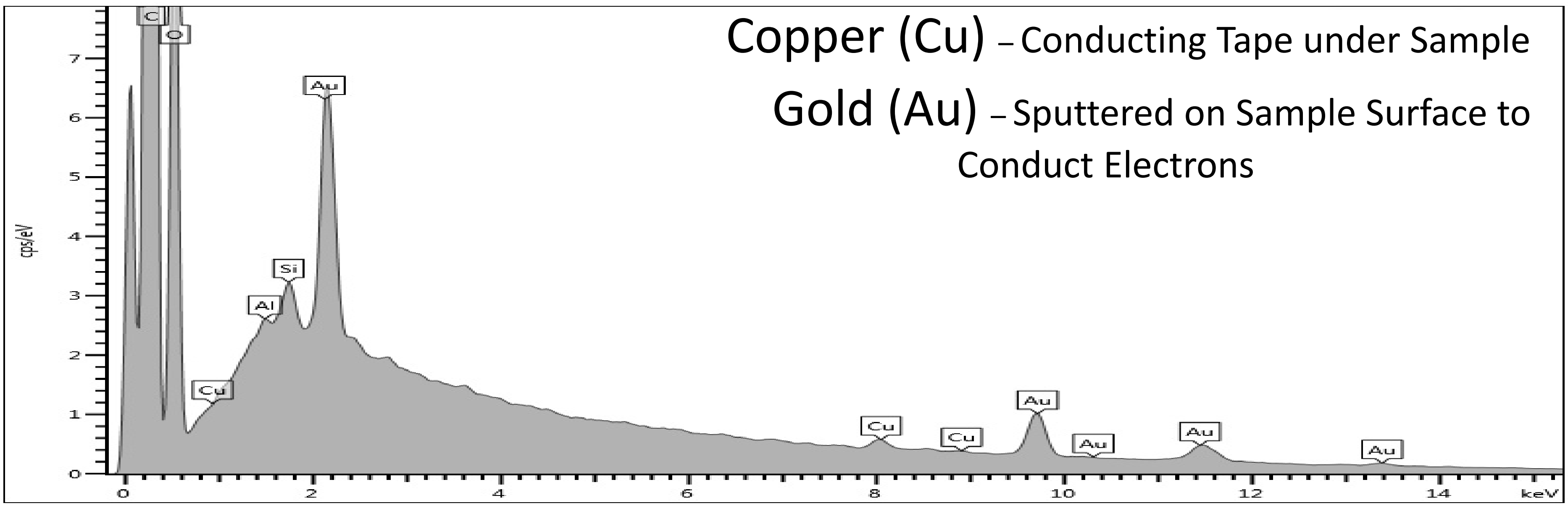
EDS Allows Material Identification Based on Elemental Analysis

PEM Material Choice

1. Sulfonated Perfluorinated Polymers – $C_7HF_{13}O_5S * C_2F_4$
2. CsH_2PO_4
3. Phosphotungstic Acid (PWA) – $H_3PW_{12}O_{40}$
4. Polybenzimidazole (PBI) – $(C_{20}H_{12}N_4)_n$
5. $CsHSO_4$
6. H_3PO_4
7. $Zr(HPO_4)_2H_2O$

Key Elements to Look for:

1. Carbon, Oxygen, **Fluorine**, **Sulfur**
2. Oxygen, **Phosphorus**, **Cesium**
3. Oxygen, **Phosphorus**, **Tungsten**
4. Carbon, **Nitrogen**
5. Oxygen, **Sulfur**, **Cesium**
6. Oxygen, **Phosphorus**
7. Oxygen, **Phosphorus**, **Zirconium**



Copper (Cu) – Conducting Tape under Sample

Gold (Au) – Sputtered on Sample Surface to Conduct Electrons

Elemental Analysis Eliminates all Choices Except Possibly PBI

PEM Material Choice

1. Sulfonated Perfluorinated Polymers – $C_7HF_{13}O_5S * C_2F_4$
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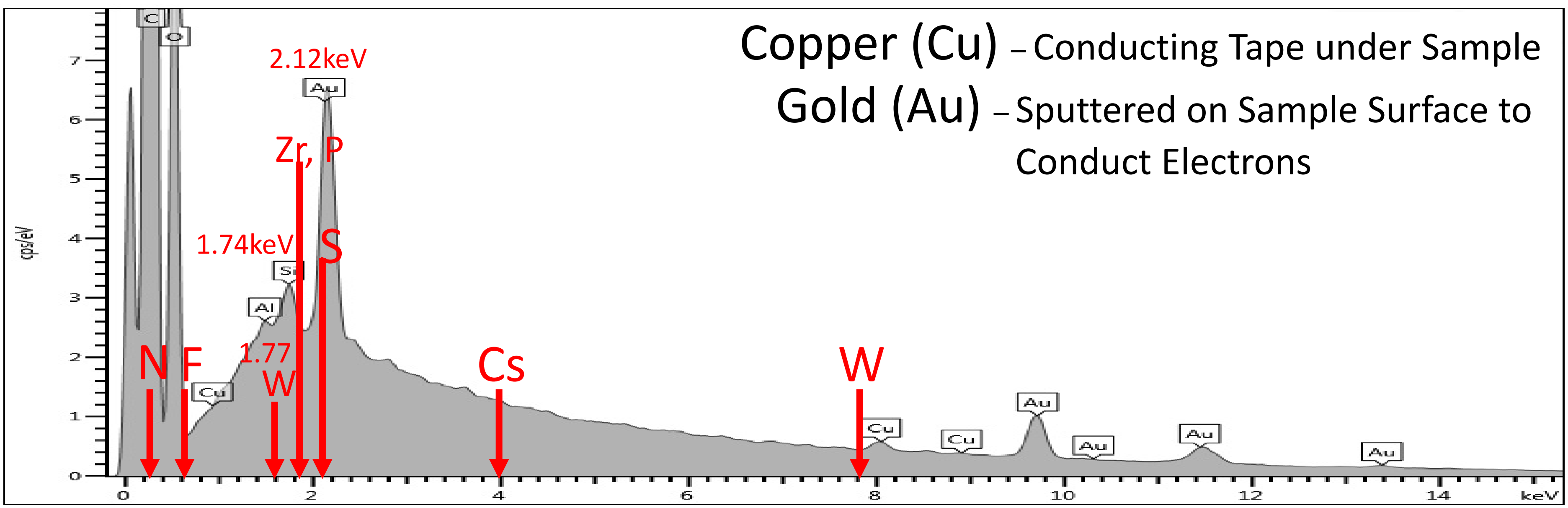


