Coal Enhanced PEEK Filament Production for Additive Manufacturing in Industrial Services

DE-FE0032146

Dr. Lakshmi Vendra, Baker Hughes

Dr. Patrick Johnson, University of Wyoming

U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
October 25 - 27, 2022

Project Overview

- Project Duration: 24 months
- Start Date: July 12, 2022
- Kick-off meeting: September 8, 2022

$1,118,348	**$829,573**	**$288,775**
Total Project Cost	Federal Commitment	Cost Share

Project Objectives

- **Performance Period 1**: 12 months
  - Development of coal-enhanced PEEK filament
  - Integration of coal-enhanced PEEK filament with commercially available 3D printer
- **Performance Period 2**: 12 months
  - Print and test a product to quantify properties of coal-enhanced PEEK filament
  - Compare & Contrast performance to quantify benefits

Scope: ***Successfully print product using coal-enhanced PEEK filament***

Project Team

Baker Hughes Team

- Dr. Lakshmi Vendra (PI)
- Brian Wieneke
- Dr. Wei Chen
- Ryan Antle
- Maggie Lowry

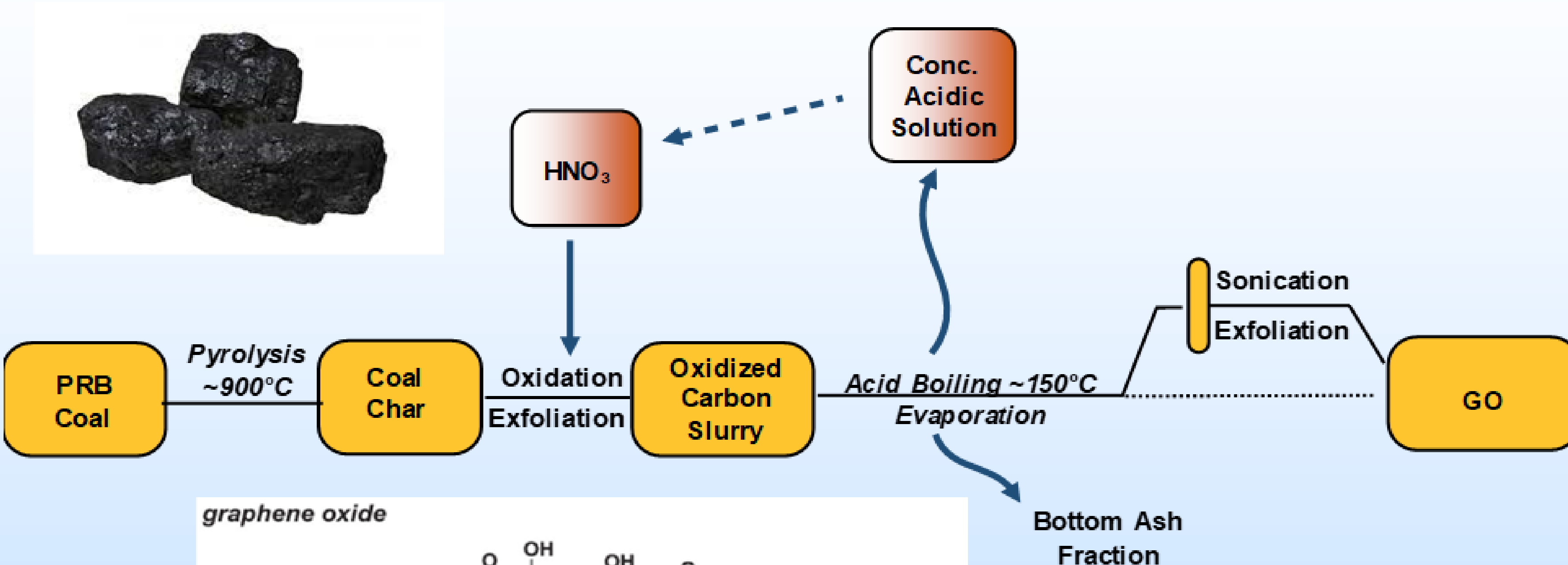
University of Wyoming Team

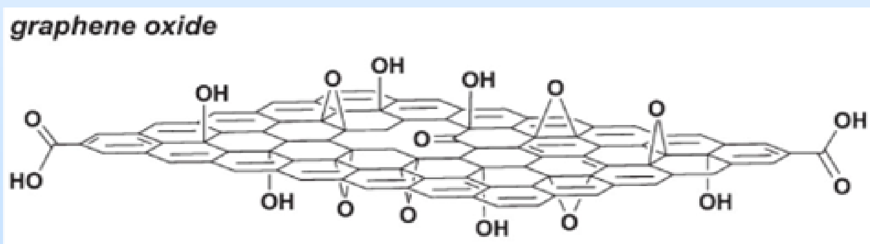
- Dr. Patrick Johnson
- Maxwell Rathweg
- Jacob Wozny

Technology Background

- Previous work on ‘Carbon Engineering’
  - State funded effort for alternative uses of coal
  - Johnson group has several publications / provisional patents on coal-derived graphene oxide, hard carbon, polyurethanes, epoxides
  - Groundbreaking on 9/2/2022 for a state / university run pilot plant for pyrolysis / solvent extraction to generate materials from coal for downstream processing

GO Process Diagram from Coal

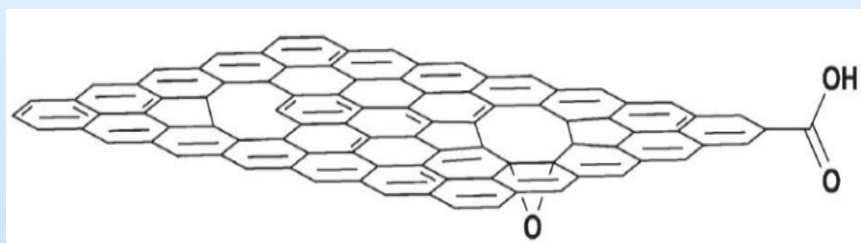




Scale-up focused lab process:

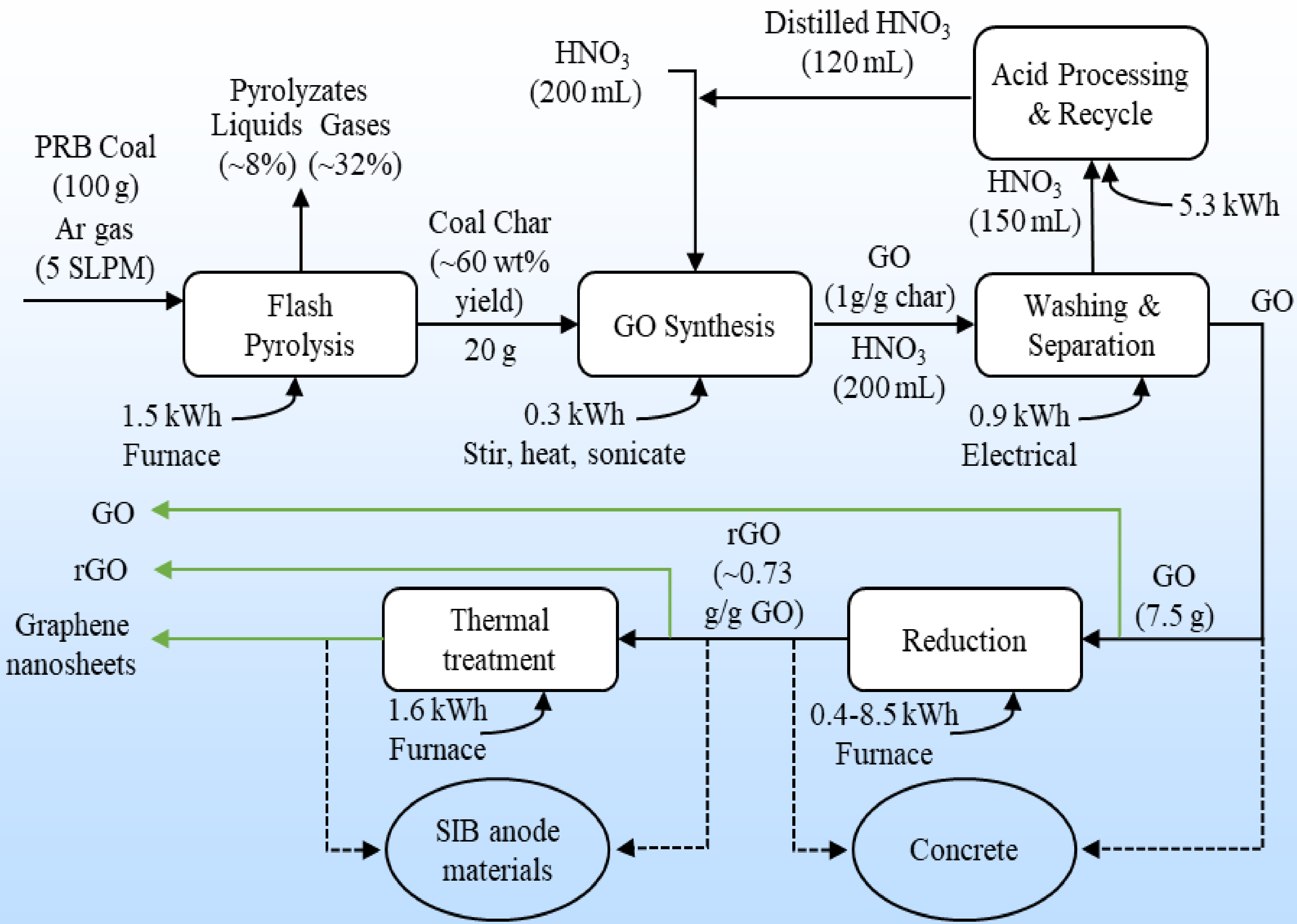
- Flash pyrolysis – improved sp2 content over tube furnace
- Separation critical – large scale processes can be faster than lab
- Recycling acid - multiple passes, distillation demonstrated

GO Thermal Treatment



reduced graphene oxide

- Small scale: Tube furnace (1200C), graphite furnace (2500C)
- Induction furnace – faster turnaround, larger quantities



PRB Coal
(100 g)
Ar gas
(5 SLPM)
Pyrolyzates
Liquids Gases
(~8%) (~32%)
Flash Pyrolysis
1.5 kWh
Furnace
Coal Char
(~60 wt% yield)
20 g
HNO3
(200 mL)
Distilled HNO3
(120 mL)
Acid Processing & Recycle
GO Synthesis
0.3 kWh
Stir, heat, sonicate
GO
(1g/g char)
HNO3
(200 mL)
HNO3
(150 mL)
5.3 kWh
Washing & Separation
0.9 kWh
Electrical
GO
GO
rGO
Graphene nanosheets
Thermal treatment
1.6 kWh
Furnace
rGO
(~0.73 g/g GO)
Reduction
0.4-8.5 kWh
Furnace
GO
(7.5 g)
SIB anode materials
Concrete

Contaminant Analysis

Table 5. Contaminant levels measured from coal feedstock, coal char, and GO.

Element	Raw Coal (wt%)	Coal Char (wt%)	GO (wt%)
Hg	ND	ND	*
As	0.0001	0.0001	ND
Se	ND	ND	ND
Cd	ND	ND	ND
Sb	ND	ND	ND
Pb	0.0001	0.0002	ND
F	0.0054	ND	ND
Cl	0.0012	ND	ND
Br	0.0016	ND	ND
S	0.34	N/A	N/A
N	0.76	N/A	N/A

* EPA Method 7473 (SW-846) will be applied to test the %Hg in the future.

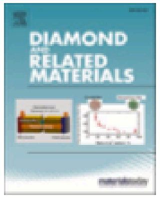
Technology Background

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

ELSEVIER



Check for updates

Evolution of structural and electrical properties in coal-derived graphene oxide nanomaterials during high-temperature annealing

Ana Paula Martins Leandro, Michael A. Seas, Kaitlyn Vap, Alexander Scot
Hud Wahab *, Patrick A. Johnson *

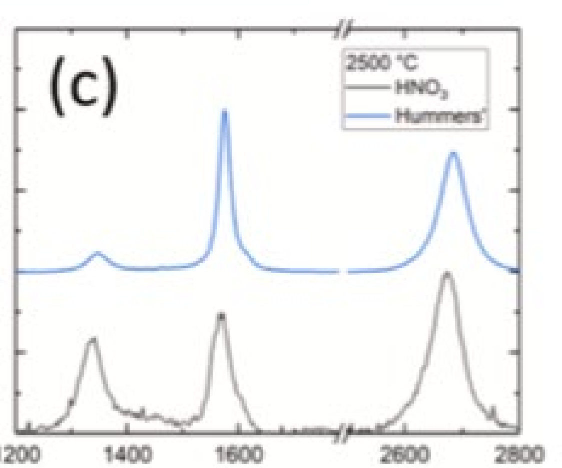


Table 3
Comparison of powder electrical conductivity with literature.

Material	Annealed temperature [°C]	Conductivity [10^3 S m^{-1}]	Ref.
Ordered mesoporous carbon	1500	2.82	[39]
Graphite	–	2.12	[38]
Graphene		0.26	
Graphite	–	2.50	[66]
Reduced GO		2.42	
Reduced GO	–	1.50	[67]
Anthracite	950	1.00	[34]
Flake graphite	–	10.6	[42]
Natural graphite		19.7	
Graphene microflower	2000	4.5	[60]
	3000	21.2	
Catalytic-microwave exfoliated graphite oxide	–	53.1	[63]
Graphite	2500	8.98	This work
HNO_3 rGO nanocrystals	2000	2.38 (2.63)	
(Hummers' rGO nanocrystals)	2500	4.81 (4.34)	

US 20210214231A1

(19) **United States**
(12) **Patent Application Publication**
JOHNSON et al.
(10) **Pub. No.: US 2021/0214231 A1**
(43) **Pub. Date: Jul. 15, 2021**

PP1

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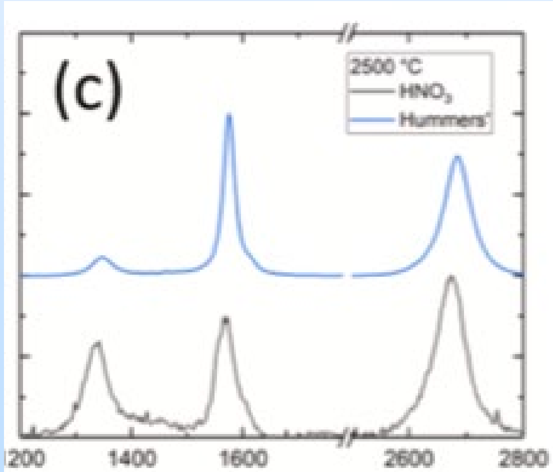

