UIC ENGINEERING

Argonne NATIONAL LABORATORY

SCALABLE MANUFACTURING OF NANOSCALE MATERIALS AND INTERFACES

EDGE TO EXASCALE COMPUTING AND IN-SITU MEASUREMENTS

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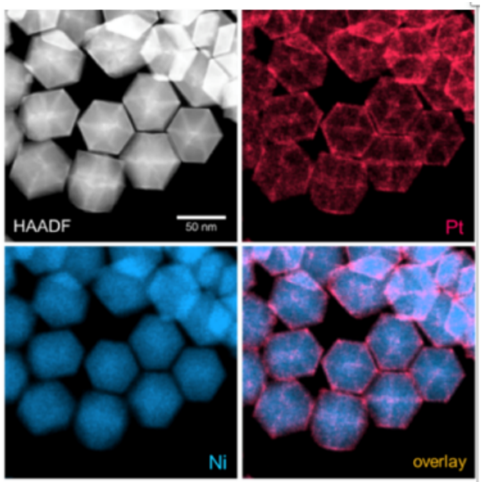
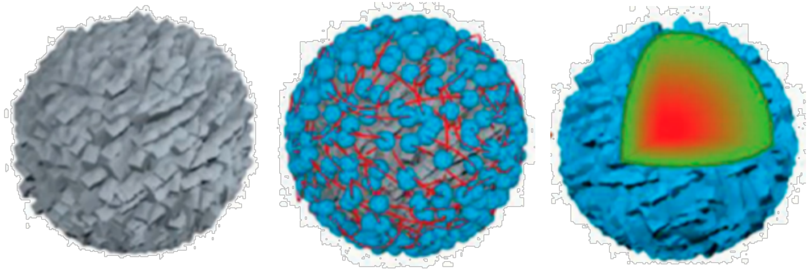
Director, Manufacturing Science and Engineering, ANL

HIGH-PERFORMANCE ENERGY MATERIALS ARE OFTEN HARD TO SYNTHESIZE AND MANUFACTURE

Advanced materials are increasingly complex, requiring control of many synthesis steps



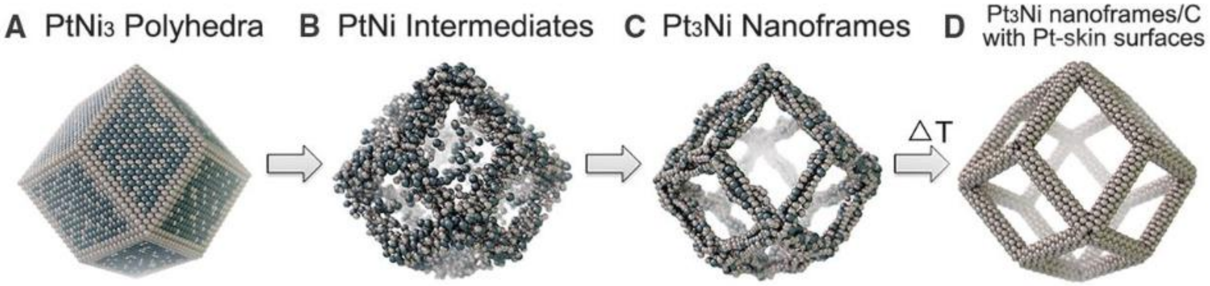
Pt-Ni nanoframe electrocatalysts for fuel cell applications: tightly controlled geometry and composition



Nickel-manganese-cobalt particles for cathode materials: multiple components, stratified

ADVANCED ELECTROCATALYSTS: SYNTHESIS OF NANOFRAME CATALYSTS WITH HIGH ACTIVITY

C. Chen et al., *Science* 343, 1339–1343 (2014)



- Promising catalyst with potentially ground-breaking performance was discovered by an Argonne-Berkeley collaboration, through research funded by BES-MSED
- Gain in activity is attributed to the catalyst’s complex three-dimensional geometry, which was created using a difficult, multi-step synthesis

Initial synthetic methods were unable to produce this catalyst in sufficient quantity or uniformity to fully characterize its performance

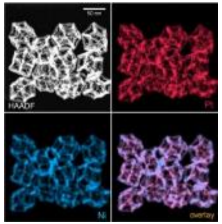
ADVANCED ELECTROCATALYSTS: FROM DISCOVERY TO PROCESS R&D, WITH FEEDBACK TO SUPPORT DISCOVERY

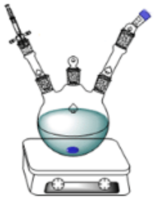
Materials Engineering Research Facility (MERF)

Discovery Science

Material Discovery

- Poor batch-to-batch reproducibility
- Small quantities (mg) did not allow for full material characterization





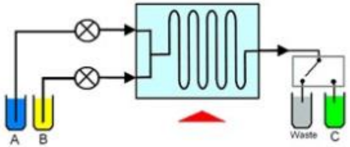
Innovative Batch Process

- Reproducible, gram-quantity samples
- Limited scalability
- Not suitable for manufacturing

Gram-quantity samples enabled full characterization of the new material

Continuous-Flow Process

- Practically unlimited quantities
- Uniform quality of material
- **Suitable for manufacturing**