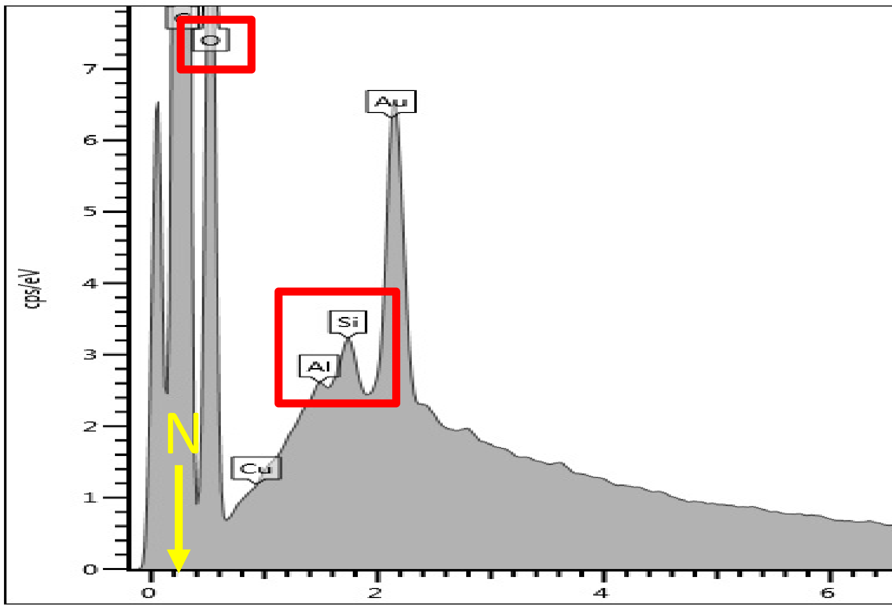
Additional Elements May Indicate PBI was Doped

PEM Material Choice

1. Sulfonated Perfluorinated Polymers – $C_7HF_{13}O_5S * C_2F_4$
2. CsH_2PO_4
3. Phosphotungstic Acid (PWA) – $H_3PW_{12}O_{40}$
4. Polybenzimidazole (PBI) – $(C_{20}H_{12}N_4)_n$?
5. $CsHSO_4$
6. H_3PO_4
7. $Zr(HPO_4)_2H_2O$

Key Elements to Look for:

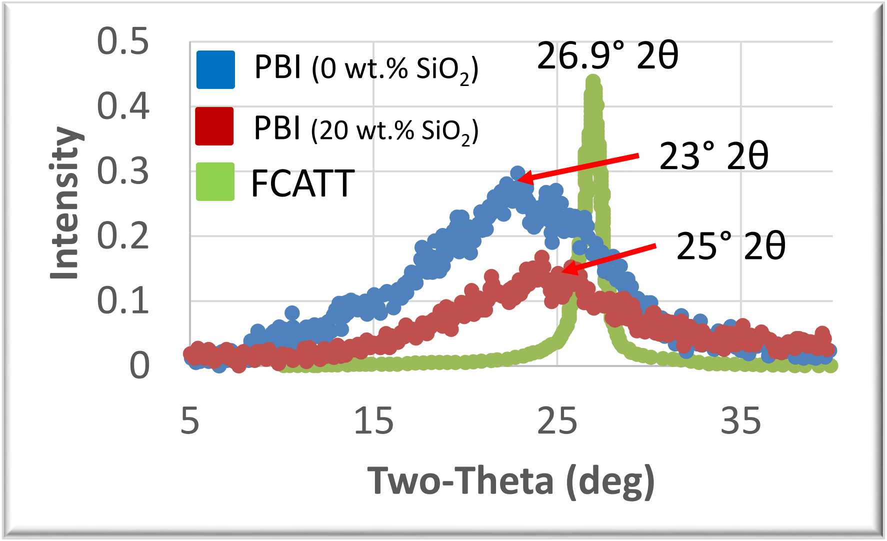
1. Carbon, Oxygen, **Fluorine**, **Sulfur**
2. Oxygen, **Phosphorus**, **Cesium**
3. Oxygen, **Phosphorus**, **Tungsten**
4. Carbon, **Nitrogen**
5. Oxygen, **Sulfur**, **Cesium**
6. Oxygen, **Phosphorus**
7. Oxygen, **Phosphorus**, **Zirconium**

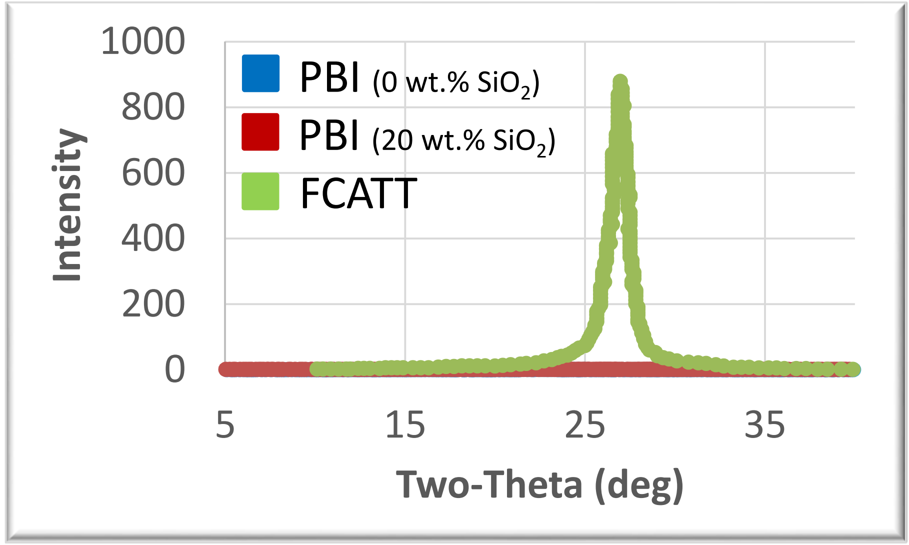


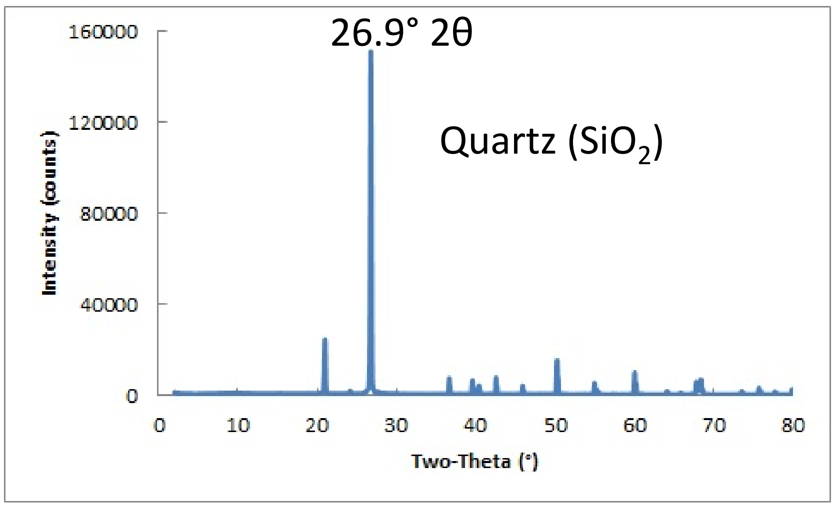
Copper (Cu) – Conducting Tape under Sample

Gold (Au) – Sputtered on Sample Surface to Conduct Electrons

Quartz Doping Shifts Main Peak Location and Increases Crystallinity







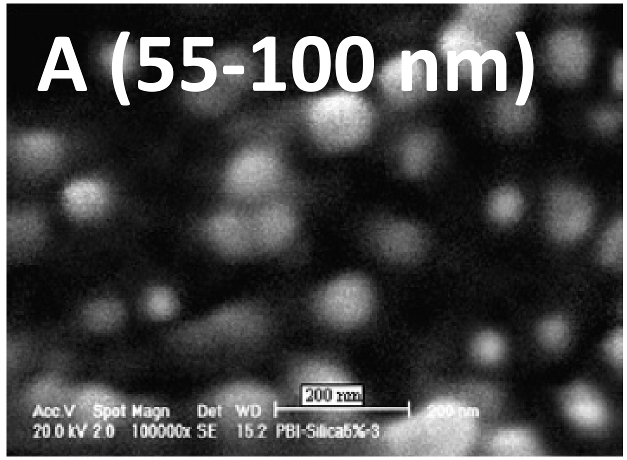
Sadeghi, J. Membrane Sci., 331, (2009), 21-30