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PP1

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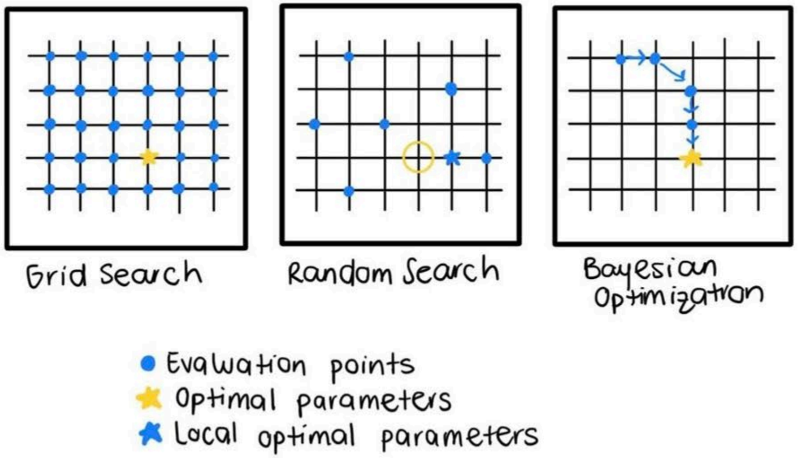
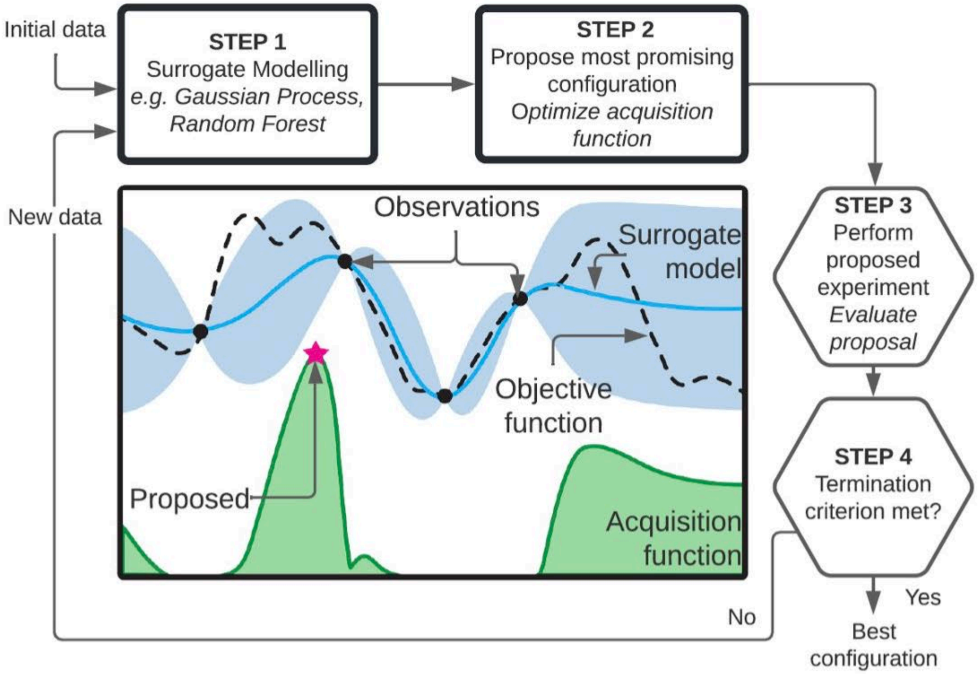
Bayesian optimization

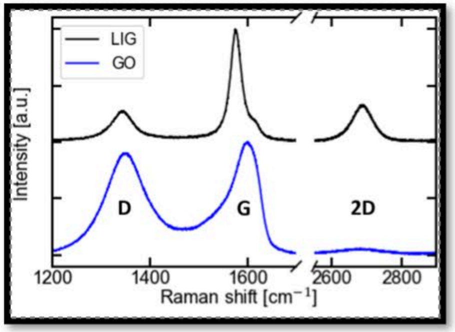


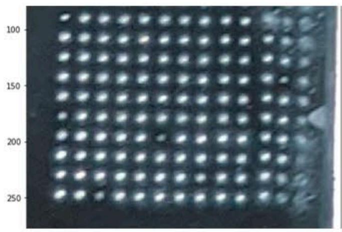
mlrMBO



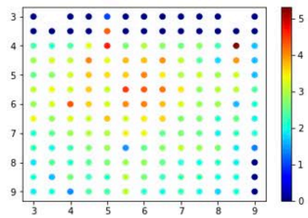
- **Grid search:** +interpretable -costly
- **Random search:** +efficient -miss optima

Single-proposal optimization of Raman



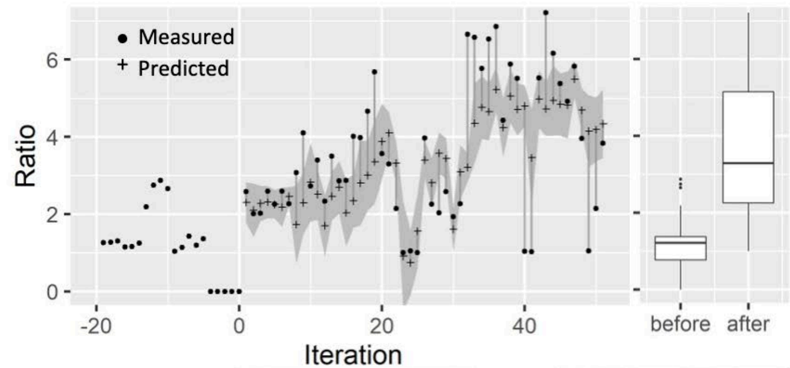


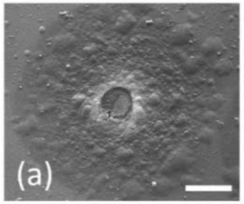
Patterned sample



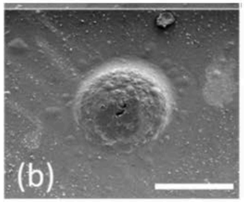
Raman G/D ratio

GO/Quartz





Before / random



After / AI

Mat.	Camp.	Median Value				Best Value			
		Random	40 Random	MBO first 20	all MBO	Random	40 Random	MBO first 20	all MBO
GOQ	1	1.27	1.23	1.95	2.09	2.57	2.87	2.55	3.54
GOQ	2	1.22	1.23	2.86	3.18	2.87	2.87	5.68	7.21
GOQ	3	1.3	1.23	1.69	2.32	2.39	2.87	5.83	5.83

Wahab 2020, Carbon, https://doi.org/10.1016/j.carbon.2020.05.087

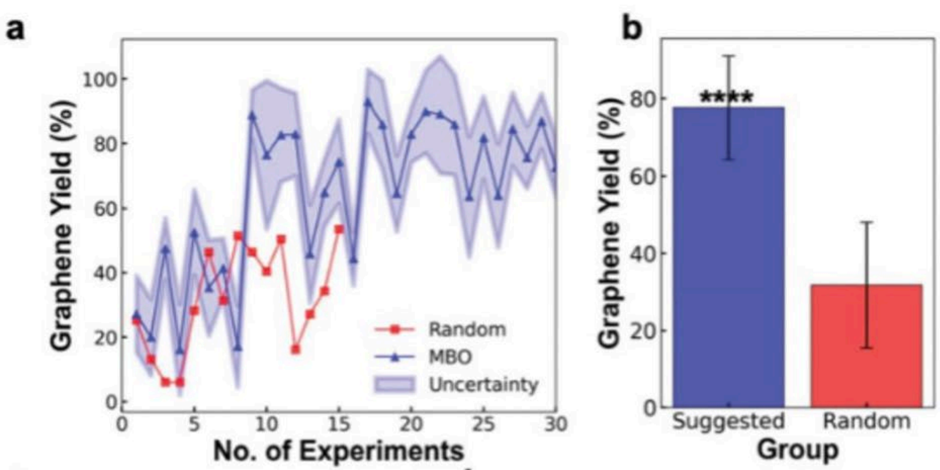
ADVANCED MATERIALS

Research Article | Full Access

Machine Learning Guided Synthesis of Flash Graphene

Jacob L. Beckham, Kevin M. Wyss, Yunchao Xie, Emily A. McHugh, John Tianci Li, Paul A. Advincula, Weiyin Chen, Jian Lin, James M. Tour

