Low Cost, Durable Seals For PEM Fuel Cells

Jason Parsons
UTC Power Corporation
May 21, 2009

FC_42_Parsons

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

DOE Hydrogen Program

Timeline

- Start: Apr 2007
- End: Sept 2009
- 70% Complete

Barriers

- A: Fuel cell seal durability
- Fuel cell seal cost is also being evaluated

Budget

- Total Project Funding
  - DOE: $1,980K
  - Contractor: $1,320K
- Funding Received in FY08
  - $600K
- Funding for FY09
  - $630K

Partners

UTC Power
A United Technologies Company
(Project Lead)

Henkel
A Brand like a Friend

Freudenberg NOK

Virginia Tech
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Collaborators

DOE Hydrogen Program

Collaborator	Project Role	Team Leads
UTC Power, A United Technologies Company	•Material specification •Seal interactions •Modeling •Seal design •Stack design	•Jason Parsons
Henkel, A Brand like a Friend	•Materials development •Development support and consulting	•Dr. Matthew Burdzy
Freudenberg NOK	•Seal concept evaluation •Rapid prototyping •Process development	•Mark Belchuk
Virginia Tech, Virginia Polytechnic Institute and State University	•Material characterization •Accelerated testing	•Dr. David Dillard

UTC Power
A United Technologies Company

Objectives – Relevance to DOE Targets

DOE Hydrogen Program

The Goal: Develop a low cost, non-silicone, durable seal material and sealing techniques amenable to high volume manufacture of PEM cell stacks.

DOE Targets/Goals/Objectives	Project Goals
Durability ***Barrier A*** Transportation: 5,000 hr Stationary: 40,000 hr	Durability - 4000 hr bulk material testing at up to 90 °C - Up to 4000 hr air aging and CSR at up to 120 °C - 4000 hr accelerated out-of-cell testing - 2000 hr in-cell verification testing
Low Cost ***Barrier B*** - Barrier not explicitly identified for seals - DTI study suggests target of \$3.91/kW @ 500k stacks/year - Fuel Cell Tech Team suggests \$2.00/kW @ 500k stacks/year	Low Cost - Evaluate seal material and production method against suggested targets

UTC Power
A United Technologies Company

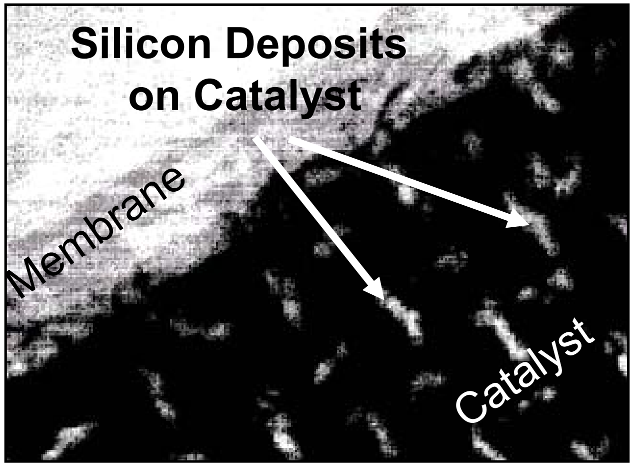
Background

Material selection concept

Material Category	Stress Relaxation	Chemical Stability	Processibility	Low Cost
LIM Silicone	–	–	+	+
Fluoropolymers	O	+	O	–
Existing Hydrocarbons	+	+	O	O
LIM Hydrocarbon	+	+	+	+

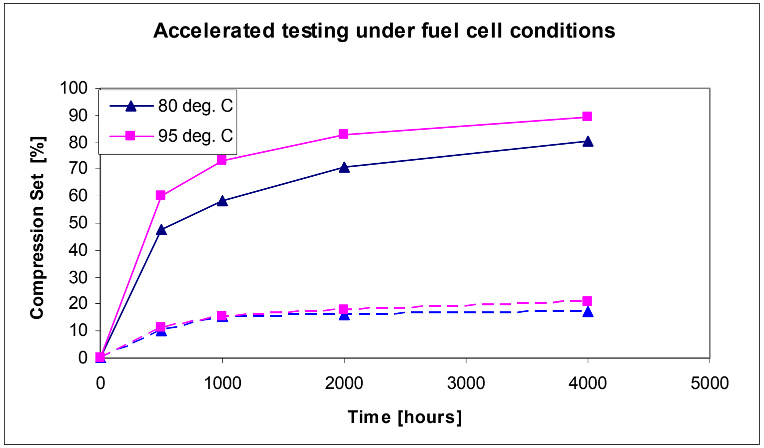
+ Excellent **O Fair** **– Poor** *LIM = Liquid Injection Moldable

Silicones are know to breakdown and chemically contaminate the fuel cell



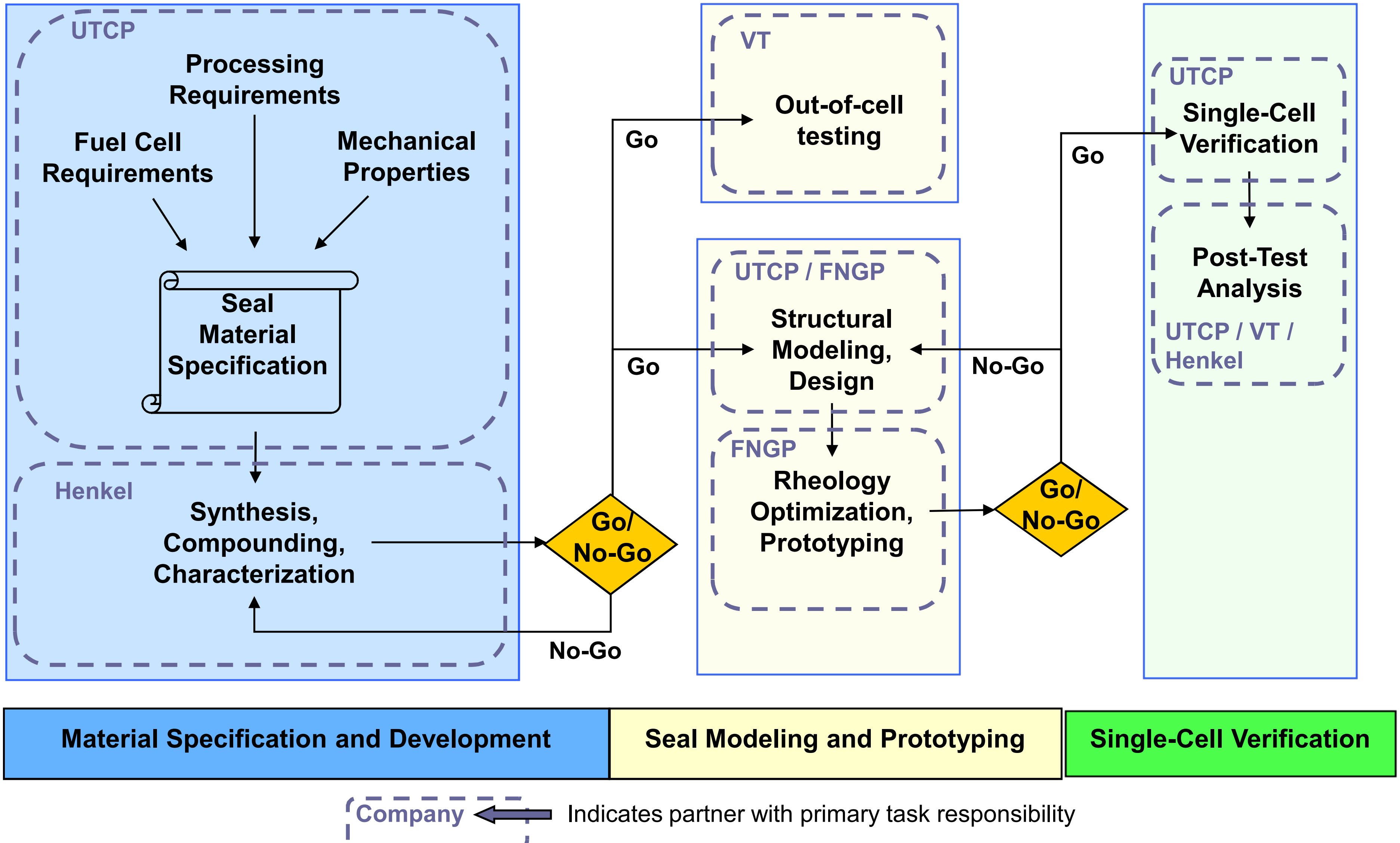
Source: M. Schulze, et. al., Journal of Power Sources 127 (2004) 222-229