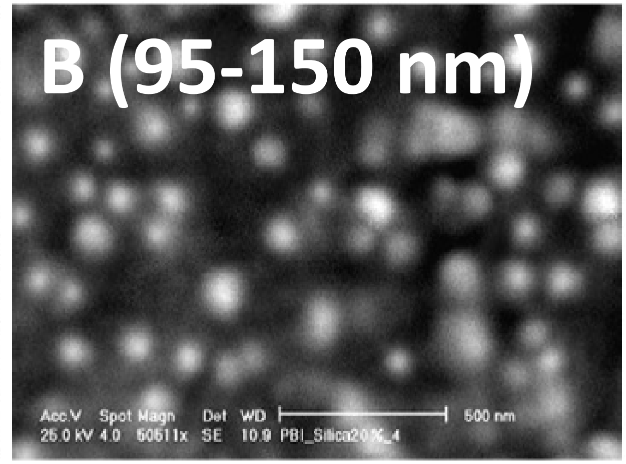
Rigaku XRD Material Database # 1532512

1. PEM Material Peak Close to PBI. Addition of SiO_2 Shifts PBI Main Peak in Literature Closer to PEM Material.
2. PEM Material Significantly more Crystalline than PBI Literature Results
3. Quartz XRD Results also Indicted a Very Crystalline Structure, which is SiO_2
4. Quartz XRD Results Indicate Quartz has the same Main Peak Position as PEM Material
5. Literature Reports Addition of SiO_2 Increased Thermal Stability and Mechanical Strength of PEM Material

Large Particles with Silicon and Oxygen are Present in Samples

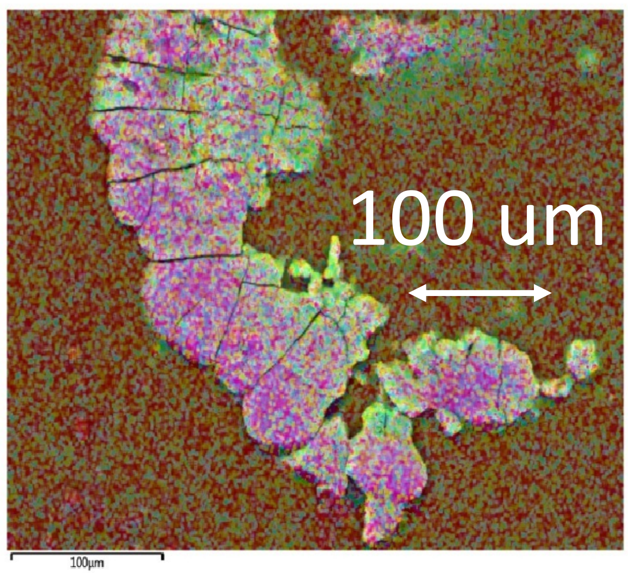
1. Literature XRD Data has Shown Doped SiO_2 Nanoparticles can be Observed vis EDS
2. Particle Sizes are:
    1. 55-100 nm (**A**) 5 wt.% SiO_2
    2. 95-150 nm (**B**) 20% wt.% SiO_2

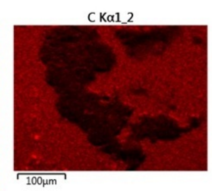




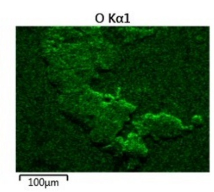
1. FCATT PEM Material Contained both Silicon & Oxygen in Similar Quantities
2. Trace Amount of Aluminum was Present too
3. Particles are Large (100's um's) and Agglomeration may have Occurred