First published: 22 January 2022 | https://doi.org/10.1002/adma.202106506



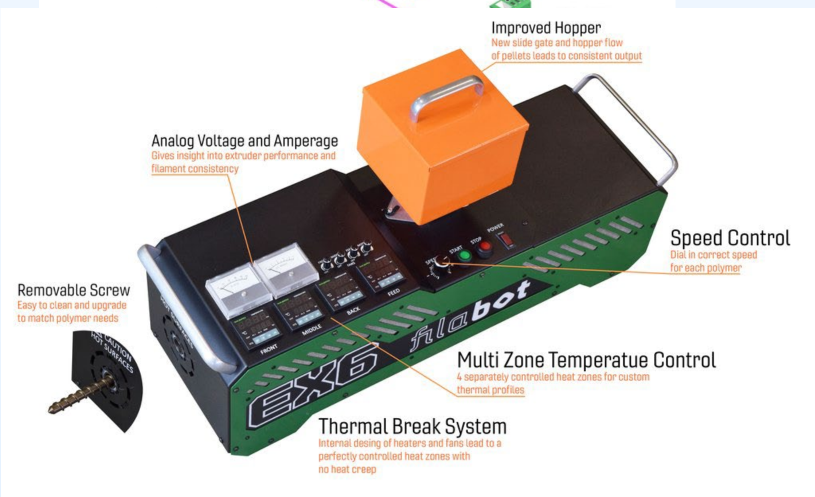
- Our ML work has inspired key researchers in the graphene field
- By following FAIR guidelines to ensure reproducibility, researchers can follow our Bayesian optimization code directly and independently
- Do come and chat for potential collaboration

Technical Approach

Characterization Capabilities

- Chemical characterization
  - Raman, UV-Vis, FTIR, XRD, TGA, CHNO, ICP-MS
- Advanced instrumentation
  - FIB TEM, SEM, XPS
- Polymer characterization
  - GPC, DSC (glass transition temp)
- Mechanical instrumentation
  - Tensile, bend, impact, compression

Equipment



Extruder and pelletizer

a. Mixes additives with pellets
b. Produces filament
c. Produces pellets
d. High temperature capabilities
e. Abrasion resistant

Injection molder

a. Tests material, not 3D printer
b. High mold and operating temperature

PP1

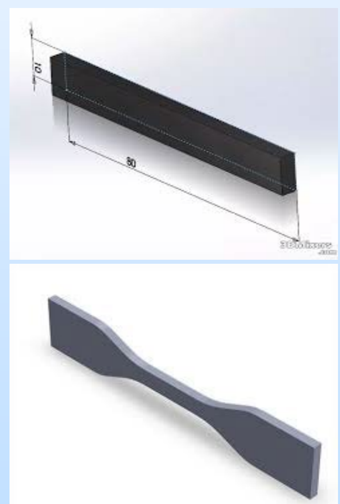
Materials Processing

Extruder

Pelletizer

Pelletized composite

Injection Molder



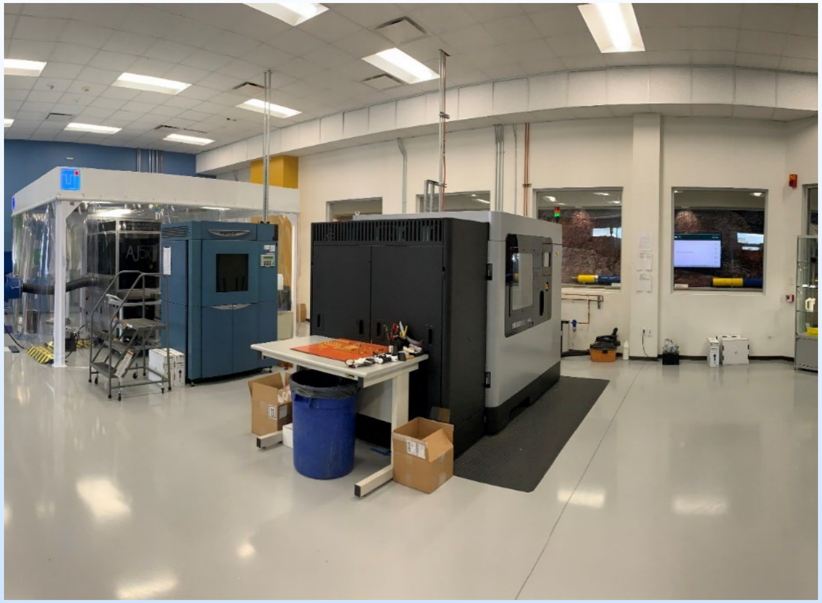
Test coupons

Mechanical	DSC/TGA
SEM	DMA/XRD/FT IR
Rheology	

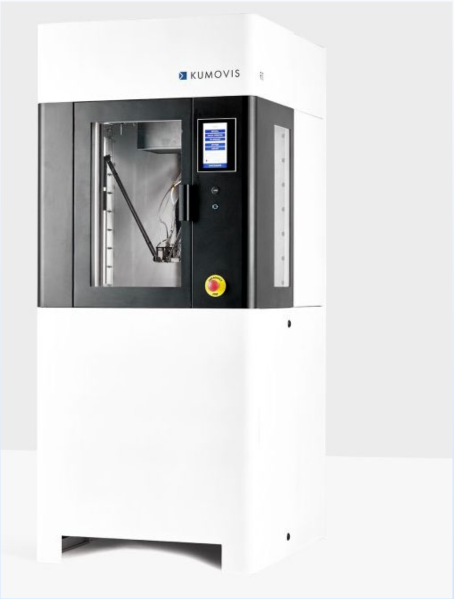
Testing

Additive Manufacturing Global Footprint

Additive Polymers Lab (Houston)