Continuous-flow reactor and instrumentation provide unique insights into synthetic mechanisms

FLAME SPRAY PYROLYSIS: A VISION FOR MOVING FROM PREDICTIONS TO DIRECT MATERIALS SYNTHESIS

High-temperature synthesis (FSP) enables scalable synthesis of metastable materials

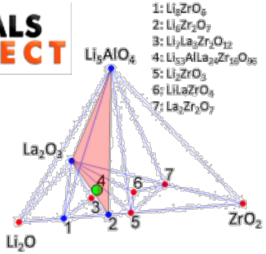
Materials Engineering Research Facility (MERF)

Discovery Science

Material Discovery: LLZO

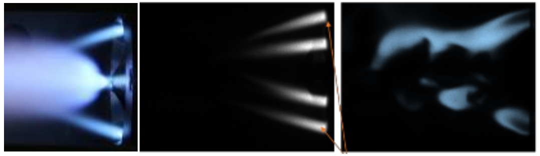
- Al-doped LLZO (lithium lanthanum zirconium oxide) is a solid electrolyte
- Desired phase is metastable and requires careful synthesis

Materials Project is supported in part by BES



Flame Spray Pyrolysis (FSP)

- *In situ* diagnostics and *ex situ* analysis provide insights into complex phase behavior and gas-phase chemistry, enabling intelligent process manipulation



FSP with *in situ* diagnostics will aid understanding synthetic pathways and improve materials databases

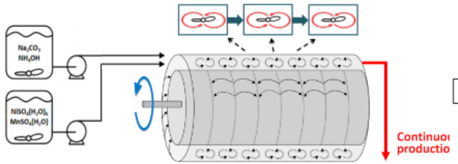
Scalable Synthesis and Validated Industry Interest

- Cabot uses FSP to manufacture relatively simple materials
- Now partnering with Argonne to advance this technology for complex battery materials