Sadeghi, J. Membrane Sci., 331, (2009), 21-30

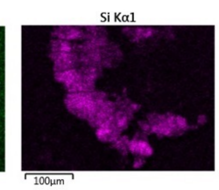




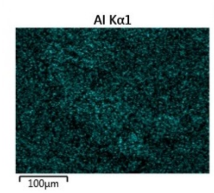
Carbon



Oxygen



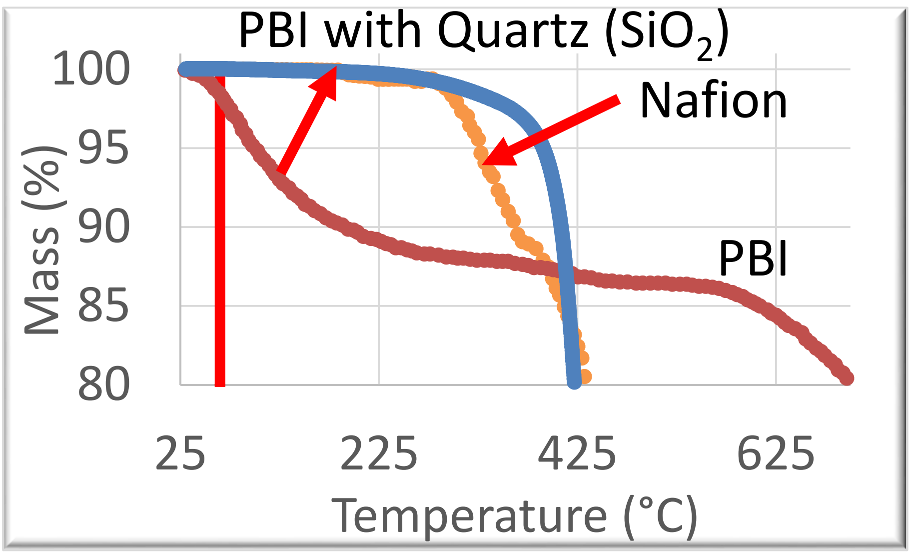
Silicon

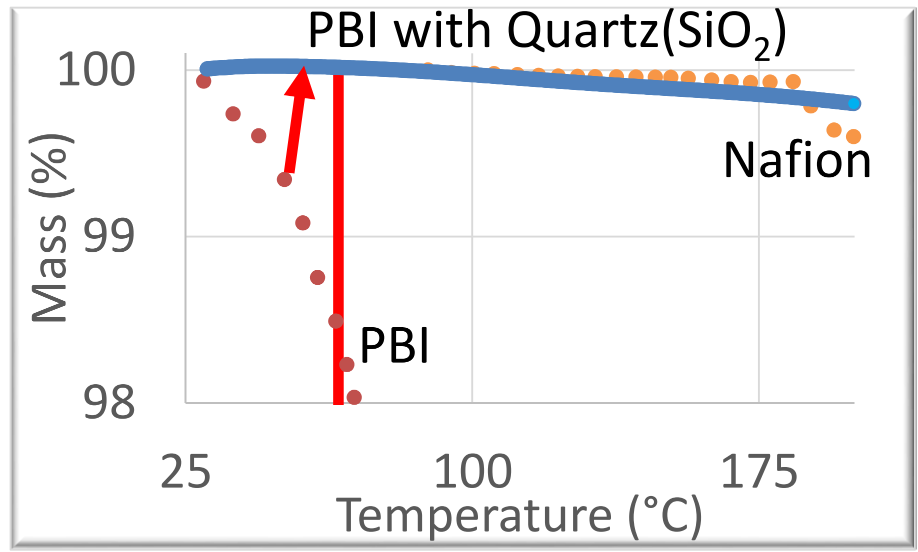


Aluminum

Addition of Quartz Enhanced Thermal Stability Significantly

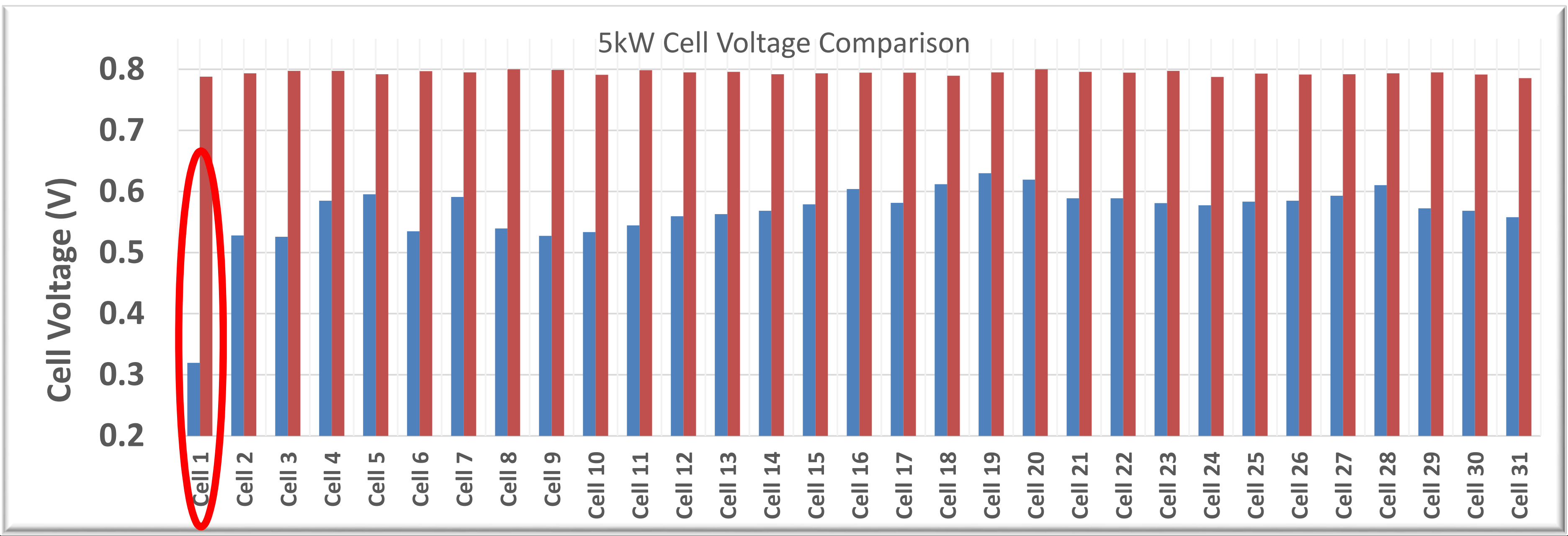
1. Addition of Quartz Enhanced Thermal Stability Similar to that of Nafion
2. Mass Loss was Reduced from 1.5 wt.% to ~0 wt.% at the Operating Temperature of 65°C, when Compared to PBI from Literature
3. Thermal Stability was Significantly Improved over Previous Material Properties Results, so why did the PEM Material Produce Acetic Acid from Degradation?



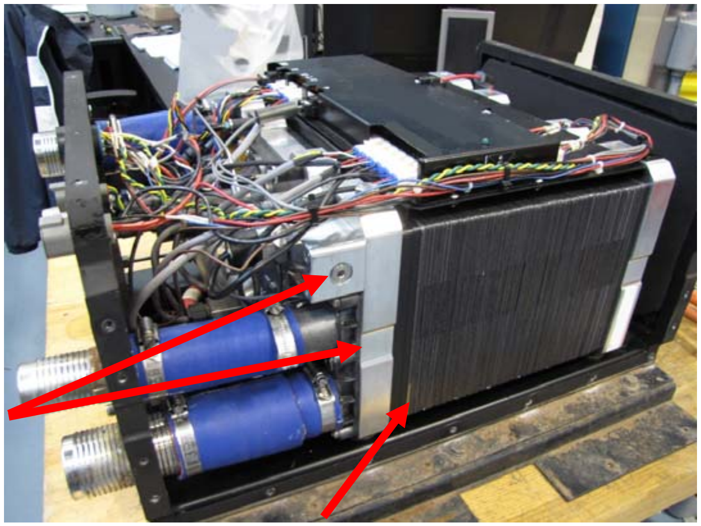


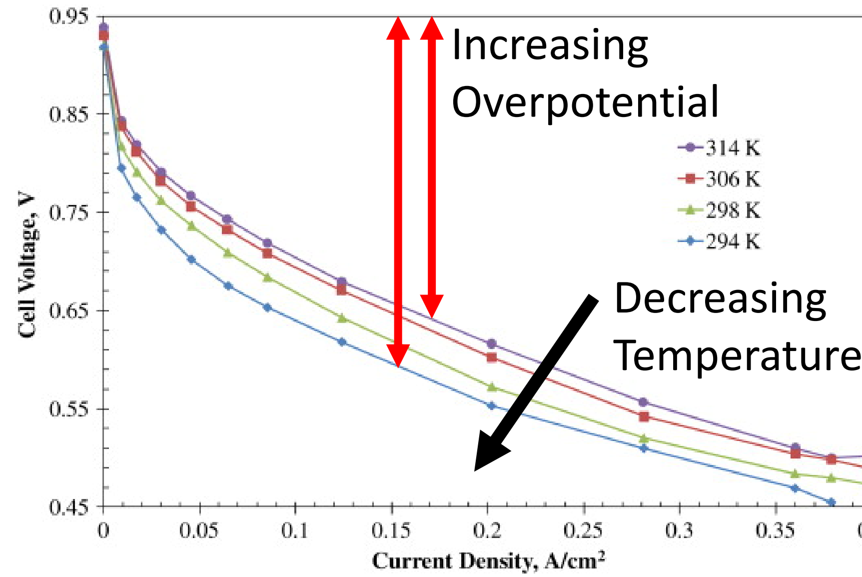
Possible Reasons for the Overall Stack Degradation

- The Recommended Maximum Manufacturer Operating Temperature was 65°C
  1. PEM stack, at 5 kW, was Operated between 71-75°C
- There were Times where the FCATT was Operated in Summer Temperatures of 37°C, which put an Additional Heat Load on the Stack
- The Stack was Thermally Cycled Frequently (Returned Stack from Operating Temperature to Ambient Temperature). Thermal Cycling Degrades Stacks Faster than Continuous Operation.
- But What About Cell 1??? Largest Contributor of Acetic Acid and 40-50% Lower Cell Voltage