Hydrocarbon elastomers can retain load better than silicones in PEM environments



Source: UTCFC-DOE Topic 1, Contract #DE-FC36-04GO14053 , Merit Review, PEM Cell Stack Activities, 2005

Approach



UTC Power
A United Technologies Company

FY08 / FY09 Milestones - Revised

DOE Hydrogen Program

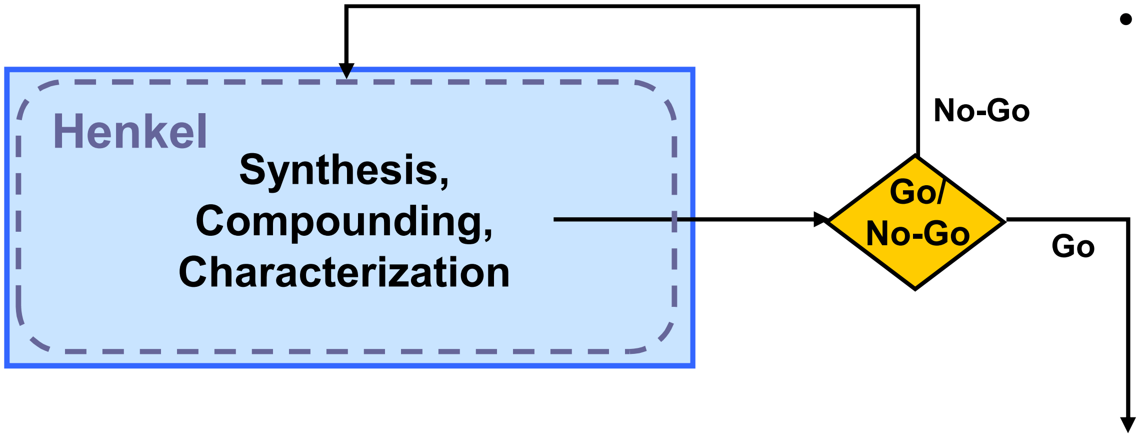
Milestones or Go/No-Go Decision	Progress Notes	% Comp
Go/No-Go: Down-select candidate to carry forward for in-cell testing	FCS2 chosen for validation	100
Milestone: Material characterization report for the leading candidate material	Most required data has been collected	90
Go/No-Go: Full-size prototype design selection	No-Go for 1st design choice, evaluating 2nd choice and a low-risk alternative	75
Milestone: 4000 hr bulk material testing	Substantial bulk material testing completed.	80
Milestone: 4000 hr accelerated out-of-cell testing	Equipment fabricated and/or acquired; Check-out complete; Sub-scale seal testing ready to begin	10
Milestone: 2000 hr In-Cell verification testing	Waiting for full-size parts	0

UTC Power
A United Technologies Company

Accomplishments and Progress

Summary of Materials

- 100's of experiments
- Most promising candidates released for additional evaluation



Iteration	Description
FCS0	One-part material meeting all minimum material requirements
FCS1	Two-part material with improved curing and mechanical characteristics
FCS2	One-part material based on FCS1; purpose: to eliminate the potential for shot-to-shot mixing variability in the production of SMORS
FCS3	One-part material with improved tear strength and elongation; expected to meet all program requirements (not yet released)

Accomplishments and Progress

Material properties vs. specification

- All three material candidates meet or exceed all minimum project goals
- In terms of key initial properties, all three also meet or exceed most of the ultimate project goals

Henkel LIM Hydrocarbon Elastomer Property Table for DOE					
Properties	Project Requirements		FCS0	FCS1	FCS2
	Minimum	Ultimate			
Process Properties					
LIM processable	Yes	Yes	Yes	Yes	Yes
Viscosity @ room temperature (cPs)	<= 700,000	<= 600,000	~ 500,000	~ 543,000	~ 543,000
Mold temperature (°C)	< 135	<= 110	120 to 130	120 to 130	120 to 130
Mold time (second)	<= 400	<= 60	60 to 120*	60 to 120*	60 to 120*
Mechanical Propreties					
Hardness (Shore A)	15 to 68	30 to 55	31	30	30
100% Modulus (Mpa)	0.25 to 3.5	1 to 2.5	0.75	0.68	0.69
Tensile strength (Mpa)	>= 0.5	>= 0.8	1.3	1.3	1.1
Elongatin (%)	> 125	> 150	163	171	160
Tear strength Die C (kN/m)	>= 2.7	>= 5.0	3.7	3.7	3.9
Environmental Requirements					
Temperature resistance (°C)	-40 to 85	-40 to 90	-40 to 90	-40 to 90	-40 to 120
Notes					
*cure schedule: 120 second in the mold @ 120°C and then 1 hour post cure @ 130°C					

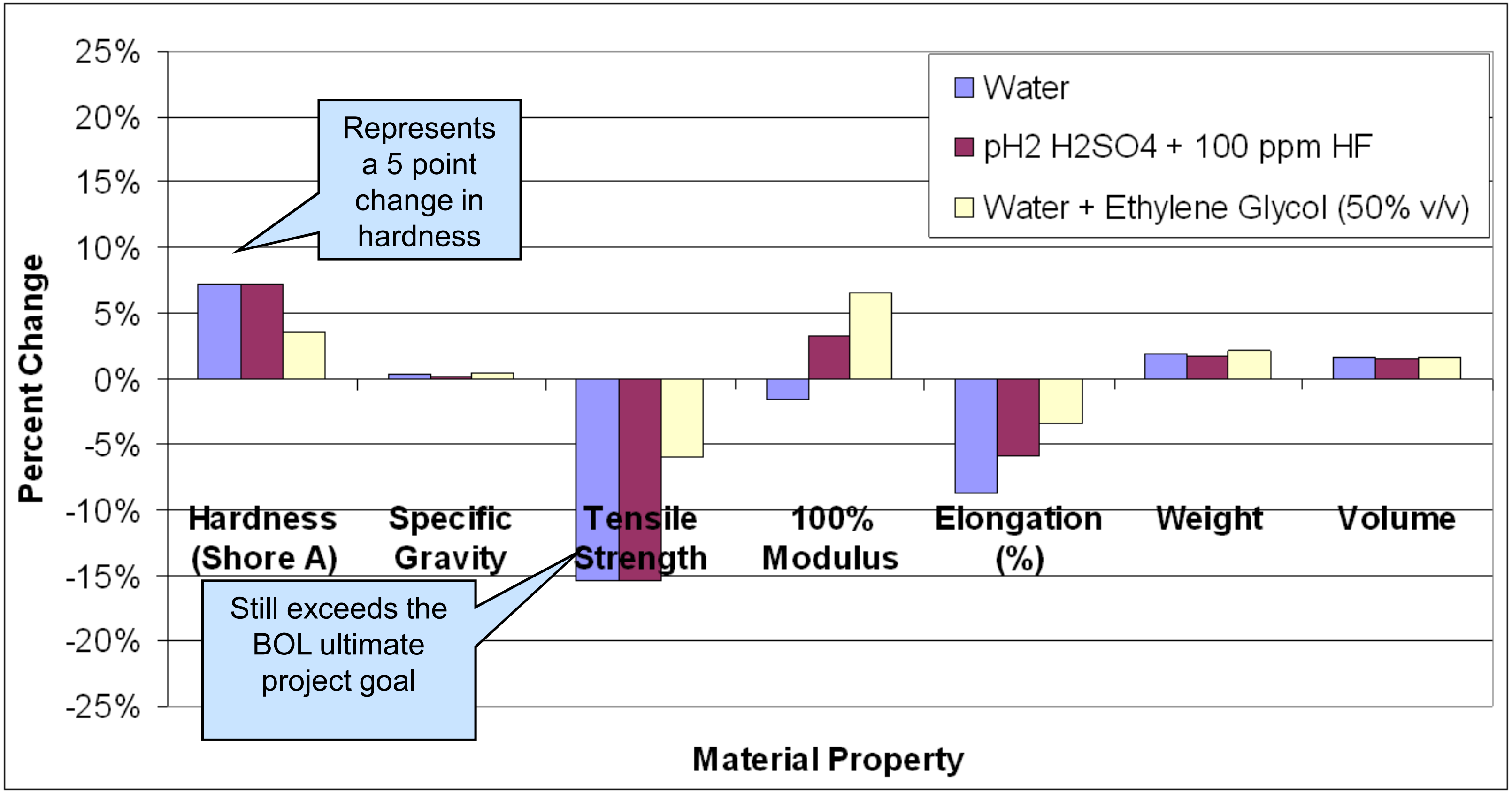
Green: meets minimum & ultimate requirements
Yellow: meets minumum requirements
Red: below minimum requirements