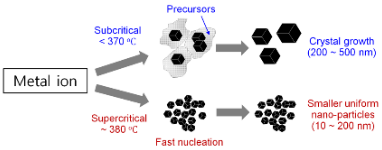
ADVANCED MATERIALS MANUFACTURING RESEARCH

Expanding focus to advanced materials synthesis and processing

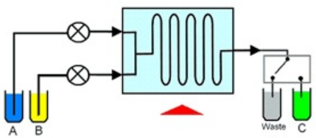
Taylor Vortex



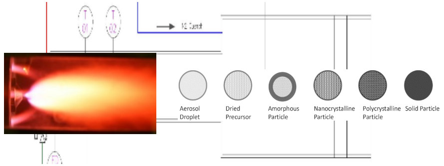
Hydrothermal



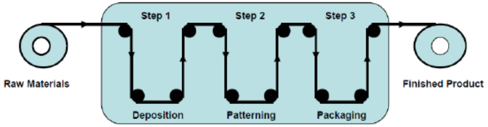
Continuous Flow



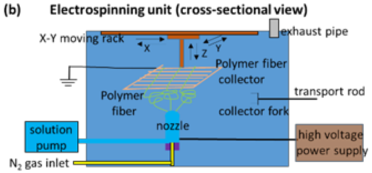
Flame Spray



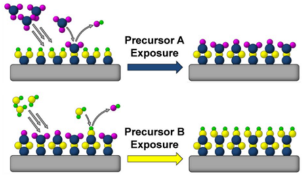
Roll to Roll



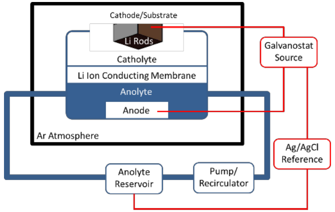
Electrospinning

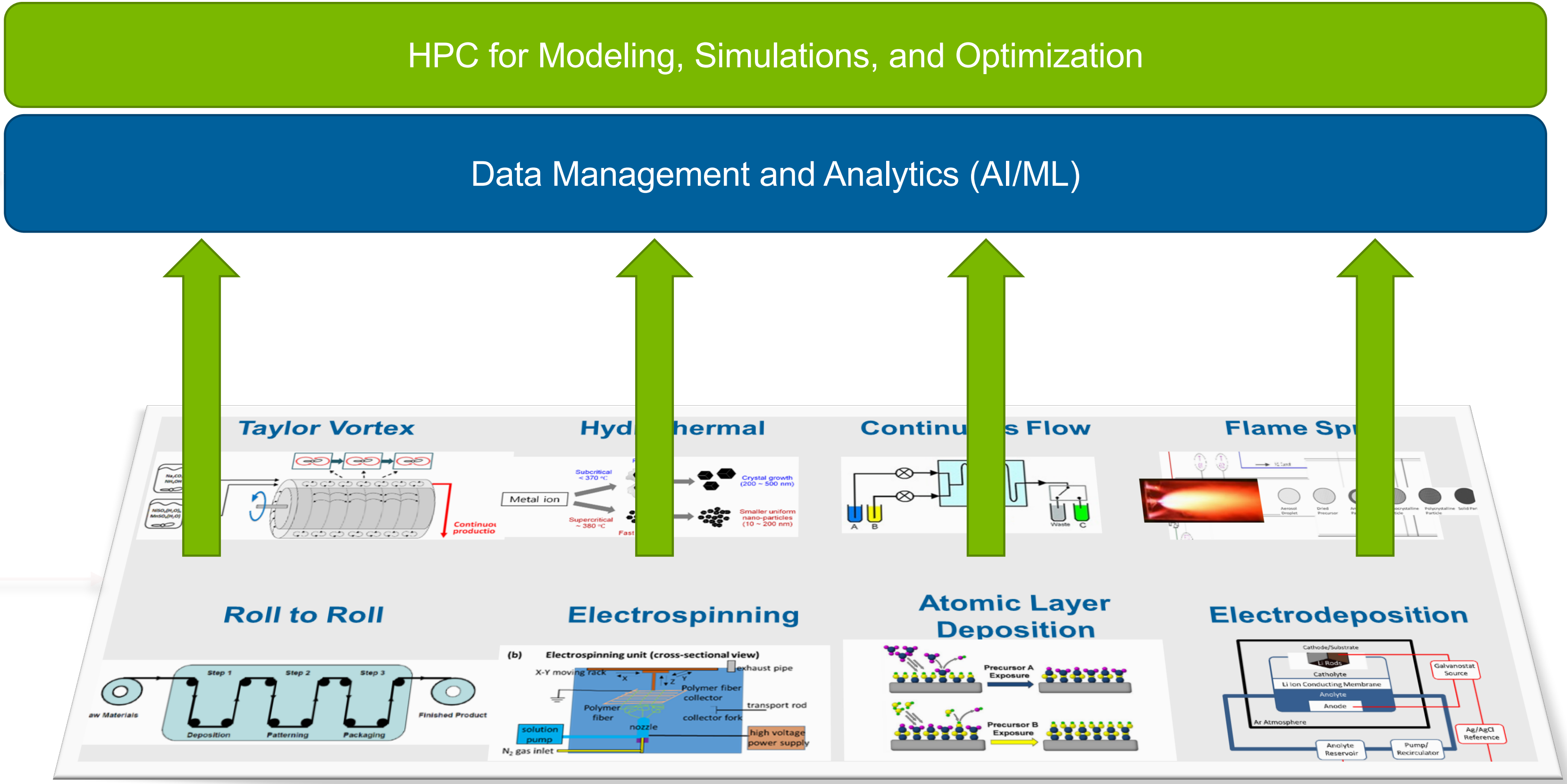


Atomic Layer Deposition



Electrodeposition





HPC for Modeling, Simulations, and Optimization

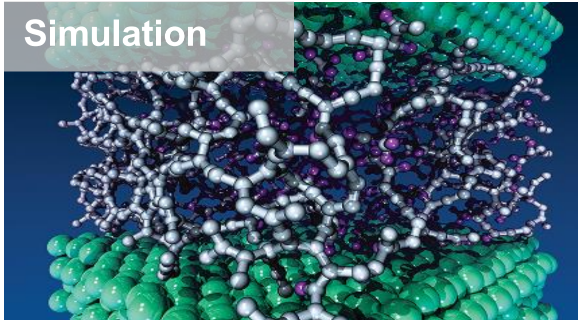
Data Management and Analytics (AI/ML)

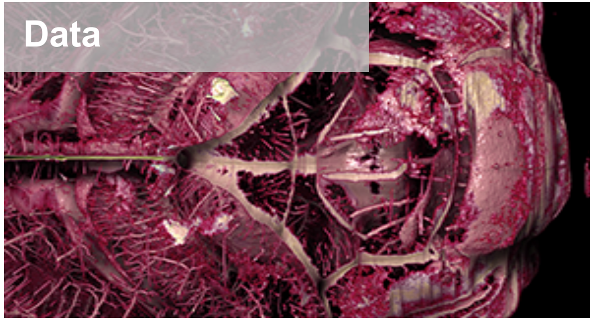
ALCF 2021 EXASCALE SUPERCOMPUTER – A21

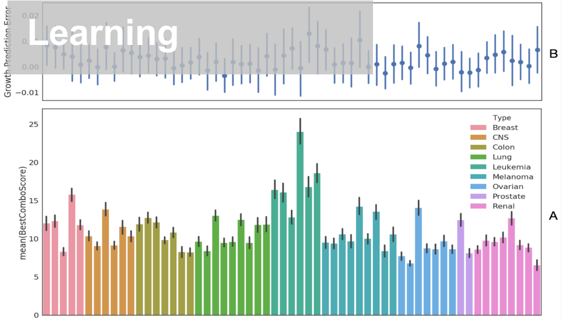
Aurora supercomputer planned for 2021

Scaled up to over 1000 PF

Support for three “pillars”







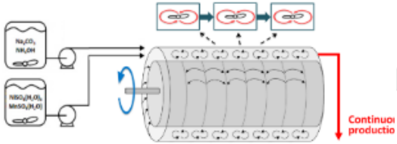
MANUFACTURING SCIENCE AND ENGINEERING INITIATIVE

MERF + ALCF *Computing (AI, ML, HPC) for modeling, simulation, and learning*

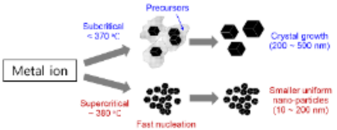
MERF + APS *Characterization (sensing, imaging, spectroscopy)*