- **AON M2 (17”x17”x25”)**
  - **Virgin PEEK**
- M400
- F900
- Elegoo Mars 2



- **3D printer**
  - **Coal-enhanced PEEK**

PP2

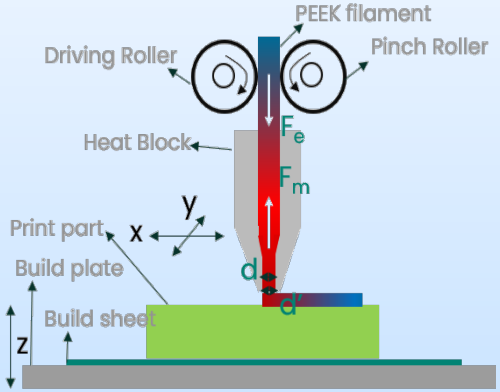
Technology Background

Fused Deposition Modeling

- Developed AM process to produce virgin PEEK

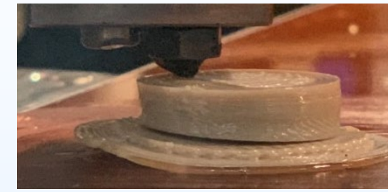
Build volume: 400x400x650mm

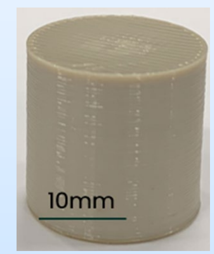
FDM PEEK

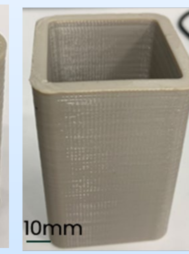


Scheme

Printing





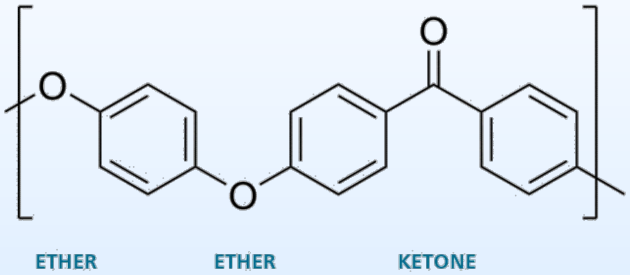


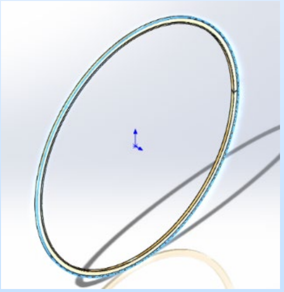
PEEK filament is fed into a heated extruder that melts the polymer and deposits it layer by layer

AM Coal-Enhanced PEEK

PEEK

- Semi-crystalline thermoplastics, PAEK family
- Mechanical, chemical, temperature resistance
- Widely used in oil & gas
- Hard to manufacture
- $MM Market Potential





Seals & Back-up rings

Success Criteria

- Develop AM PEEK with isotropic properties
- Potential to have better printability compared to carbon-fiber PEEK
- Enhance corrosion performance
- TRL 4-5

Technical/Economic Challenges

Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
Financial Risks:				
Raw material supply risk	Low	High	High	Well-established relationships with raw material suppliers. Look for alternative suppliers as applicable
Cost/Schedule Risks				
Cost estimates could be affected by delays in project schedule	Low	Medium	High	Regular report-outs to ensure the project is on schedule and doesn't impact cost estimates
Technical/Scope Risks				
Coal derived material is not compatible with PEEK	Medium	Medium	High	Robust test matrix for blending parameters. Go/No go decision
Modified PEEK filaments cannot be extruded	Medium	Medium	High	Leverage Univ. of Wyoming extrusion expertise. Go/No go decision
Modified part performance is not improved	Low	Medium	High	Explore economic impacts, consider other end use applications
Health, Safety, & Environmental Risks:				
Competency of operators working on 3D printers and handling coal-enhanced PEEK material	Low	High	High	AM process and procedures handling 3D printers and polymer materials following HSE guidelines and standards are well established at Baker Hughes.

Project Status

Task/ Subtask	Milestone Title & Description	Planned Completion Date	Verification Method
1.0	**Kick-off meeting**	**Sep 8, 2022**	**Project kick-off meeting**
2.3	Successful integration of coal in PEEK filament	Apr 2023	Being able to extrude filament with coal and inspecting for desired volume fraction
2.4	Successful printing of test coupons using modified PEEK	Jul 2023	Print test coupons to desired shape and size using commercial 3D printer and coal-enhanced PEEK filament. Verified for dimensional accuracy. Go/No go decision
	Annual Meeting	Aug 2023	Report out on project status.
3.1	Tabulate mechanical properties of coal-enhanced PEEK specimens	Mar 2024	Complete testing of specimens and analysis of results
3.4	Successful printing of baseline part	May 2024	Print functional part using commercial 3D printer and coal-enhanced PEEK filament. Verified for dimensional accuracy and CT scanned for volumetric inspection
	Final Report Out	Jul 2024	Final Report on project outcome

Plans for future testing/development/ commercialization

After the project:

- Partnering with raw material suppliers to commercialize enhanced PEEK filament fabrication
- Collaborating with OEMs to address scalability challenges
- Wyoming state investing in pilot plant for graphene oxide material generated from coal wastes – improves future availability, utilization and applications of the material

Outreach and Workforce Development Efforts or Achievements

- Workforce Development
  - 1-2 post-doctorate students to be hired at University of Wyoming
  - 2 undergraduate students currently working on the project

Summary Slide

Project Scope

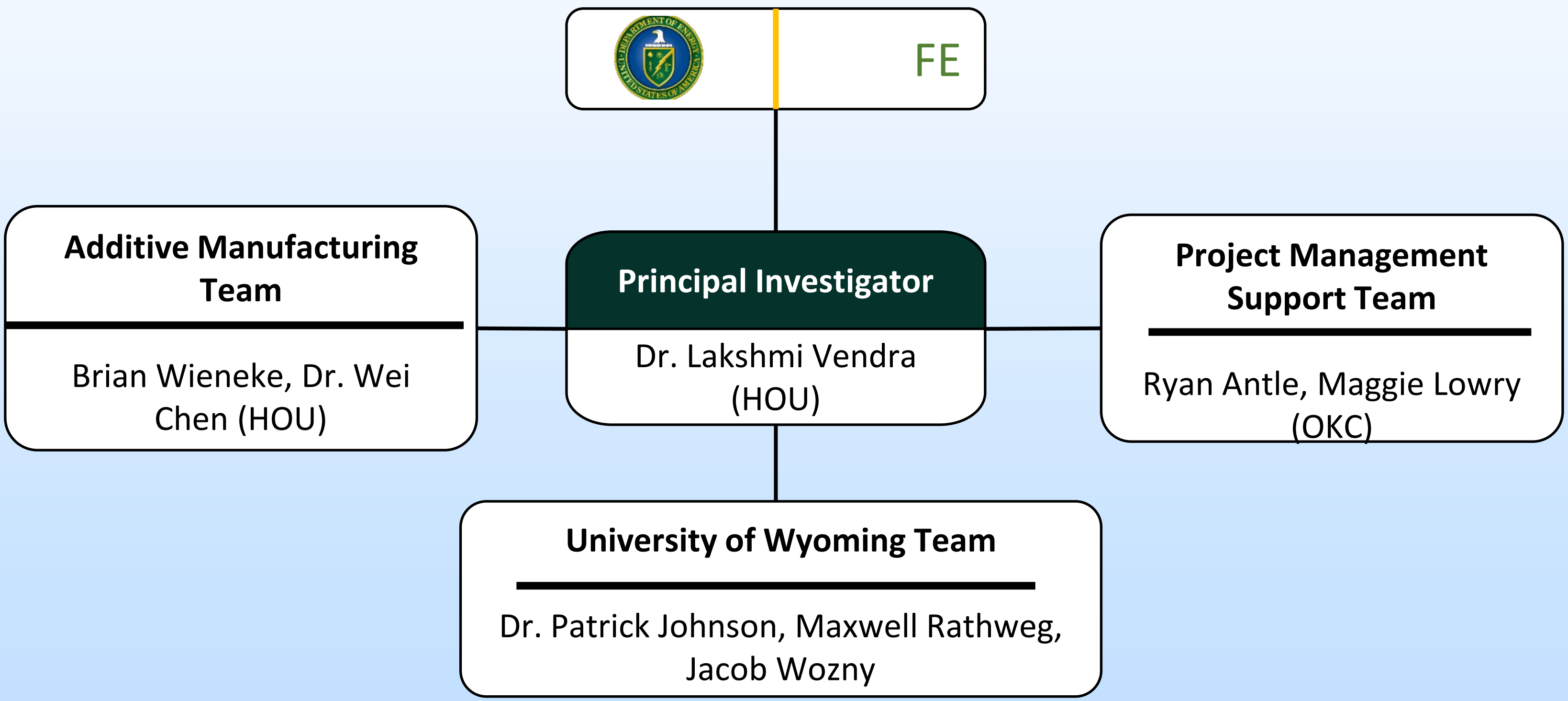
- Development of coal-enhanced PEEK filament
- Integration of coal-enhanced PEEK filament with commercially available 3D printer
- Print and test a product to quantify properties of coal-enhanced PEEK filament
- Compare performance & quantify benefits