The Manifold is Hypothesized to Lower Cell Voltage in Cell 1

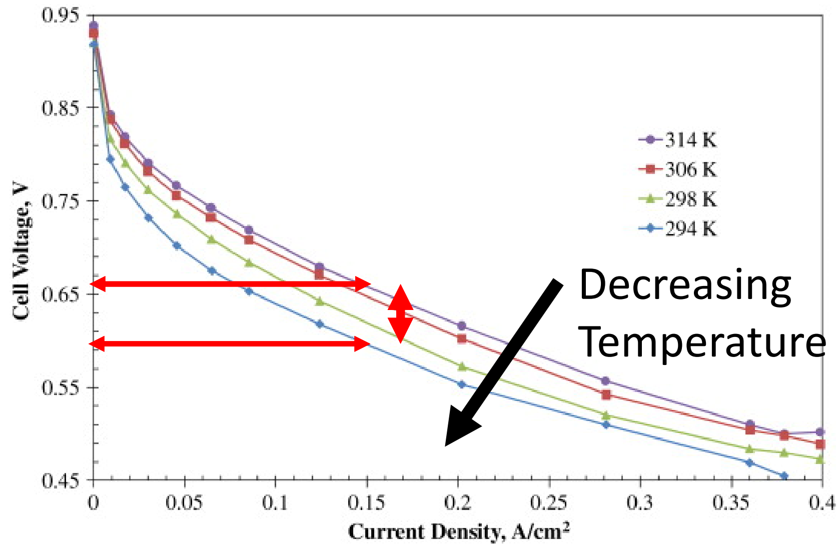


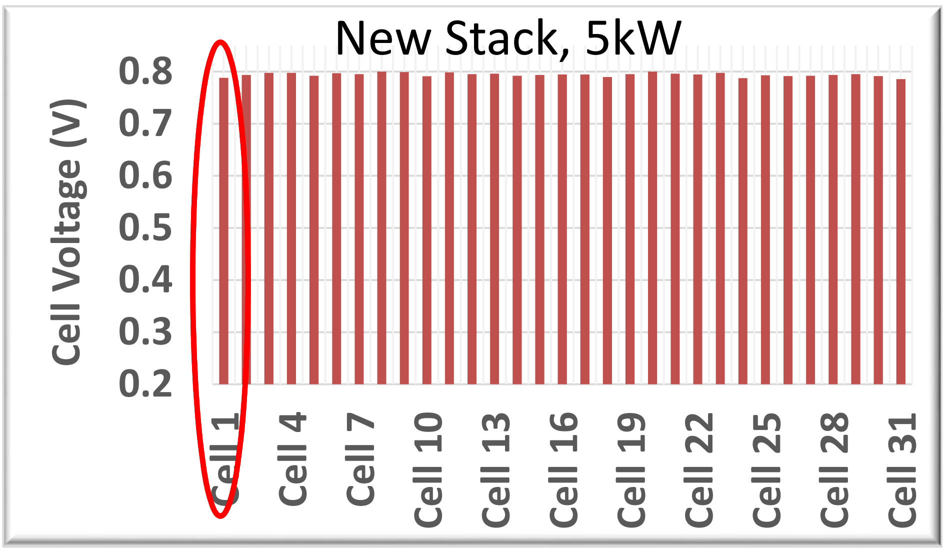


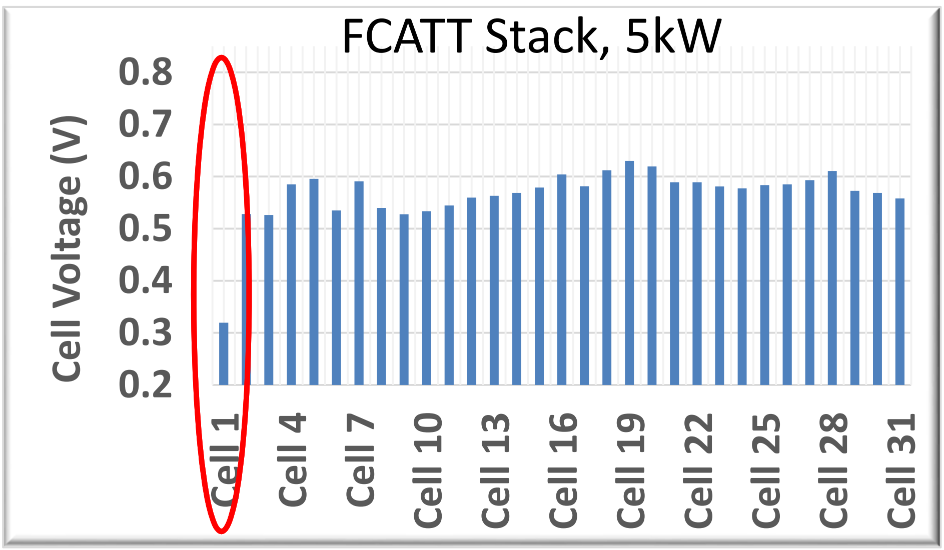
1. The Manifold and other Metal Attachments Cool the Topmost Cell, Cell 1.
2. Operating a Cell at a Lower Temperature Increases its Overpotential (i.e. difference in voltage between actual and thermodynamically derived). Higher overpotential means lower cell voltage efficiency.
3. Higher Overpotential is Caused Primarily due to Increased Ohmic Resistance Losses at Electrode Surfaces and Interfaces.
   1. The Interface between the Manifold and Cell 1
4. The Cell uses More Energy to Overcome those Increased Inefficiencies than Thermodynamically Required. That Additional Energy is Lost to the Cell as Heat, Locally and Degrades the Cell.