MERF *Advanced materials synthesis and processing technologies*

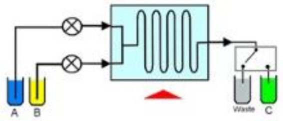
Taylor Vortex



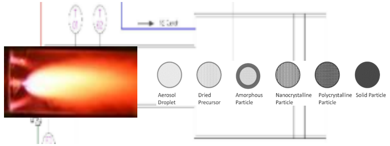
Hydrothermal



Continuous Flow



Flame Spray



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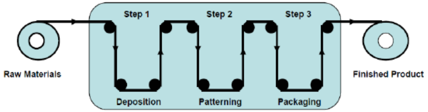
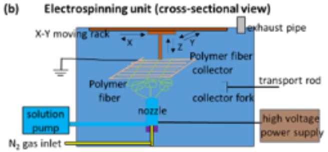


Electrospinning



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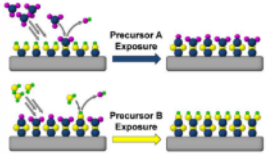
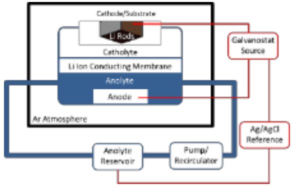


Electrodeposition



COLLABORATIONS

Internal Cross-Laboratory and External with University and Industry

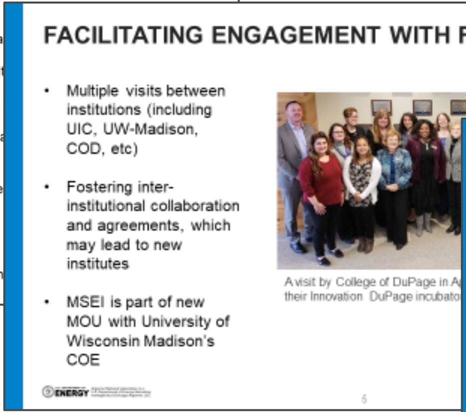
Advanced Manufacturing: Related Workshops at Argonne

RECENT

- **Advanced Manufacturing Workshop**, ANL, August 31, 2017
  - Involved scientists and engineers across laboratory divisions
  - Explored advance manufacturing interest areas
- **High Performance Computing for Manufacturing Workshop**, ANL, Ja
  - Brought together two communities: HPC and AM
  - Identified top areas of common interest: machine learning and mult
- **Additive Manufacturing Collaborative Workshop**, ANL, May 22, 2018
  - Organized by AMO, NNSA and ANL
  - Improved interactions with sponsors and expanded collaborations a

UPCOMING

- **Machine Learning and Advanced Manufacturing Workshop**, ANL, Se
  - Organized by EGS and CLS
  - Breakout discussions of strategy and future project ideas
- **Artificial Intelligence Workshop**, ANL, November, 2018
  - Participation of DOE, Industry and Academia
  - Sessions dedicated to intelligent materials design and advanced m



FACILITATING ENGAGEMENT WITH FOCUS UNIVERSITIES

- Multiple visits between institutions (including UIC, UW-Madison, COD, etc)
- Fostering inter-institutional collaboration and agreements, which may lead to new institutes
- MSEI is part of new MOU with University of Wisconsin Madison's COE

A visit by College of DuPage in A
their Innovation DuPage incubato

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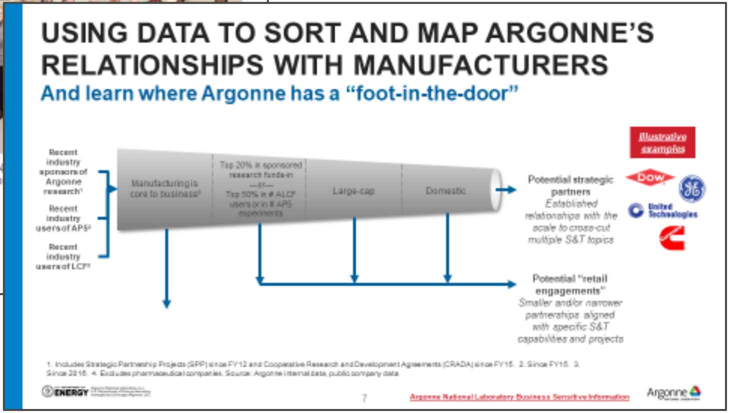

USING DATA TO SORT AND MAP ARGONNE'S RELATIONSHIPS WITH MANUFACTURERS

And learn where Argonne has a "foot-in-the-door"

Recent industry sponsors of Argonne research[1]

Recent industry users of APS[2]

Recent industry users of LCF[3]

Manufacturing is core to business[4]

Top 20% in sponsored research funds-in —or— Top 50% in # ALCF users or in # APS experiments

Large-cap

Domestic

Potential strategic partners
Established relationships with the scale to cross-cut multiple S&T topics