Deliverables

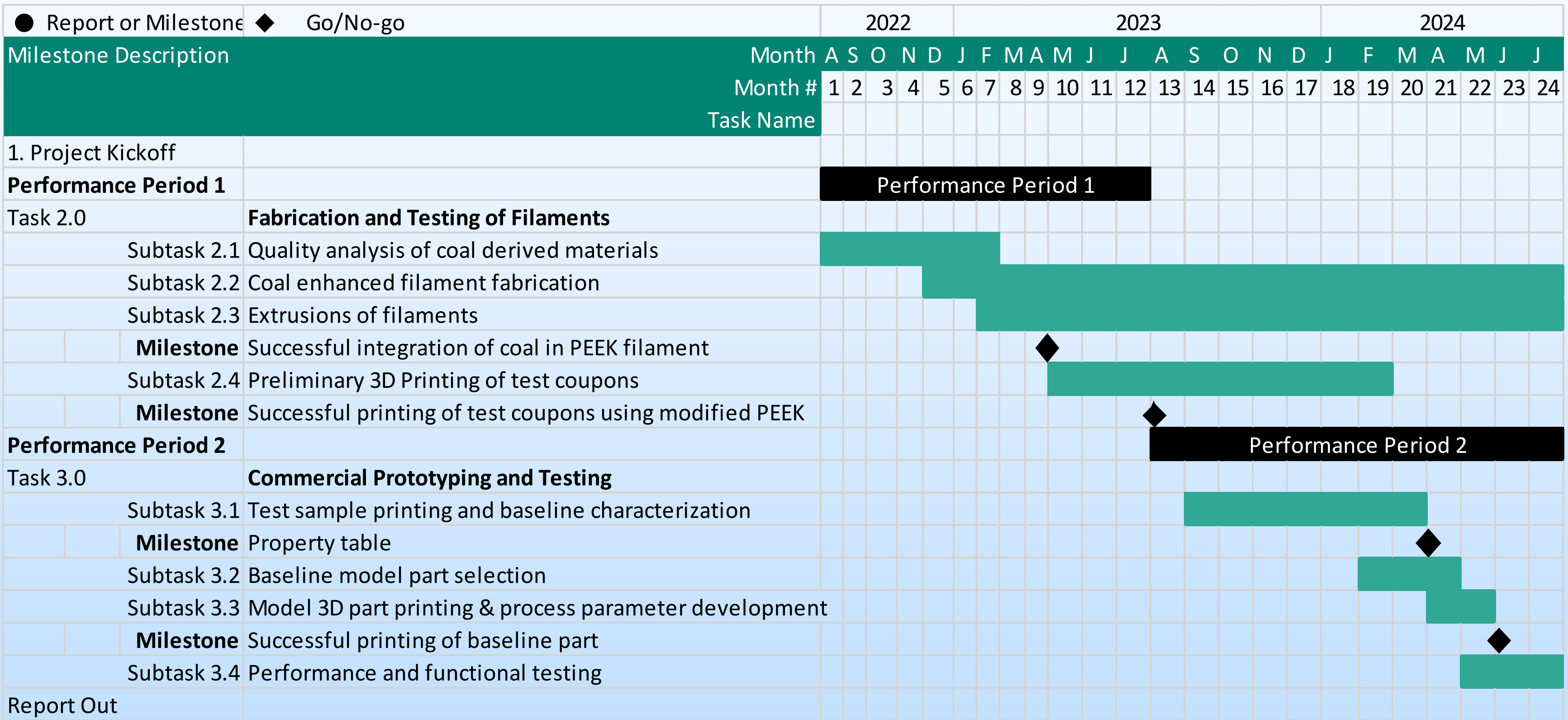
- Material formulation of coal-enhanced PEEK
- Process development
- Property tables
- Final Report
- IP creation