DOE Hydrogen Program

UTC Power
A United Technologies Company

Accomplishments and Progress

FCS1 6600 hr fluid immersion test @ 90C



Accomplishments and Progress

Compatibility testing

DOE Hydrogen Program

Overall, one of the cleanest seal materials tested by UTC Power

Organic Migration and Deposition		
Test Parameter	**Result**	
	FCS0	**FCS1**
Vapor Phase Deposition	**None detected**	
Surface Migration	**Contact transfer only – no migration detected**	

DI Water Immersion		
Test Parameter	**Result – FCS0 / FCS1**	
	500hr	**1000hr**
Surface Tension by Tensiometer (% change)	**3 / –**	**1 / –**
Total Organic Carbon (ppm)	**– / –**	**10 / –**
Total Inorganic Content by IC/ICP-AES (ppm)	**2 / 3**	**2 / –**
Volatile Organic Content by GC-MS (ppm)	**– / –**	**0 / –**
pH	**5.7 / 5.8**	**– / –**
Conductivity (µS/cm)	**4 / 3**	**– / –**

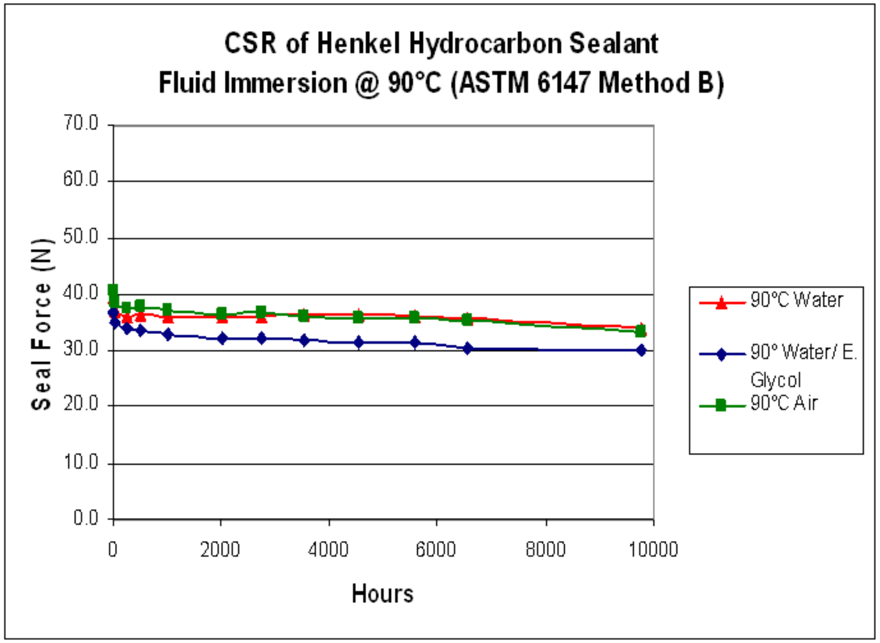
UTC Power
A United Technologies Company

Accomplishments and Progress

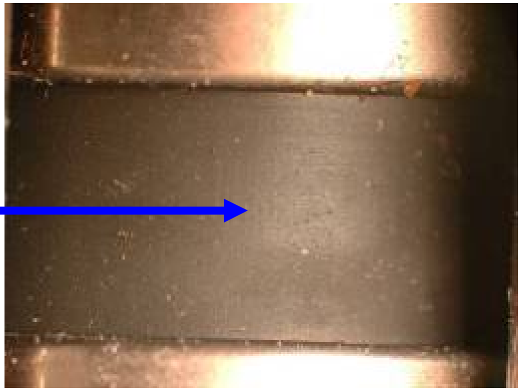
10000 hr ex-situ durability test - Sealing

DOE Hydrogen Program

- Compression Stress Relaxation (CSR)
  - 10,000 Hour Durability
  - No visible signs of degradation
  - Less than 20% decay
- Sealing Force:
  - 25% compression, 0.5 MPa
- Henkel Technology:
  - Proprietary resin & cross-linker
  - Benefits – stable sealing force & low compression set
  - Automotive operating lifetime



CSR fixture



CSR sample

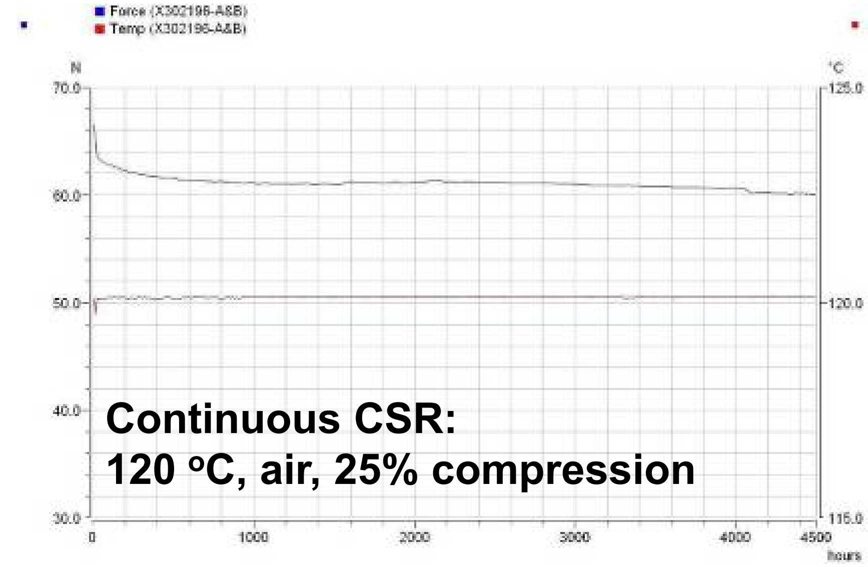
UTC Power
A United Technologies Company

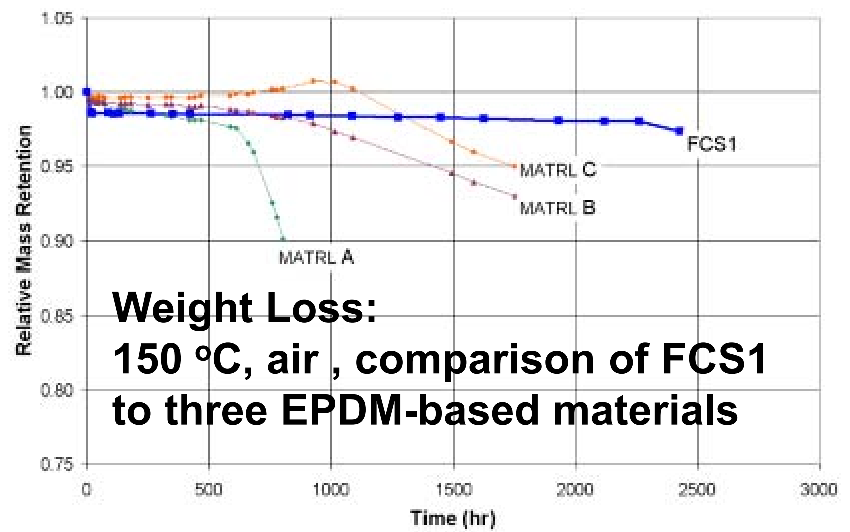
Accomplishments and Progress

Additional testing of FCS1 @ T above 90 °C

DOE Hydrogen Program

- Compression Stress Relaxation
  - 4500 Hour Durability @ 120 °C
  - Less than 10% decay
- Compression Set at 120 °C
  - Less than 10% (1000 hrs)
- Thermal stability
  - Air-aging @ 150 °C
  - FCS1 and three EPDM-based fuel cell seal materials (A, B, & C) were compared
  - FCS1 exhibits the best thermal stability and showed no sign of oxidation after more than1500 hours.