Potential "retail engagements"
Smaller and/or narrower partnerships aligned with specific S&T capabilities and projects

Illustrative examples

1. Includes Strategic Partnership Projects (SPP) since FY12 and Cooperative Research and Development Agreements (CRADA) since FY15. 2. Since FY15. 3. Since 2015. 4. Excludes pharmaceutical companies. Source: Argonne internal data, public company data

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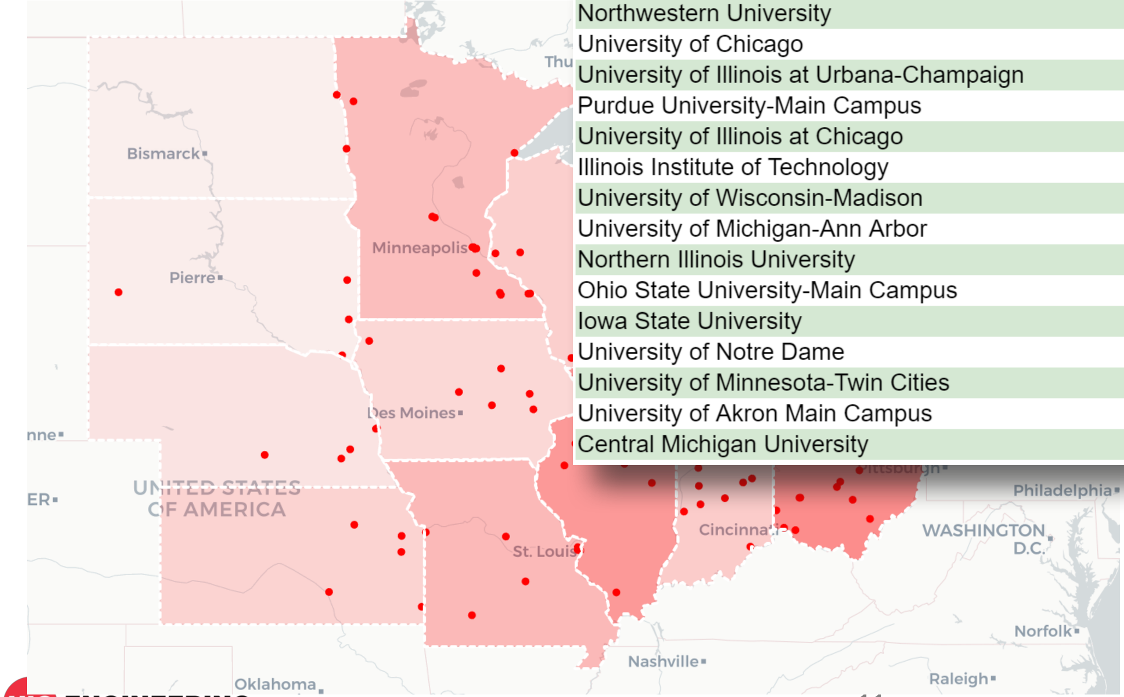
Argonne National Laboratory Business Sensitive Information