S. Haji, Renewable Energy, Vol. 36, 2, (2011), 451-458

Lower Operating Temperature did not Reduce Cell 1 Voltage



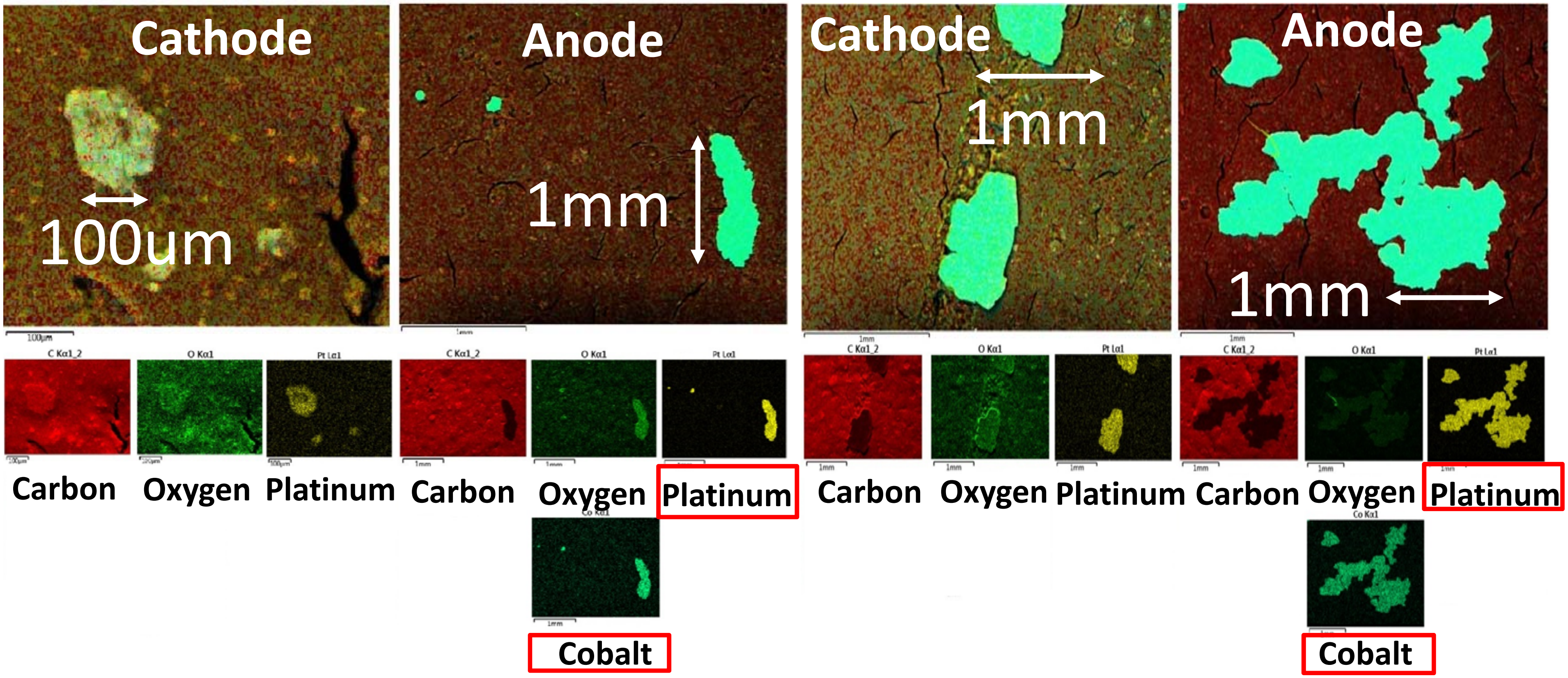




S. Haji, Renewable Energy, Vol. 36, 2, (2011), 451-458

Loss of Electrocatalyst Active Areas Lowers Cell Voltage

Cell 1 Electrocatalyst Element Map   Cell 31 Electrocatalyst Element Map



Two Degradation Mechanisms Appeared to have Occurred which Lowered Cell 1 Voltage:

1. Electrocatalyst Particle Size Agglomerated (normally 5-10 nm) (less total active area)
2. Electrocatalyst Particle Detach from Polymer Surface (less active surface area)

Conclusions

1. FCATT PEM Stack was Producing Acetic Acid from PEM Material in Stack
2. PEM Material was Found to most likely be PBI which was Doped with Quartz and Aluminum
3. The Addition of Quartz Improved the PEM Material's Thermal Stability and Reduced its Thermal Degradation at Lower Operating Temperatures
4. FCATT PEM Fuel Cell Failure was Found to most likely be the Result of:
   1. Operating the Stack at 5-10° C Above the Manufacturer's Recommended Maximum Temperature and Repeated Thermal Cycling Resulted in Overall Stack Performance Loss
   2. The Cell Closest to the Stack Manifold was Less Efficient due to being Cooled by Manifold. This Resulted in the Cell being Less Efficient, Increasing Energy Consumption which was Lost as Heat to the PEM Material Interface.
   3. Increased Heating at the Interface Promoted the following, which Lowered Stack Performance:
      1. Increased PEM Material Mass Loss and Acetic Acid Production
      2. Lower Electrocatalyst Active Area through Agglomeration/Detachment

Questions?

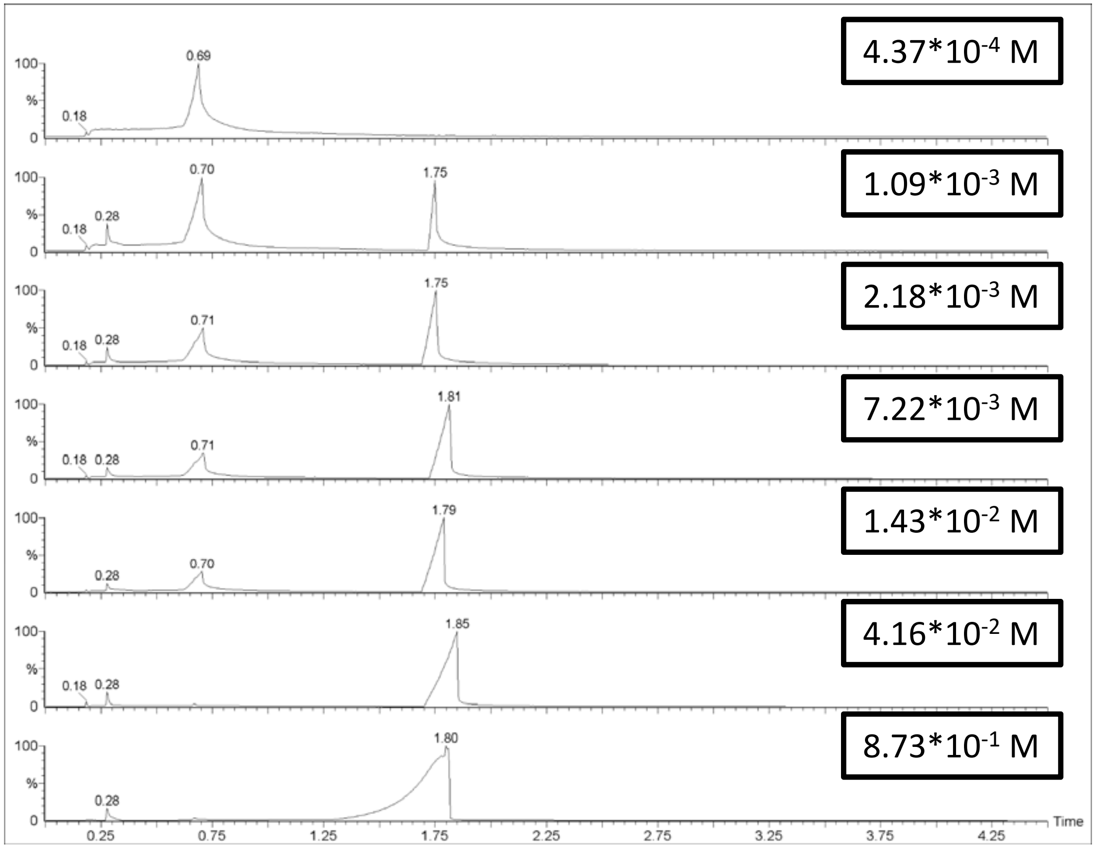
GC/MS Data Collected from the Fuel Cell Laboratory