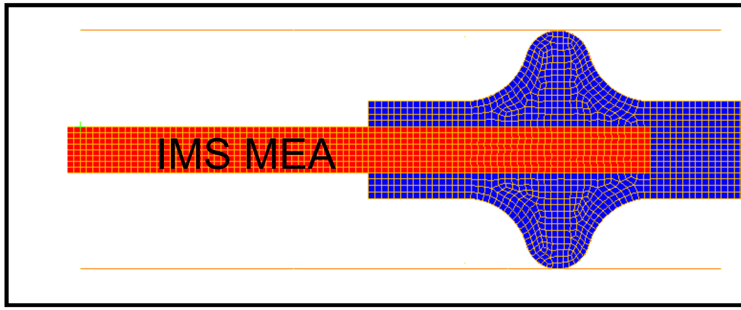
UTC Power
A United Technologies Company

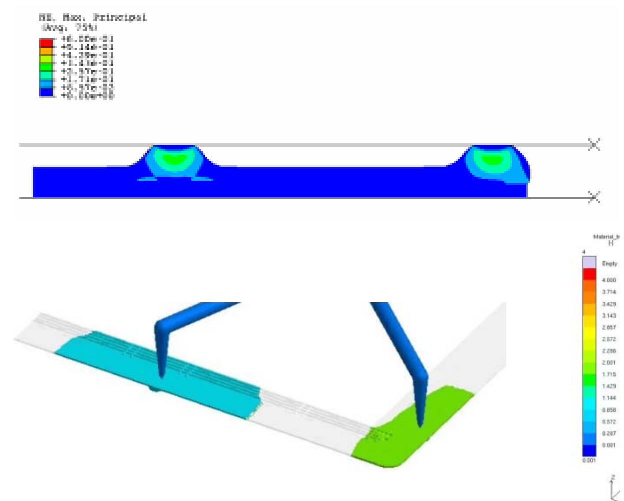
Accomplishments and Progress

Full-Size proto-type development

DOE Hydrogen Program

- Integrated Molded Seal (IMS) MEA
  - Benefit: Addresses cost by combining
    - Unitization of the MEA
    - Molding of the seal
    - Placement of the sealing features
  - Multiple designs considered
  - Preferred Design: low-profile seal (1st Choice)
    - Rejected based on FEA modeling and tolerance analysis
  - Alternative Design (2nd Choice)
    - Taller seal beads mitigate effects of tolerance stack-up
    - FEA evaluation and mold-flow analysis underway
- Parallel Effort
  - In-cell evaluation of seals over-molded on Polyethylene Naphthalate (PEN) film
  - Benefit: Industry alignment





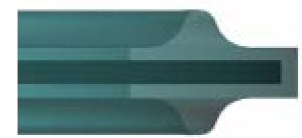
FEA and Mold-flow analysis underway for Alternate IMS Design

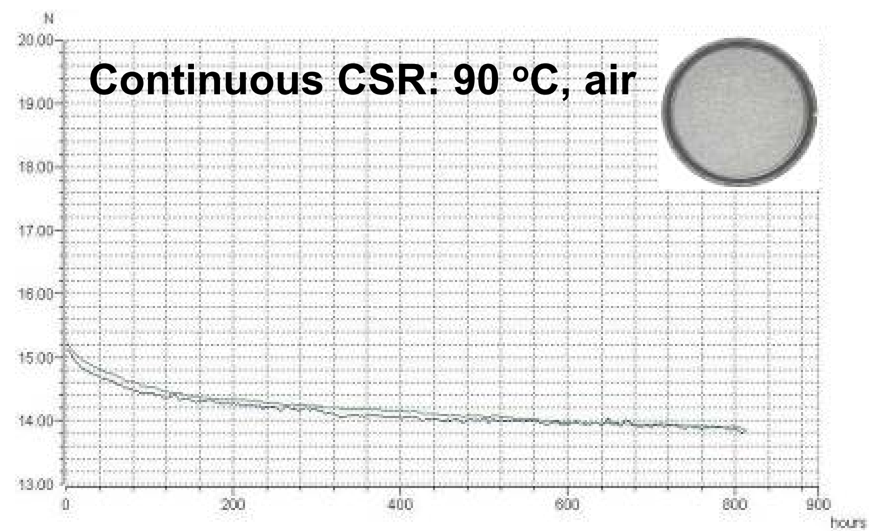
UTC Power
A United Technologies Company

Accomplishments and Progress

Subscale seal testing

- **Sub-scale Molded O-ring Seals (SMORS)**
  - Seal liquid injection molded over substrate by FNGP
  - Used for compression and leak testing
  - Single bead facilitates detection of leaks
  - Cross-section mimics full-size part
  - Used to verify results obtained in bulk material tests
- **Progress**
  - Initial CSR test by VT showed higher than expected sealing force decay
  - Analysis by Henkel revealed the causes
    - Over-compression of the porous substrate
    - Differences between the ideal FEA model and the molded parts
    - Sub-optimal cure
- **Solution & results**
  - Cure (1 min @ 120 °C) & post cure to achieve short cycle time and optimal cure.
  - With 15% compression, measured sealing pressure is three times the maximum fuel cell design pressure and effects of the GDL are negated.
  - Resulting CSR tests on SMORS show the expected result of less than 10% load decay over 800 hrs.





UTC Power
A United Technologies Company

DOE Hydrogen Program

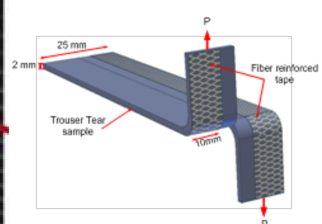
Accomplishments and Progress

DOE Hydrogen Program

Testing at VT - Overview

Test	Standard	Equipment	Specimen	Properties of Interest
Tensile	ASTM D638	Instron MicroTester	Dogbone	Tensile strength, Elongation to break
Tear	ASTM D624 Type T	Instron MicroTester	Rectangular Tear Sample	Seal material resistance to crack propagation
Mass Uptake	ASTM D570	Mettler Toledo Analytical Balance	Cylindrical Disks	Diffusion Coefficient, Solubility
Compression Stress Relaxation	-	Custom Designed Jig	SMORS	Calculation of sealing force in the seal in various environments and temperatures
Leak Test	-	Custom Designed Fixture	SMORS	Leak properties in various environments at different temperatures