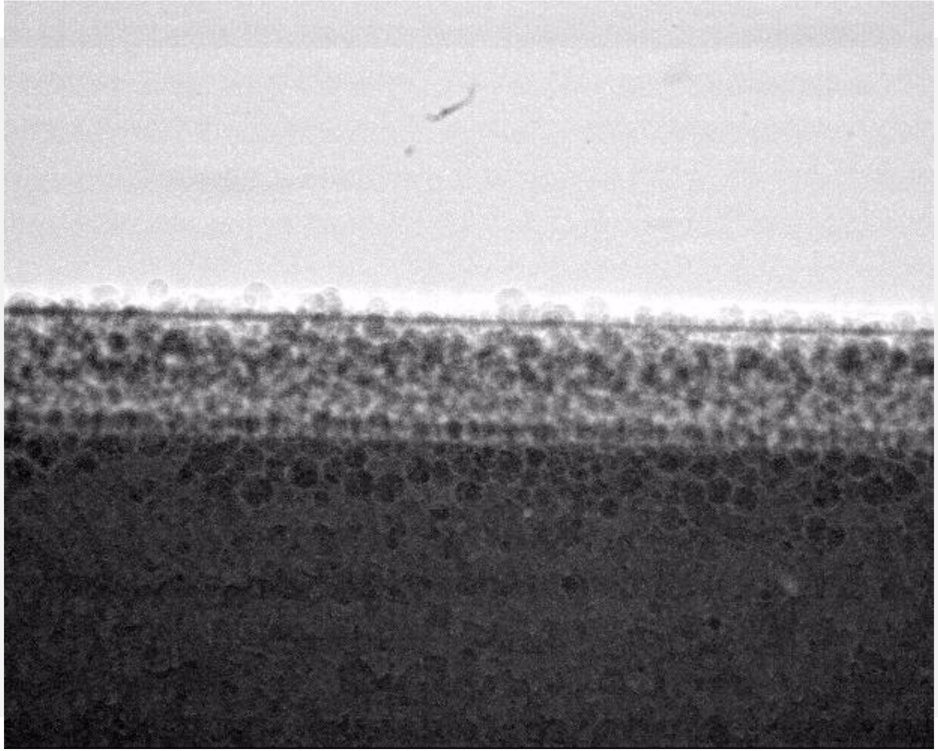
MIDWEST PARTNERSHIP IN MANUFACTURING

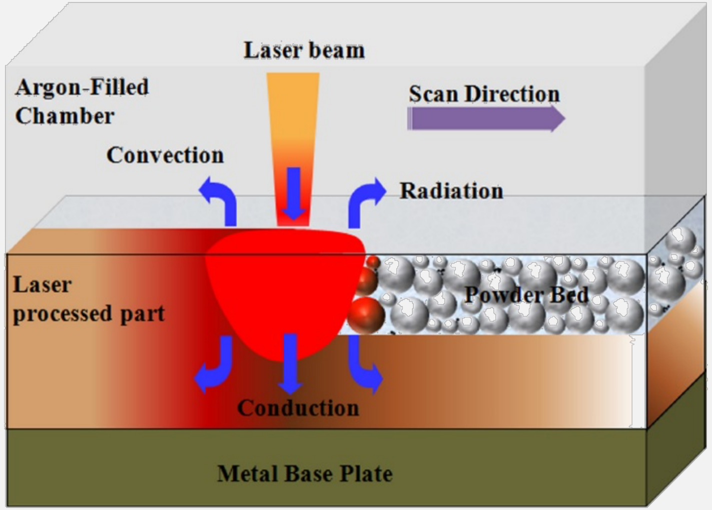


University	State	Publications
Northwestern University	Illinois	410
University of Chicago	Illinois	379
University of Illinois at Urbana-Champaign	Illinois	154
Purdue University-Main Campus	Indiana	108
University of Illinois at Chicago	Illinois	95
Illinois Institute of Technology	Illinois	90
University of Wisconsin-Madison	Wisconsin	64
University of Michigan-Ann Arbor	Michigan	45
Northern Illinois University	Illinois	38
Ohio State University-Main Campus	Ohio	30
Iowa State University	Iowa	29
University of Notre Dame	Indiana	29
University of Minnesota-Twin Cities	Minnesota	25
University of Akron Main Campus	Ohio	23
Central Michigan University	Michigan	22