Appendix

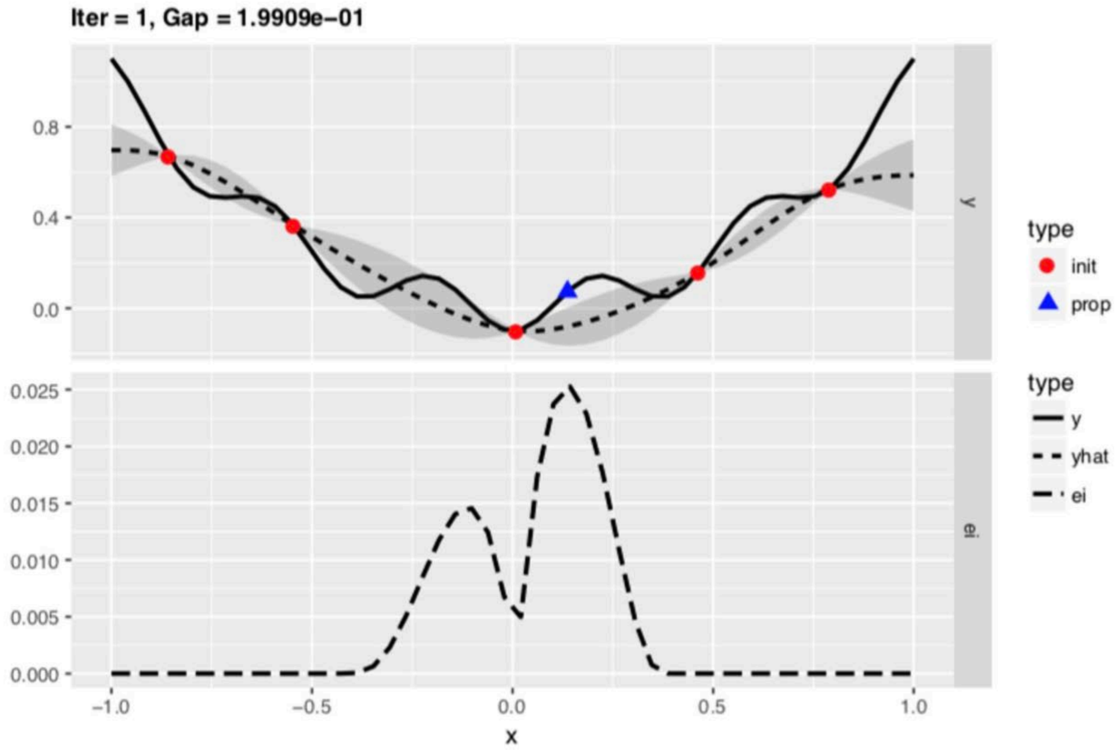
Organization Chart



Gantt Chart

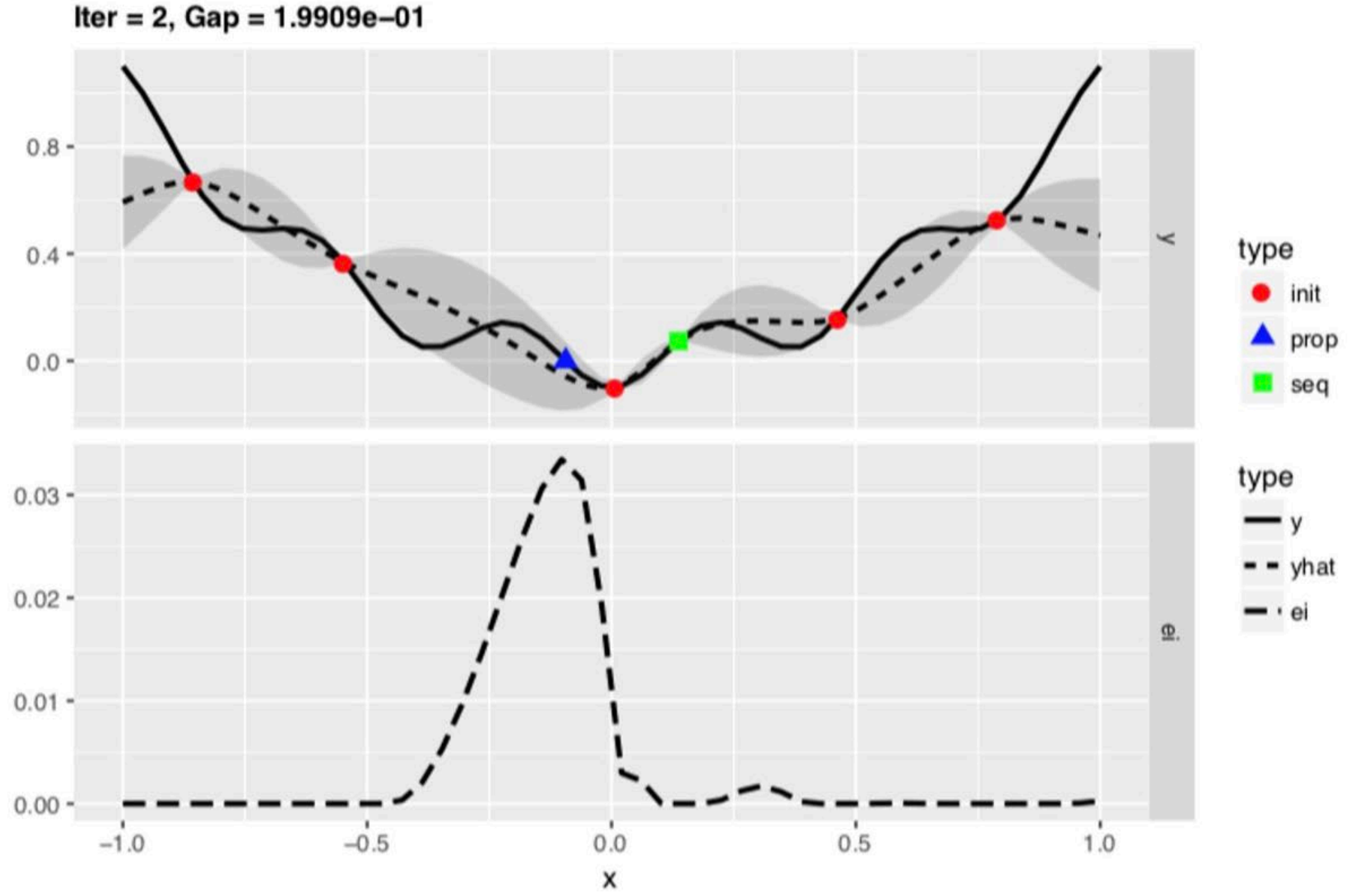

● Report or Milestone ◆ Go/No-go
2022
2023
2024
Milestone Description
Month A S O N D J F M A M J J A S O N D J F M A M J J
Month # 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Task Name
1. Project Kickoff
Performance Period 1
Performance Period 1
Task 2.0 Fabrication and Testing of Filaments
Subtask 2.1 Quality analysis of coal derived materials
Subtask 2.2 Coal enhanced filament fabrication
Subtask 2.3 Extrusions of filaments
Milestone Successful integration of coal in PEEK filament
Subtask 2.4 Preliminary 3D Printing of test coupons
Milestone Successful printing of test coupons using modified PEEK
Performance Period 2
Performance Period 2
Task 3.0 Commercial Prototyping and Testing
Subtask 3.1 Test sample printing and baseline characterization
Milestone Property table
Subtask 3.2 Baseline model part selection
Subtask 3.3 Model 3D part printing & process parameter development
Milestone Successful printing of baseline part
Subtask 3.4 Performance and functional testing
Report Out