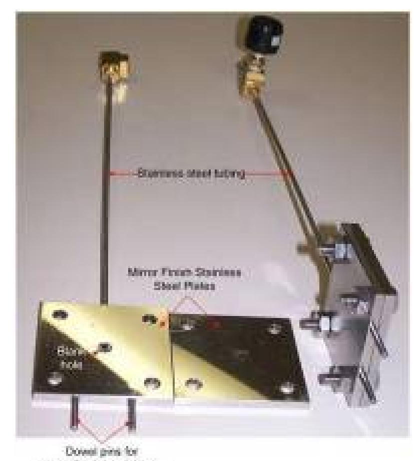
Tensile



Tear

Mass Uptake

CSR



Leak Test

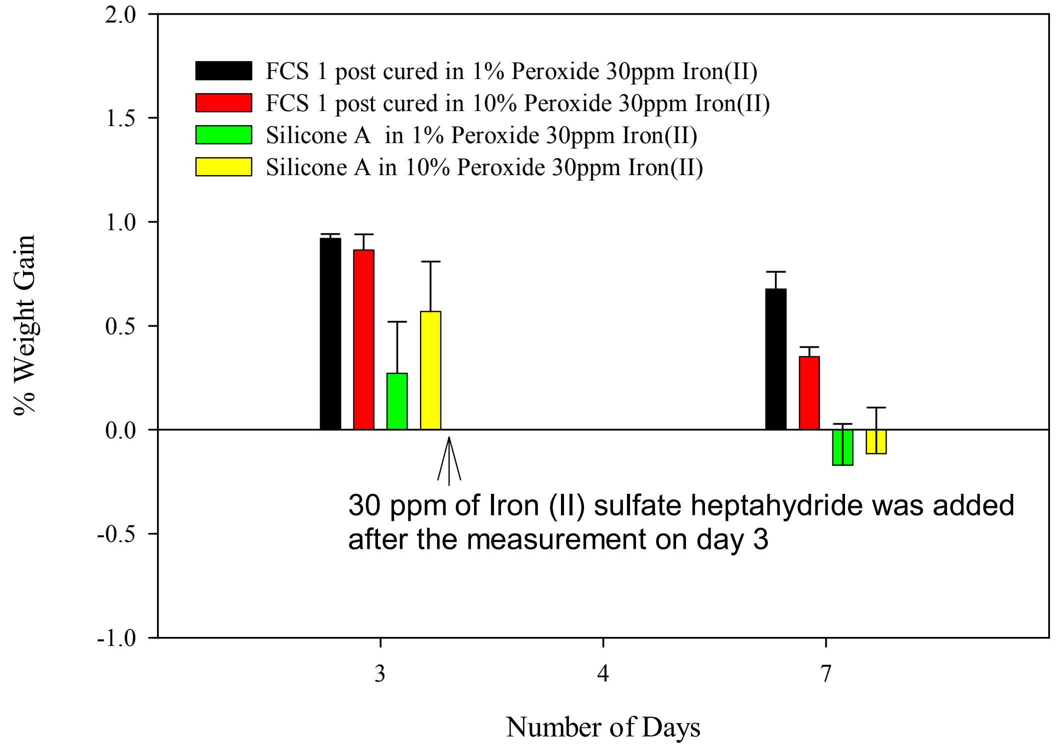
UTC Power
A United Technologies Company

Accomplishments and Progress

Testing at VT – Degradation using Fenton's Reagent

Conditions:

- T=90 °C
- 1 and 10% Hydrogen peroxide
- 30 ppm Iron(II) sulfate heptahydrate



Future Work

- Materials selection and development
  - Complete work on FCS3 (increase modulus, elongation, and tear strength)
- Out-of-Cell testing
  - Execute 4000 hr accelerated testing on SMORS
  - Verify 4000 hr aging results on FCS2 bulk samples
  - FCS3 testing up to 3000 hrs
  - Continue benchmarking against other materials
- Full-size prototype development
  - Evaluation of alternative seal design for Go/No-Go
  - Over-mold seals on PEN for full-size in-cell evaluation
  - Perform additional molding trials
    - Incorporate any lessons learned from the alternative seal design
- In-cell testing
  - Screen sub-scale MEAs with molded seals
    - Testing for seal adhesion, penetration, and specific interactions
  - Execute 2000 hr verification testing using full-size seals

Summary

DOE Hydrogen Program

- Project Goal
  - Develop a durable and low-cost PEM fuel cell seal material
- Materials selection and development
  - Material properties for available candidates meet most ultimate project goals
  - FCS3 expected to meet all project goals
- Out-of-cell testing
  - Initial data from chemical and mechanical durability tests on sheet stock and sub-scale parts are encouraging
  - More than 4000 hours of testing accumulated
    - Over 10,000 hours on FCS0
    - 4000 hr performance to be verified on SMORS
  - Nearly 5000 hours in air at 120C demonstrated
- In-cell testing
  - Full-size parts for in-cell testing on schedule for completion by the project end date

Acknowledgements

- UTC Power
  - George Roberts
  - Bhavana Bommarajpeta
- Henkel
  - Dr. Matthew Burdzy
  - Dr. Yanbing Wang
  - Dr. Younghui Zhang
- Freudenberg - NOK
  - Mark Belchuk
  - Ronnie Adams
- Virginia Tech
  - Dr. David Dillard
  - Hitendra Singh – PhD Candidate
  - Dr. John Dillard
  - Dr. Robert Moore
  - Dr. Wonho Kim – Visiting Professor
  - Gilles Divoux – PhD Candidate
  - Dr. Scott Case

Additional Slides

Accomplishments and Progress

FCS1 6600 hr immersion test

DOE Hydrogen Program

Excellent mechanical, weight, and volume stability

Change @ 6600h

- Hardness:
  1 to 6 point increase
- Weight/Volume:
  -1 to 2%
- Tensile/Elongation:
  -15 to 8%

Henkel Hydrocarbon Heat Cured Elastomer FCS1							
Condition	Property	Initial	1000 h	2000 h	3300 h	6600 h	Change @ 6600 h
Water @ 90°C	Hardness Shore A	28	29	29	29	30	2 point
	Specific Gravity	0.979	0.980	0.981	0.981	0.982	0.31%
	Tensile Strength (MPa)	1.49	1.26	1.34	1.32	1.26	-15.44%
	100% Modulus (MPa)	0.61	0.55	0.60	0.61	0.60	-1.48%
	Elongation (%)	206	190	200	190	188	-8.74%
	Weight change (%)	0%	1.27%	1.28%	1.84%	1.90%	1.90%
	Volume change (%)	0%	1.17%	1.04%	1.67%	1.63%	1.63%
pH2 H2SO4 + 100 ppm HF- @ 90°C	Hardness Shore A	28	29	30	29	30	2 point
	Specific Gravity	0.979	0.980	0.982	0.981	0.982	0.31%
	Tensile Strength (MPa)	1.49	1.30	1.23	1.29	1.26	-15.44%
	100% Modulus (MPa)	0.61	0.63	0.62	0.64	0.63	3.45%
	Elongation (%)	206	189	191	196	194	-5.83%
	Weight change (%)	0%	1.21%	1.41%	1.73%	1.79%	1.79%
	Volume change (%)	0%	1.13%	1.13%	1.52%	1.52%	1.52%
Water + E. Glycol (50% v/v) @ 90°C	Hardness Shore A	28	29	30	30	29	1 point
	Specific Gravity	0.979	0.980	0.982	0.982	0.983	0.41%
	Tensile Strength (MPa)	1.49	1.47	1.39	1.43	1.40	-6.04%
	100% Modulus (MPa)	0.61	0.64	0.61	0.62	0.65	6.73%
	Elongation (%)	206	205	204	195	199	-3.40%
	Weight change (%)	0%	-0.18%	0.17%	0.49%	2.07%	2.07%
	Volume change (%)	0%	-0.31%	-0.12%	0.17%	1.65%	1.65%
110°C (air)	Hardness (Duro A)	28	30	34	34	34	6 point
	Specific gravity	0.979	0.977	0.979	0.978	0.979	0.00%
	Tensile strength (MPa)	1.49	1.58	1.53	1.66	1.61	8.05%
	100% Modulus (MPa)	0.61	0.67	0.85	0.78	0.85	39.57%
	Elongation (%)	206	193	170	186	177	-14.08%
	Weight change (%)	0%	-1.27%	-1.21%	-1.25%	-1.23%	-1.23%
	Volume change (%)	0%	-1.10%	-1.18%	-1.19%	-1.24%	-1.24%

UTC Power
A United Technologies Company

Accomplishments and Progress

6,600 hr ex-situ durability test – H_2 stability

Test Specimens: X305543

Samples: ASTM D 638 Die IV Dog Bones
13 mm OD x 6.5mm H plugs

Conditions: Temperature = 90ºC
Hydrogen = 15 psi @ 23ºC
Water = 100 ml ASTM D 1193 Type 1 Water