SEM/EDS and XRD Data Collected from Metallurgy Laboratory

TGA Data Collected from the EFTI Laboratory

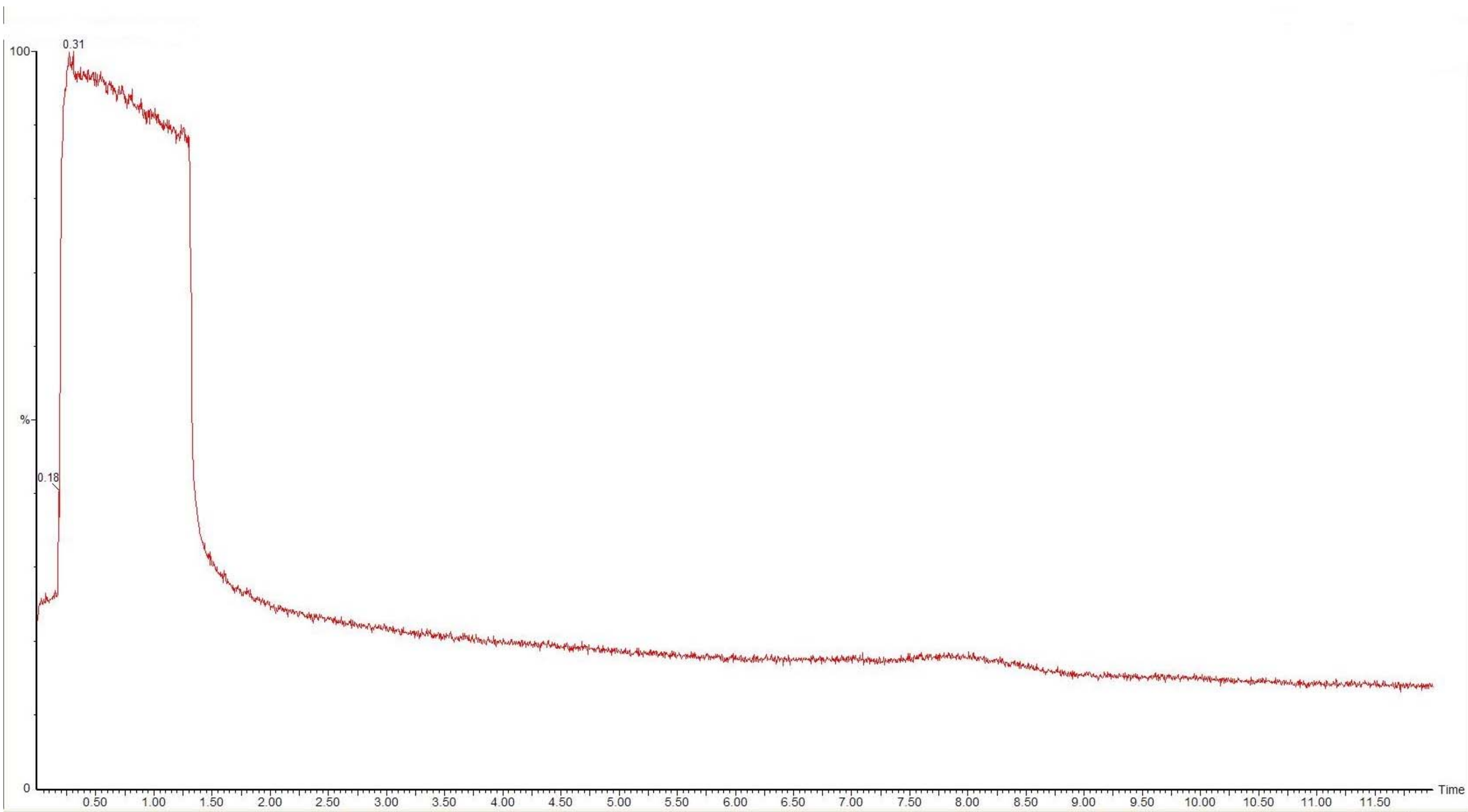
Backup Slides

Acetic Acid Peak Positions with Different Molarities

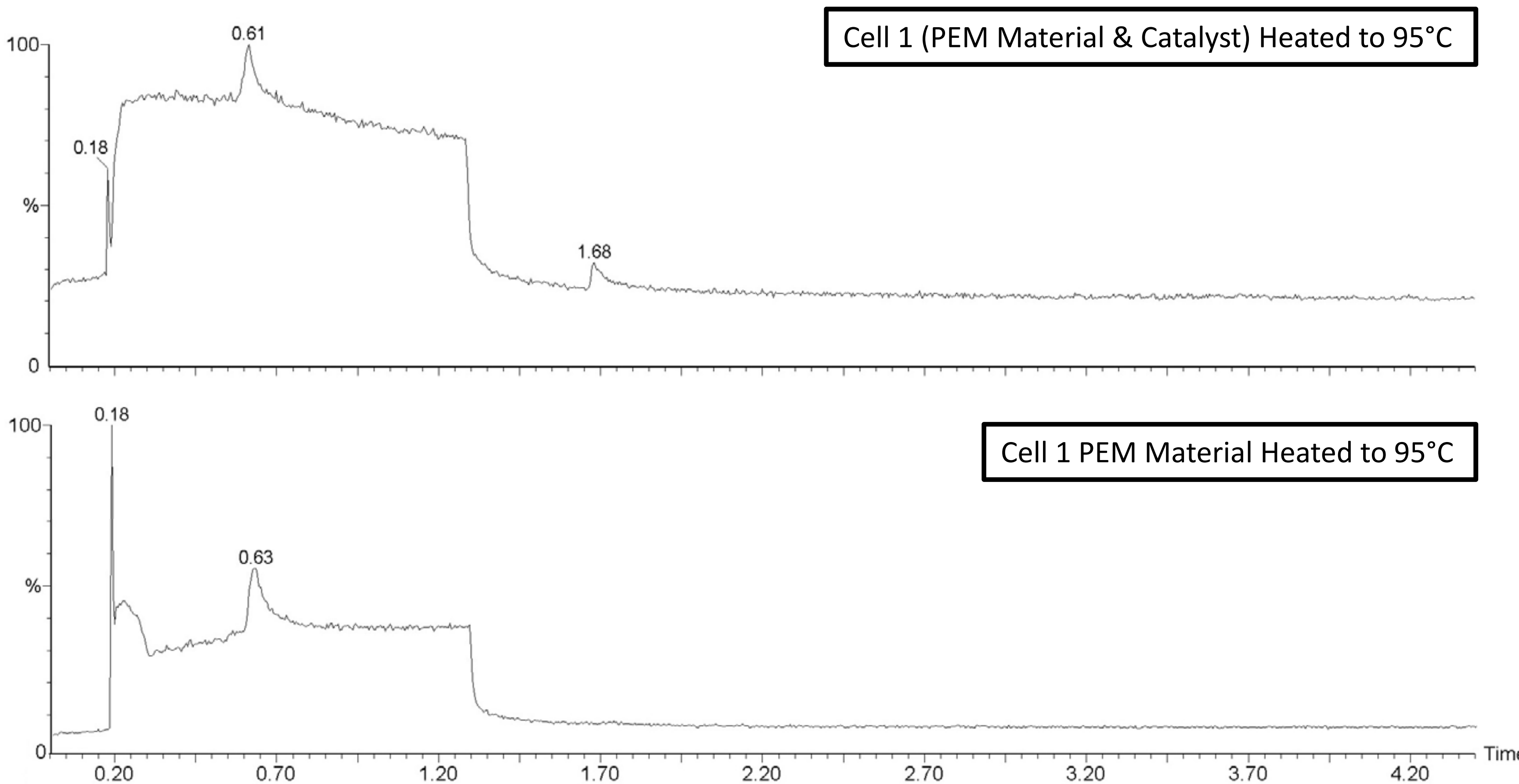


FCATT Dynalene Coolant Chromatogram

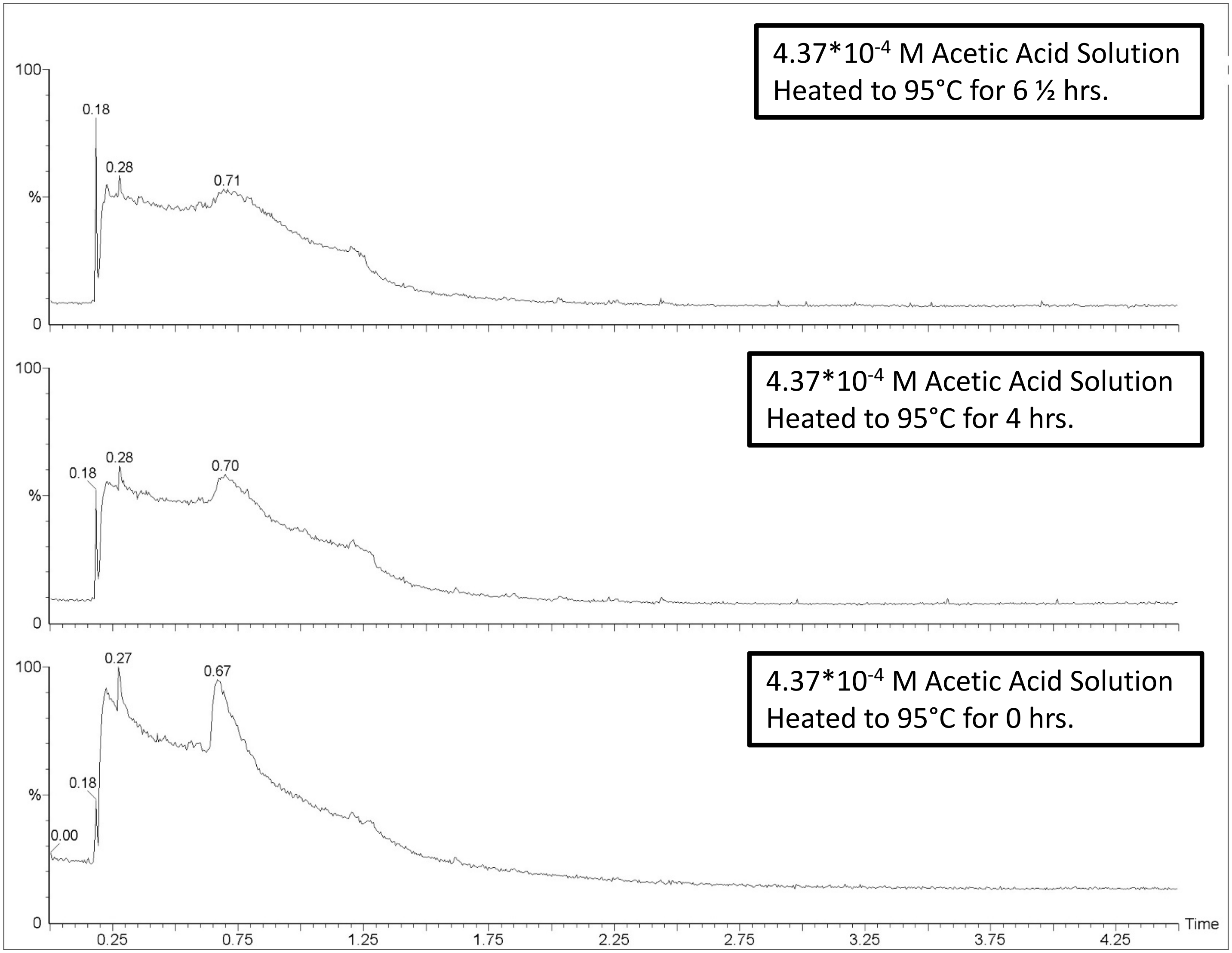