NANOSCALE CONTROL OF PROCESSING CONDITIONS FOR INTERFACES

APS IN-SITU OBSERVATION OF AM PROCESS

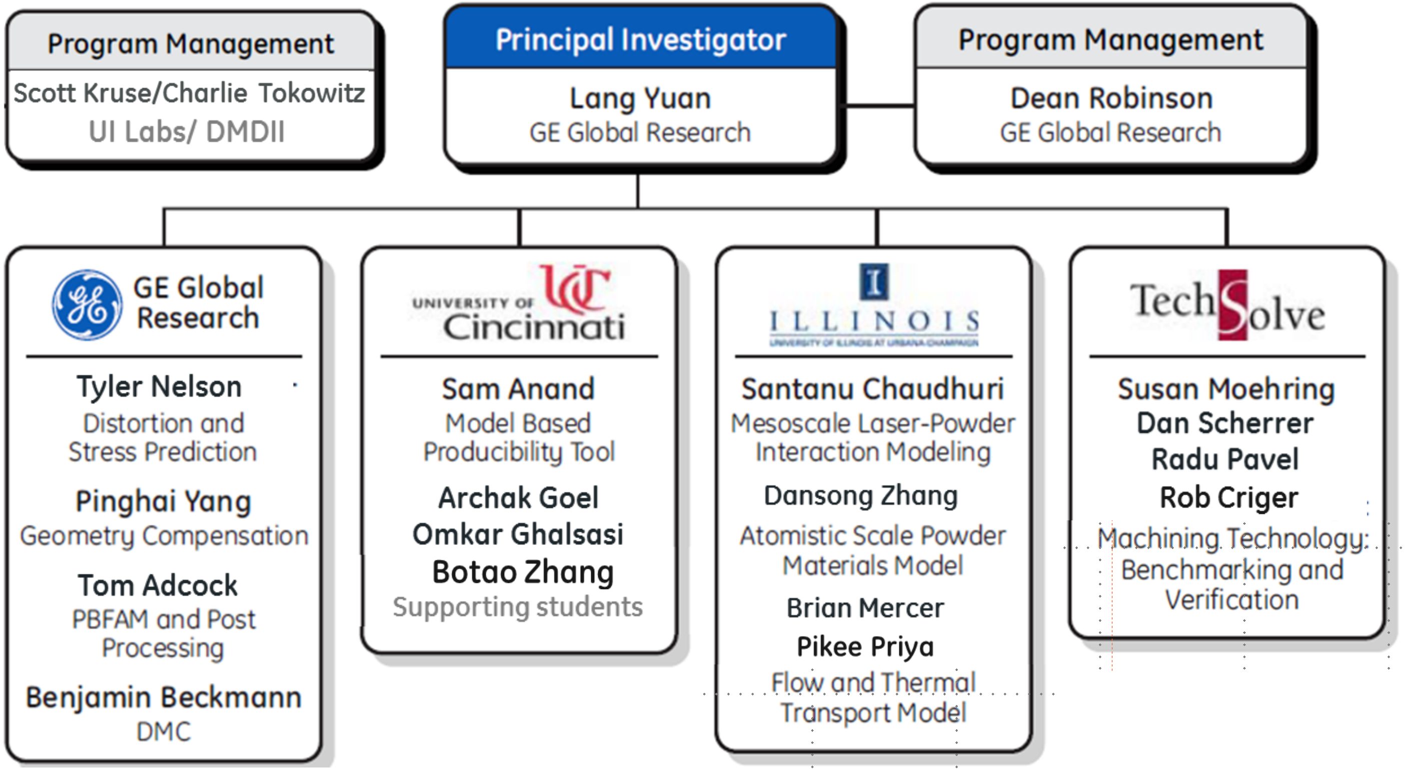




PI – Tao Sun

In-Situ x-ray observation
Side view | 8ms (45 kHz)

AM: ACCELERATING QUALIFICATION



Program Management
Scott Kruse/Charlie Tokowitz
UI Labs/ DMDII

Principal Investigator
Lang Yuan
GE Global Research

Program Management
Dean Robinson
GE Global Research

GE Global Research

Tyler Nelson
Distortion and Stress Prediction

Pinghai Yang
Geometry Compensation

Tom Adcock
PBFAM and Post Processing

Benjamin Beckmann
DMC

University of Cincinnati

Sam Anand
Model Based Producibility Tool

Archak Goel
Omkar Ghalsasi
Botao Zhang
Supporting students

ILLINOIS
University of Illinois at Urbana-Champaign

Santanu Chaudhuri
Mesoscale Laser-Powder Interaction Modeling

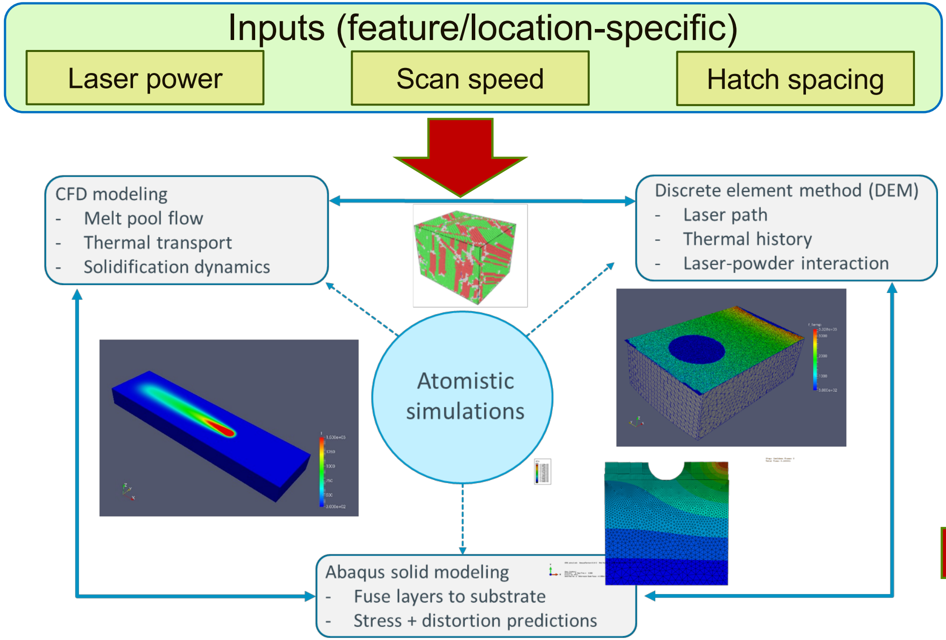
Dansong Zhang
Atomistic Scale Powder Materials Model

Brian Mercer
Pikee Priya
Flow and Thermal Transport Model

TechSolve

Susan Moehring
Dan Scherrer
Radu Pavel
Rob Criger
Machining Technology: Benchmarking and Verification

PROCESS PARAMETER OPTIMIZATION VIA MULTIPHYSICS MESOSCALE SIMULATION



Inputs (feature/location-specific)

- Laser power
- Scan speed
- Hatch spacing

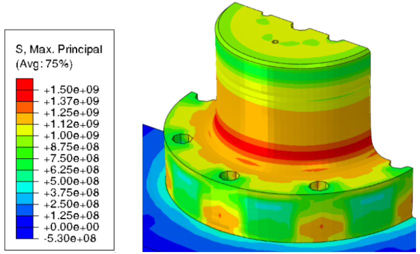
CFD modeling
- Melt pool flow
- Thermal transport
- Solidification dynamics

Discrete element method (DEM)
- Laser path
- Thermal history
- Laser-powder interaction

Atomistic simulations

Abaqus solid modeling
- Fuse layers to substrate
- Stress + distortion predictions

Coupling scheme yields affordable simulation with accurate physical representation of the process