Test Methods:

Tensile Strength	ASTM D 412 (ASTM D 638 Type IV Die)	Average of 5 specimens/ test point
100% Modulus	ASTM D 412 (ASTM D 638 Type IV Die)	Average of 5 specimens/ test point
% Elongation @ Break	ASTM D 412 (ASTM D 638 Type IV Die)	Average of 5 specimens/ test point
Hardness (Shore A)	ASTM D 2240	Average of 3 replicates per specimen/ 5 specimens
% Weight Change	ASTM D 471	Average of 5 specimens
% Volume Change	ASTM D 471	Average of 5 specimens
Density	ASTM D 471	Average of 5 specimens

Property Summary Table
Immersion @ 90°C in Hydrogen (15psi)

Property	Method	Product	0 Hours Average	100 Hours Average	500 Hours Average	1000 Hours Average	2000 Hours Average	3390 Hours Average	6652 Hours Average
Tensile Strength (Mpa)	ASTM D 412 (ASTM D 638 Type IV Die)	X305543	1.4	1.4	1.3	1.3	1.4	1.5	1.3
100% Modulus (MPa)	ASTM D 412 (ASTM D 638 Type IV Die)	X305543	0.7	0.8	0.9	0.9	0.9	0.9	0.9
% Elongation @ Break	ASTM D 412 (ASTM D 638 Type IV Die)	X305543	177	162	143	146	143	156	142
Hardness (Shore A)	ASTM D 2240	X305543	36	38	38	38	38	38	38
% Weight Change	ASTM D 471	X305543	0%	0.27%	0.38%	0.36%	0.26%	0.46%	0.62%
% Volume Change	ASTM D 471	X305543	0%	-0.93%	-1.09%	-2.05%	-0.11%	-1.01%	-0.43%
Density (g/cc)	ASTM D 471	X305543	0.963	0.975	0.978	0.987	0.967	0.978	0.974

Life time prediction at Henkel

DOE Hydrogen Program

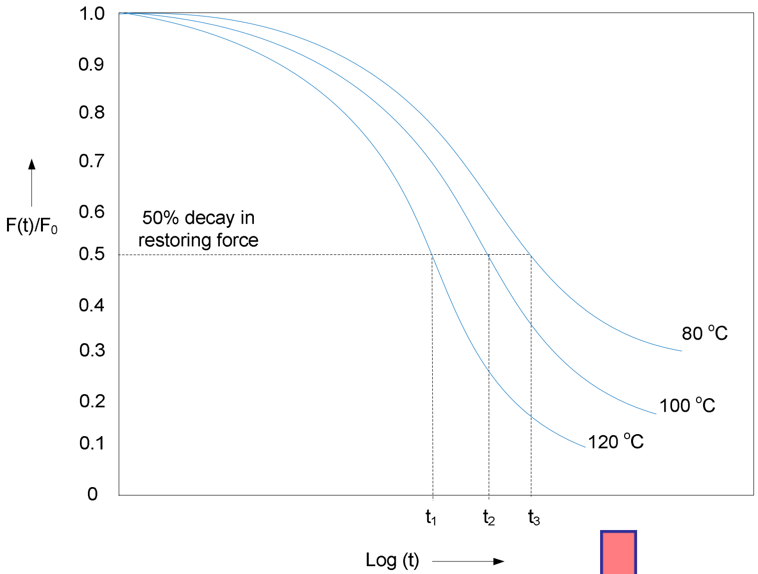
* Based upon Relaxation Test @ multiple temperatures using Arrhenius procedures

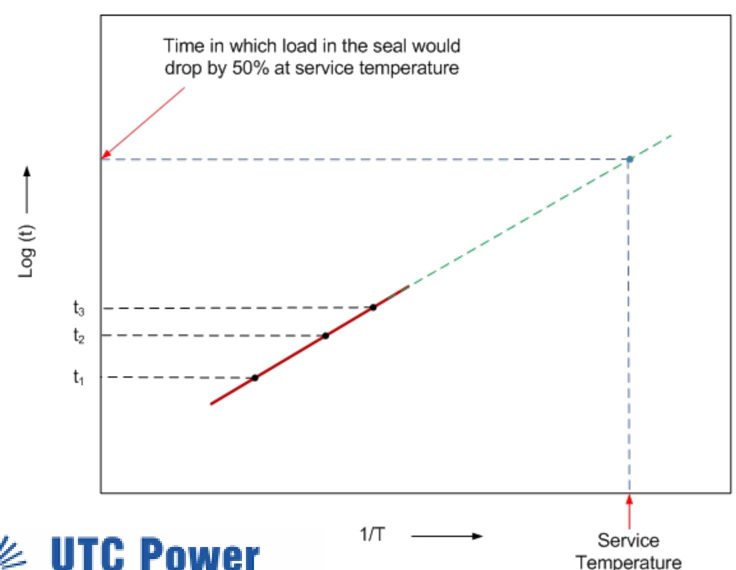
Elastocon CSR Equipment at Henkel

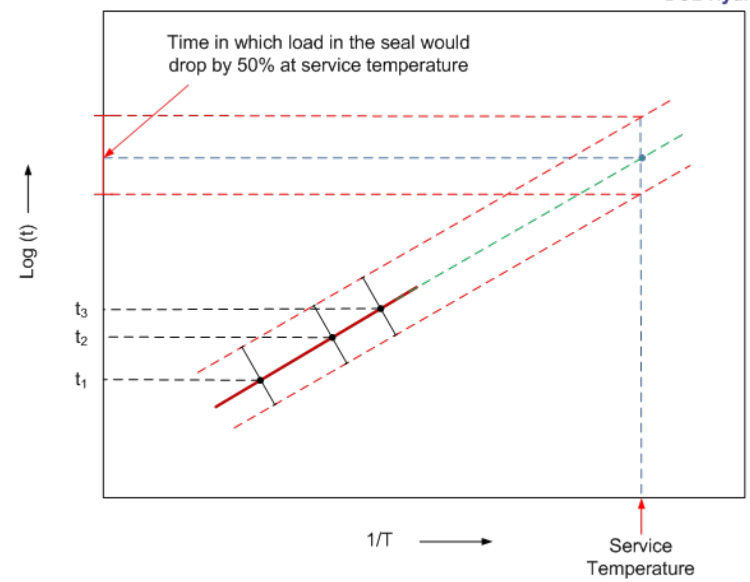
- Continuous CSR
- 80, 100, and 120 ºC
- 3 Cells / 3 Temperatures
- Hot air
- 50% sealing force decay
- Sample Life-time Estimation*