FCATT Tailpipe Chromatogram



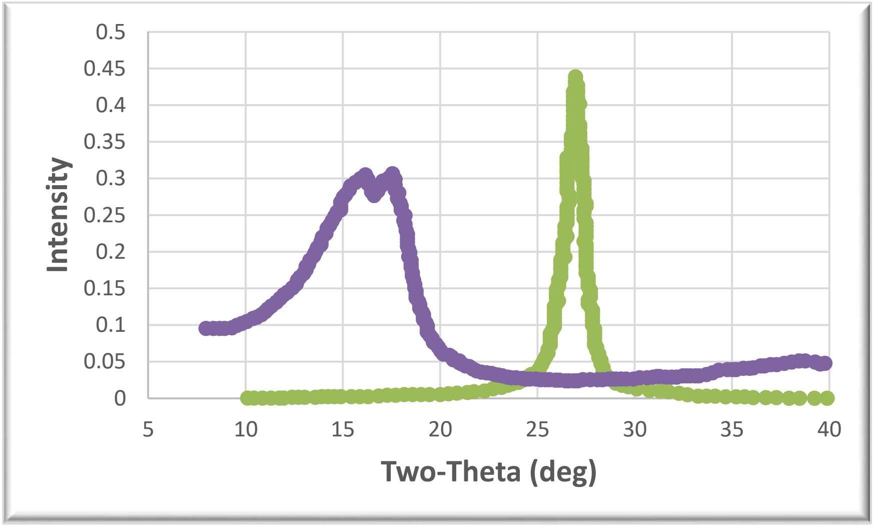
Catalyst Promotes Formation of Separate Acetic Acid Peak

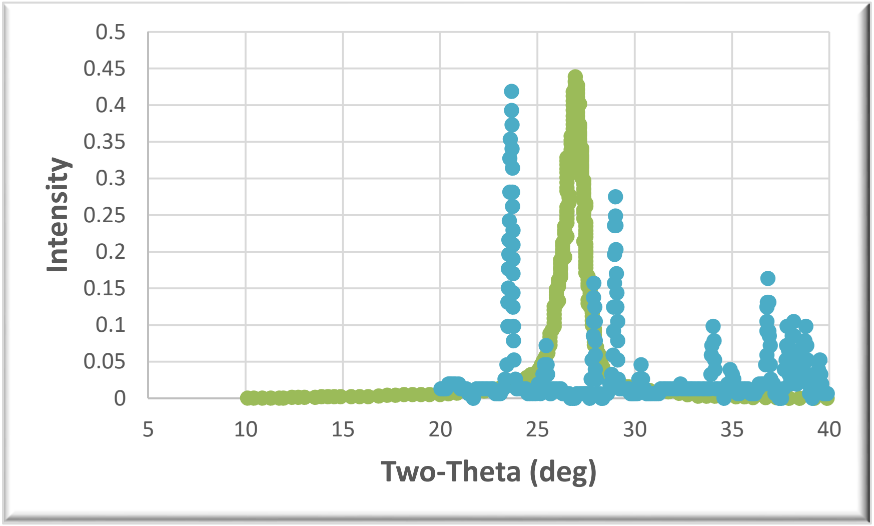


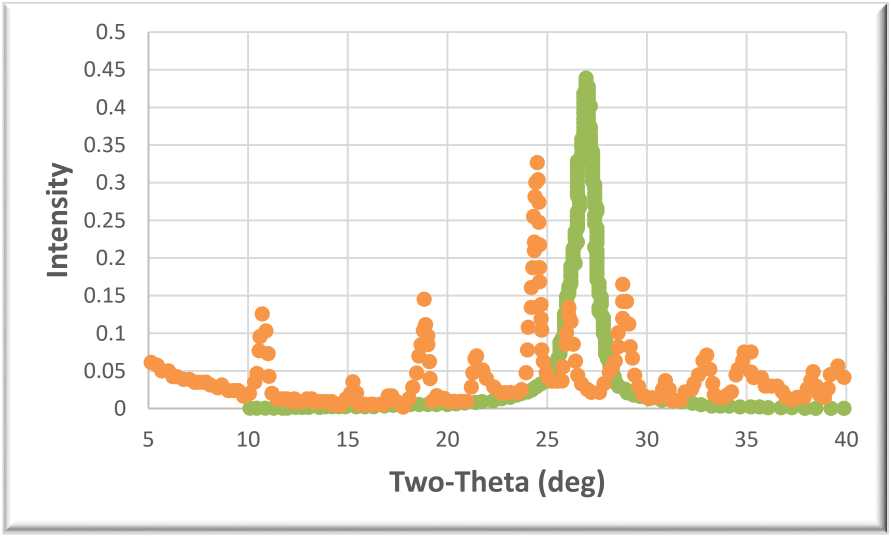
Acetic Acid Evaporates Around 100°C



Comparison of Literature PEM Materials XRD Data







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