Model-Based Search Example

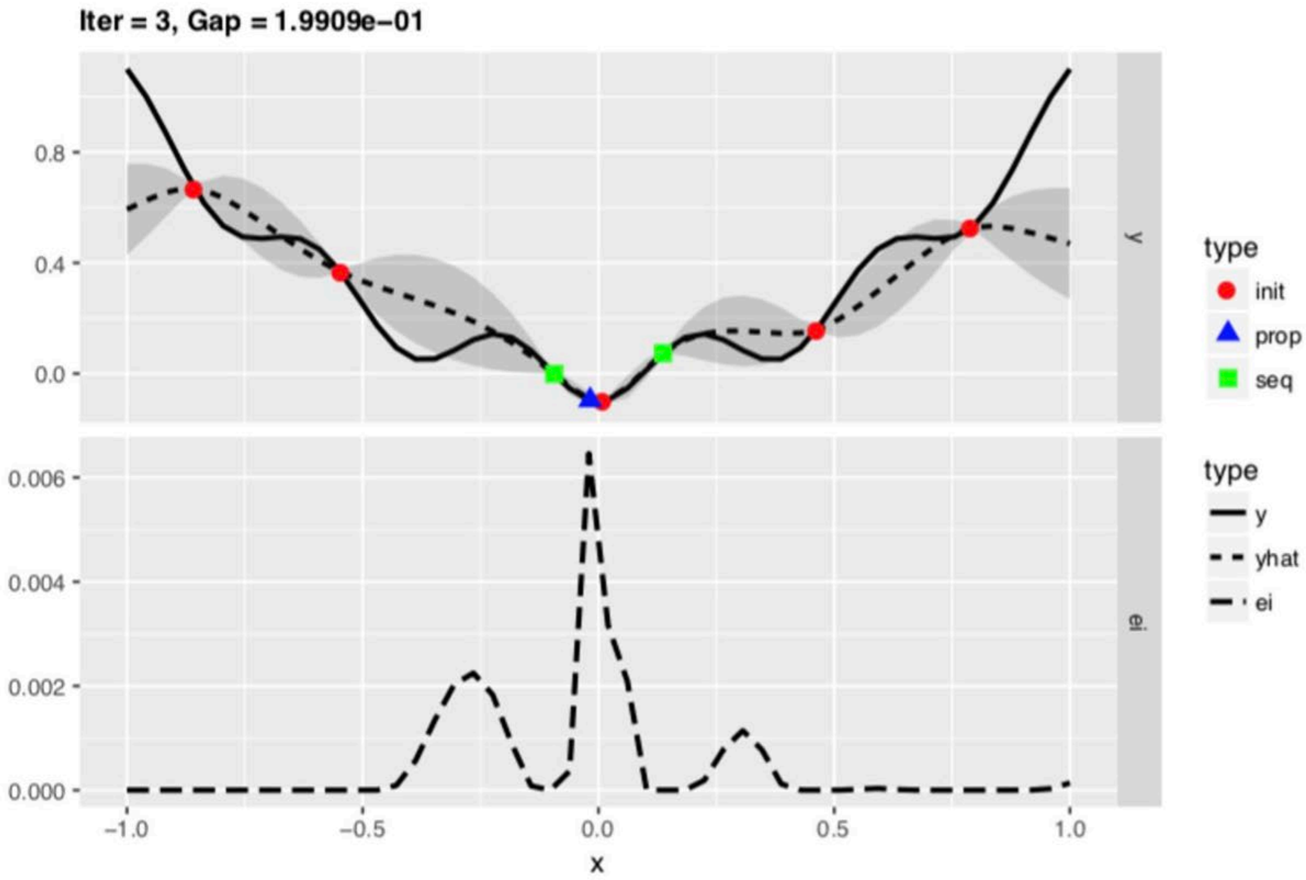


Bischl, Bernd, Jakob Richter, Jakob Bossek, Daniel Horn, Janek Thomas, and Michel Lang. "MlrMBO: A Modular Framework for Model-Based Optimization of Expensive Black-Box Functions," March 9, 2017. http://arxiv.org/abs/1703.03373.

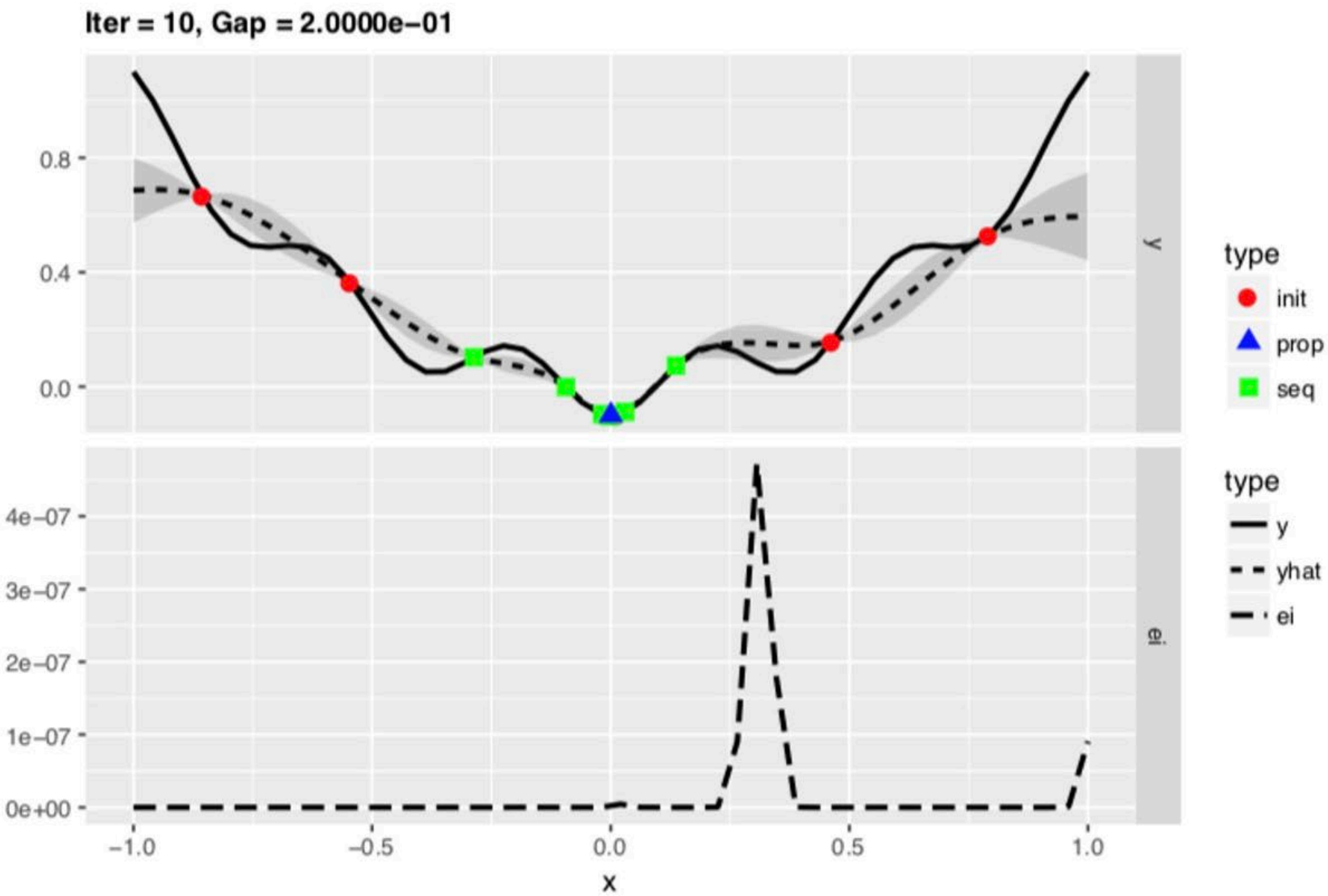
Model-Based Search Example



Model-Based Search Example

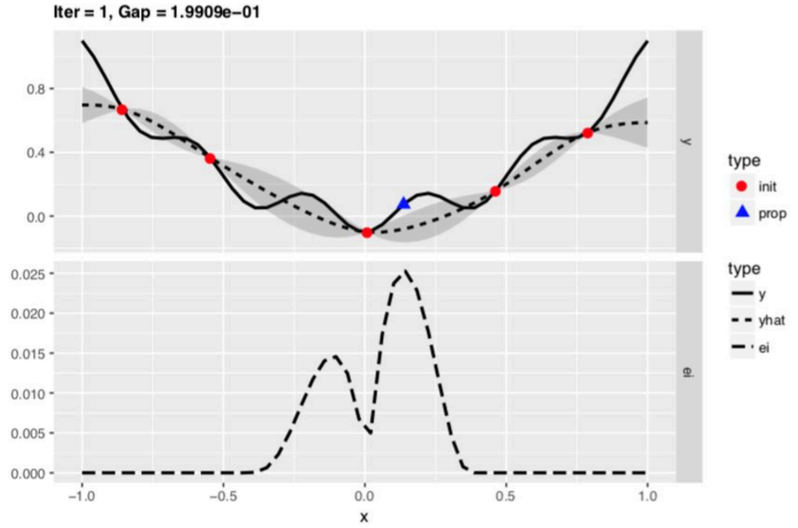


Model-Based Search Example



power	pressure	time	ratio	pred. ratio	max pred. ratio
486	53	4377	9.75	3.72	5.09
526	49	4377	4.52	9.19	10.19
629	53	4377	4.09	8.6	9.73
486	21	4377	5.14	8.53	9.61
486	50	4266	3.08	9.34	9.94
470	30	4381	3.57	5.68	7.16
876	21	13991	2.39	4.02	5.72
1124	100	9725	2.71	3.96	5.65
243	46	5146	8.29	3.92	5.6
243	46	5146	7.05	4.99	6.77
243	46	5132	5.81	5.63	7.43
224	48	5845	6.17	5.76	7.4
243	46	5153	5.98	5.93	7.59
243	27	5152	6.95	6.02	7.55
243	43	5154	5.72	6.2	7.74
331	84	1191	3.8	4.49	6.18
243	19	6689	5.49	5.93	7.44
243	26	6011	6.57	5.92	7.37
239	46	4917	5.87	6.01	7.56
243	26	5070	8.71	6.11	7.51

Predictions



Y = ratio
Yhat = predicted ratio
Max pred. ratio = pred. ratio + uncertainty