UTC Power
A United Technologies Company

Proposed Lifetime Prediction Approach at VT





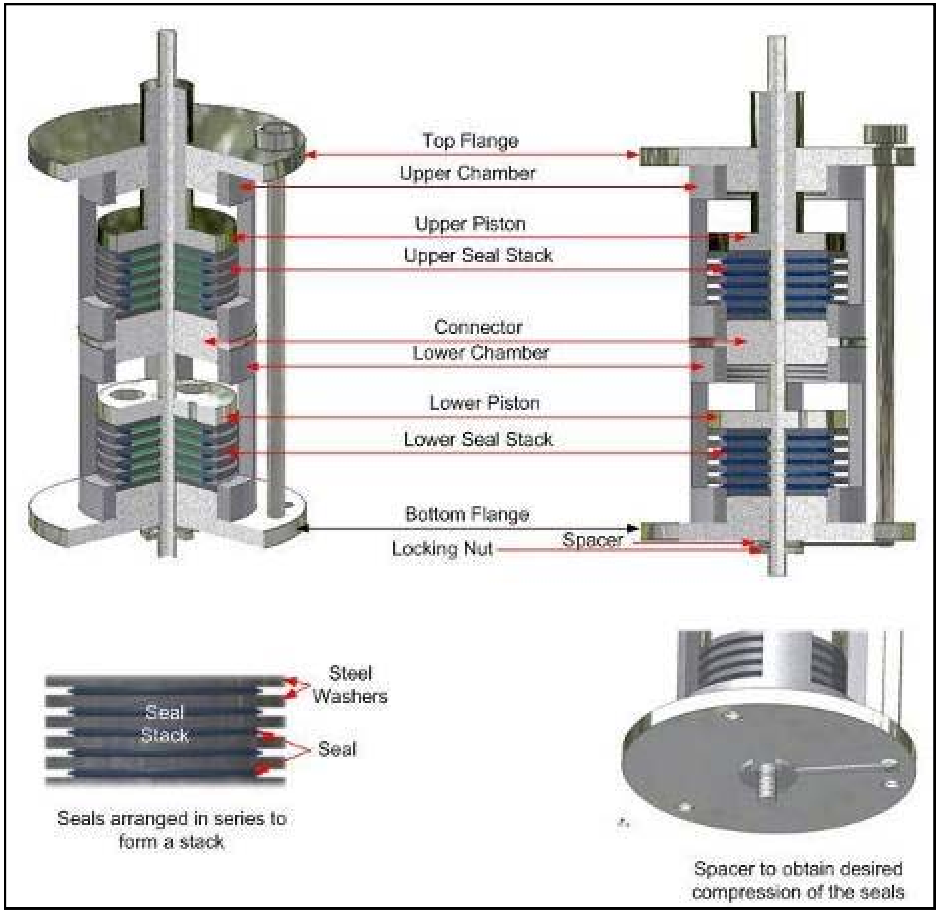


- Primary method:
  - Compression stress relaxation (CSR) experiments over a range of environmental conditions using custom fixture.
- Preparation of Arrhenius plots using The Arrhenius Equation
  - *[ISO 11346. Rubber, Vulcanized or Thermoplastic – Estimation of Life-time and Maximum Temperature of Use from an Arrhenius plot. 1997]*

UTC Power
A United Technologies Company

CSR Fixture: Original & Modified Design

DOE Hydrogen Program



Original Design

- Advantage: Tracking of both compressive properties and load relaxation over time in identical environments and one rig
- Disadvantage: Intermittent measurements introduce noise when working with low durometer seals

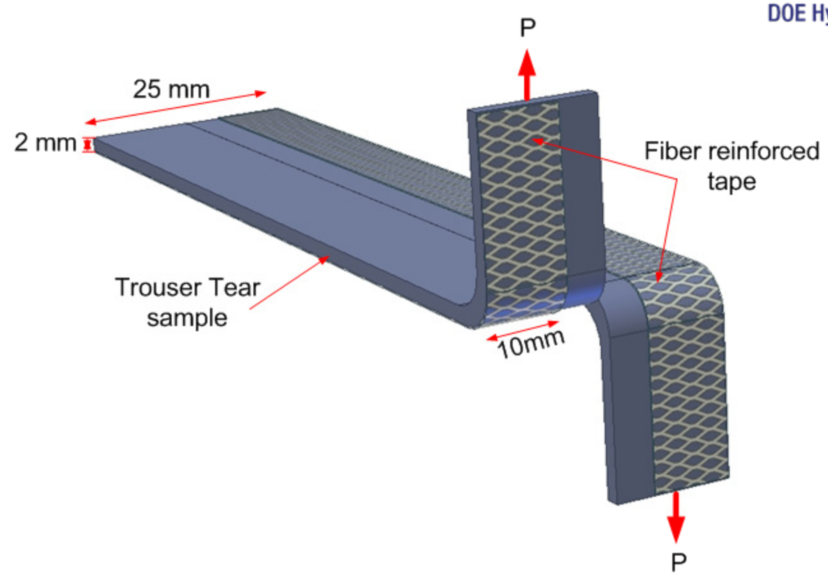
Modified Design

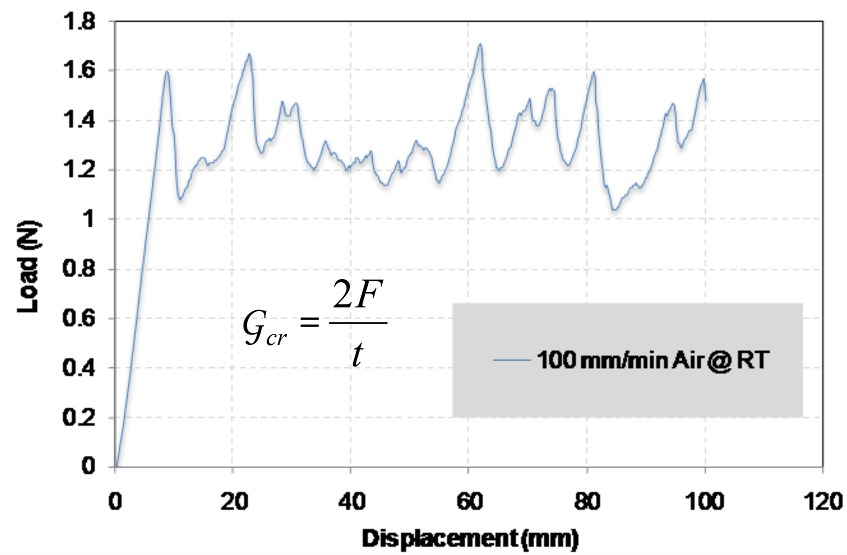
- Advantage: Continuous load relaxation measurement greatly reduces noise in the data
- Disadvantage: Samples used for tracking changes in compressive properties will need to be aged separately

UTC Power
A United Technologies Company

Trouser Tear: Test Procedure

- Properties: Critical tear energy, $\mathcal{G}_{cr}$
- Specimen Type: 2mm thick tear samples cut using ASTM D624 Type T Die
- Test Method: Trouser tear according to ASTM D624
- Loading Rate: 2 to 500 mm/min
- Load Measurement: Instron® 5865 outfitted with ± 1 kN load cell
- Material: FCS1

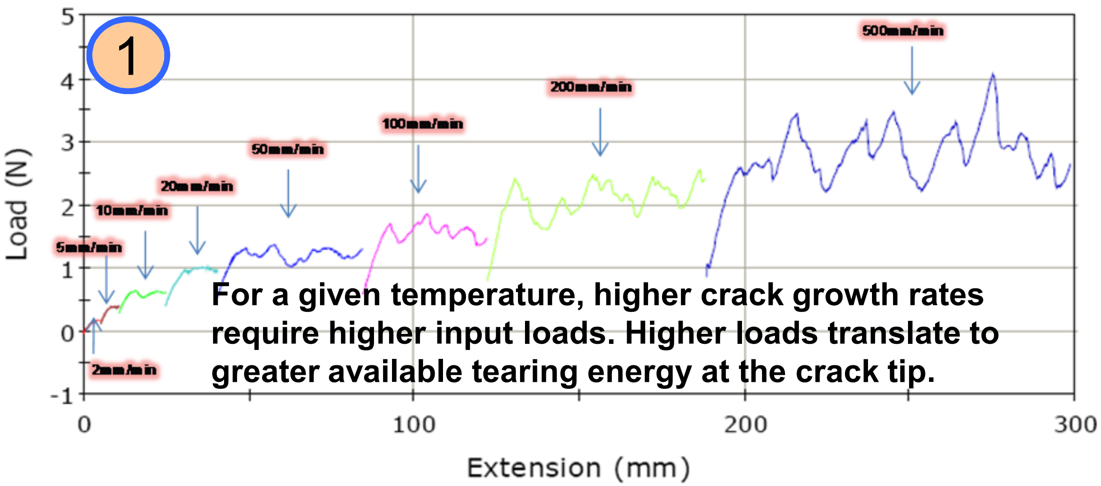


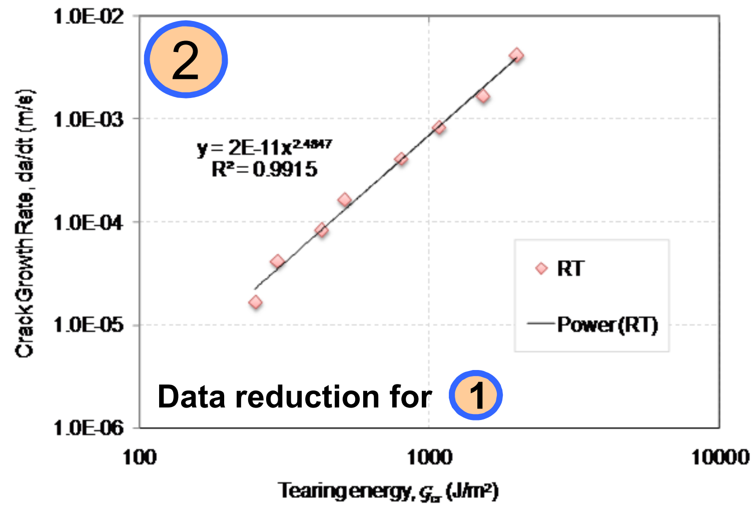


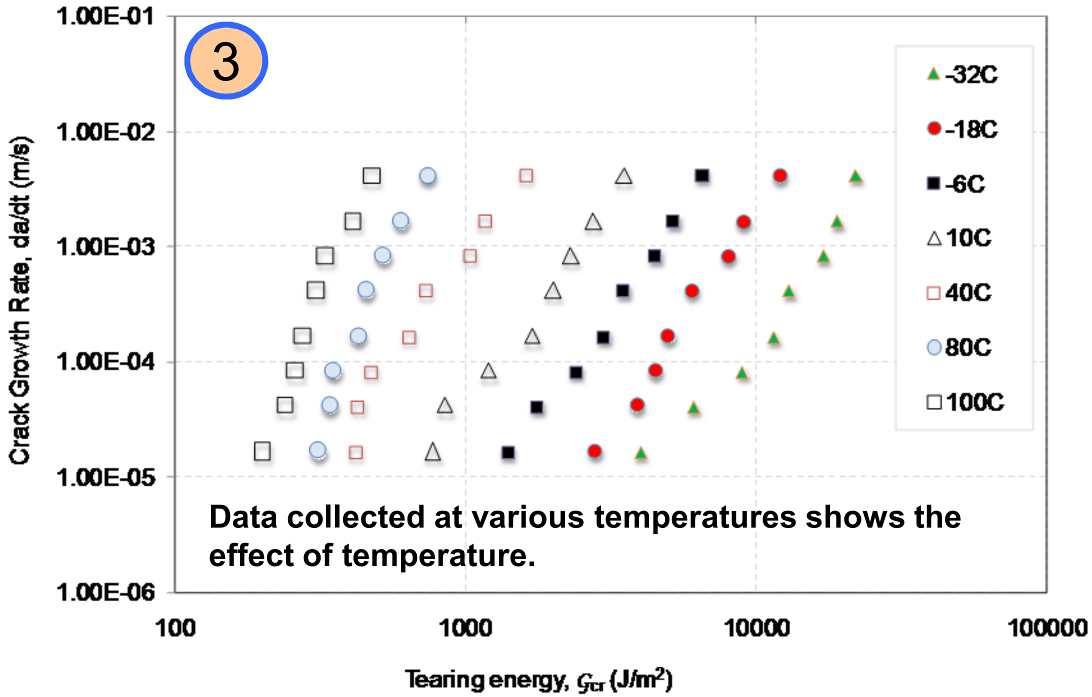
$$\mathcal{G}_{cr} = \frac{2F}{t}$$

Trouser Tear: Data acquisition method

DOE Hydrogen Program



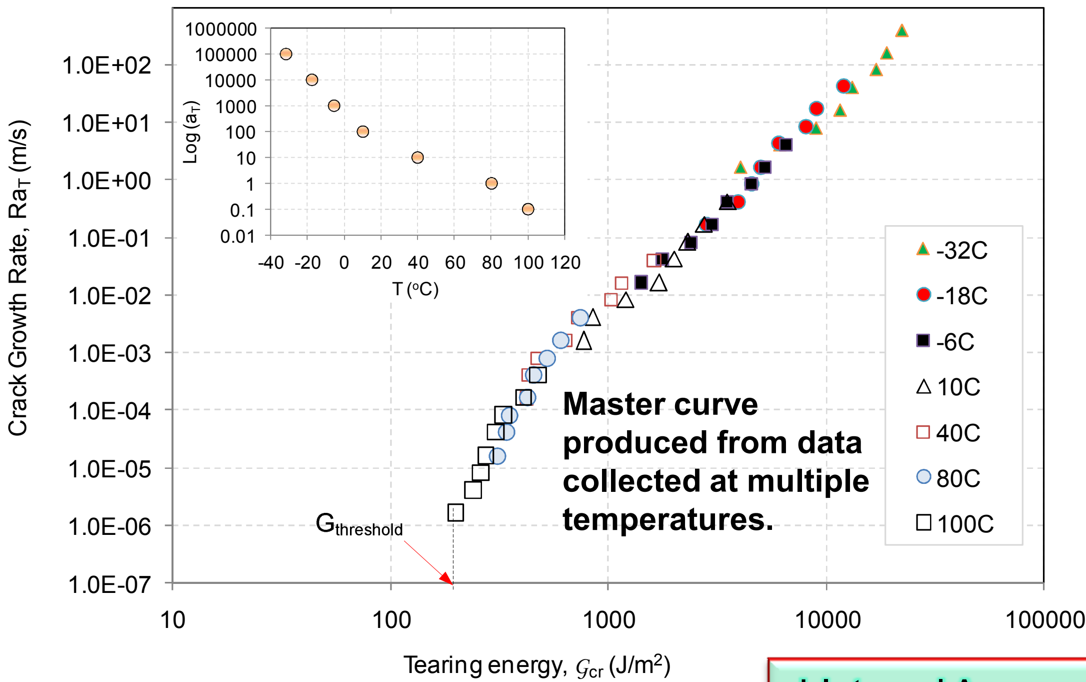


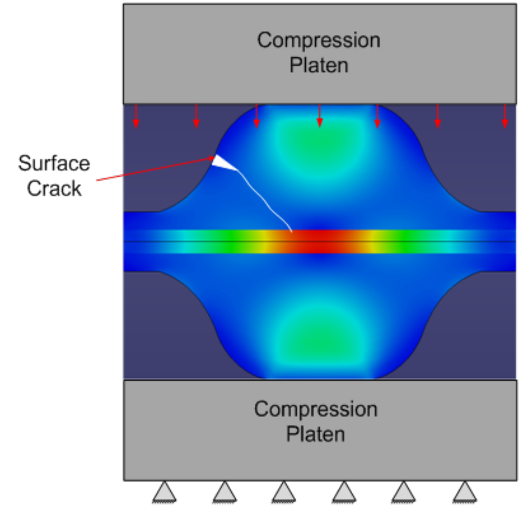


UTC Power
A United Technologies Company

Virginia Tech
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

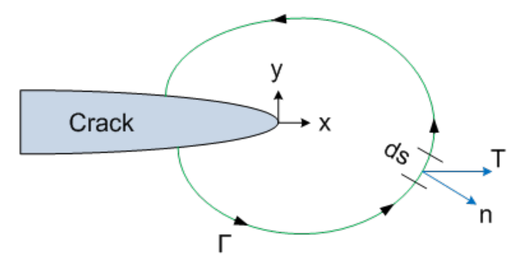
Trouser Tear: Predictions





J-Integral Approach

$$J = \int_{\Gamma} w \cdot dy - T_i \frac{\partial u_i}{\partial x} \cdot ds$$



Threshold value of tearing energy can be coupled with FEA to predict whether a crack, once formed, will propagate in the seal and at what rate.

where $w = \int_0^{\varepsilon_{ij}} \sigma_{ij} \cdot d\varepsilon_{ij}$ is the strain energy density

$T_i = \sigma_{ij} \cdot n_j$ is the traction vector

Γ is an arbitrary contour around the tip of the crack,
n is the unit vector normal to Γ
σ, ε, and u are the stress, strain, and displacement field respectively.