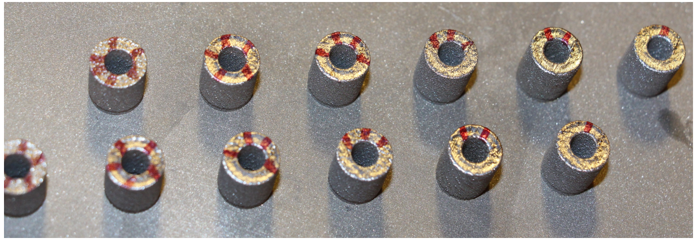


Feed optimized settings into part-scale build simulations

Use simulation tool to optimize laser settings:
- Reduce thermal stress and distortion
- Minimize surface roughness and porosity

INFLUENCE OF PROCESS PARAMETERS ON MELT POOL CHARACTERISTICS

Case	Power (W)	Speed (mm/s)	Pool width (microns)	Pool depth (microns)	Max pool velocity (cm/s)	Max temperature gradient (K/cm)	Max cooling rate (K/s)
1	300	900	273	55	238	7.10E+05	1.20E+07
2	300	600	345	60	253	7.30E+05	1.40E+07
3	280	1000	226	50	214	6.10E+05	1.00E+07
4	250	800	250	50	210	5.80E+05	9.20E+06
5	200	700	226	50	190	5.40E+05	7.60E+06
6	200	1000	178	40	175	4.40E+05	8.00E+06

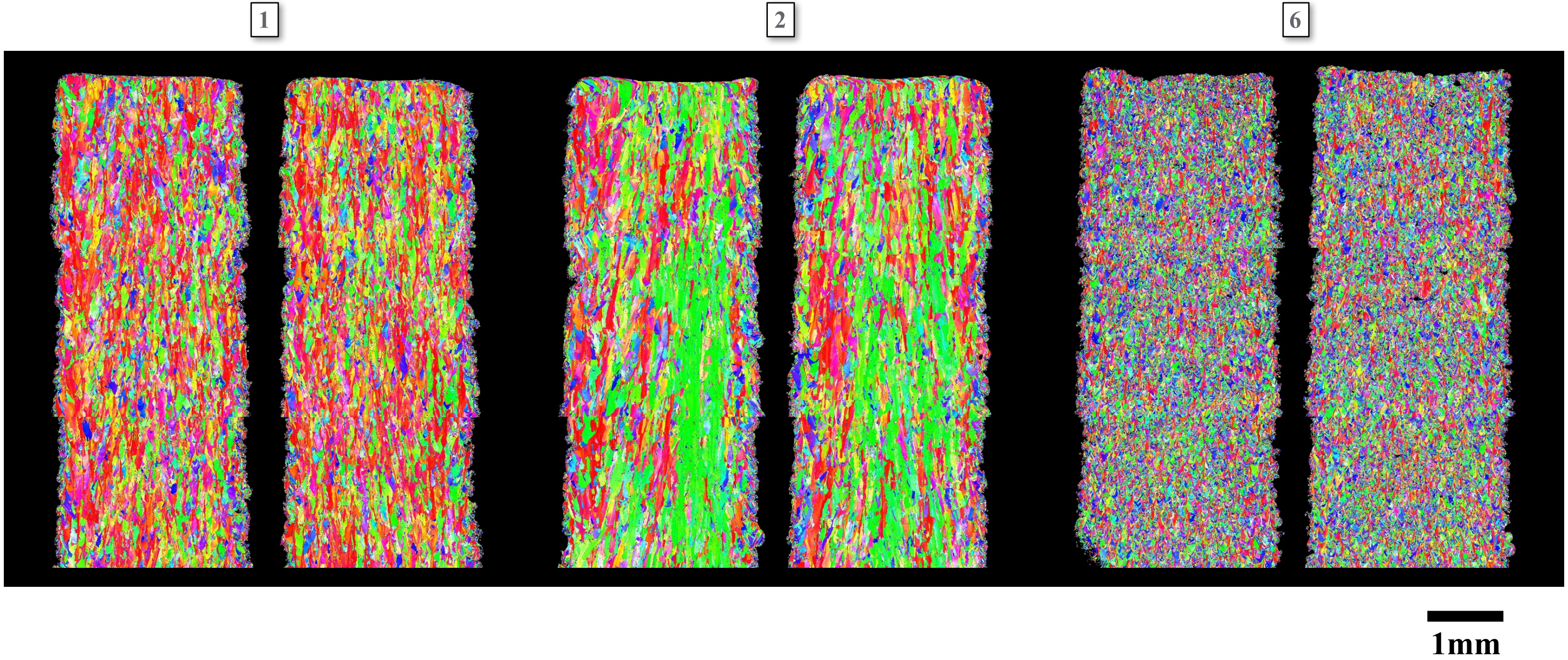


Samples are under characterization on SEM & EBSD

Data above used for microstructure prediction

- Grain Morphology
- Texture

MICROSTRUCTURE AND PERFORMANCE



Massive Differences in Microstructure in as-printed parts

Atmospheric Plasma for Surface Modification and Nanoscale Embedding of Chemistry

Santanu Chaudhuri
University of Illinois

SERDP
DOD ▪ EPA ▪ DOE

Project Team

Dr. Santanu Chaudhuri (PI)

Professor of Materials Engineering, CME, UIC
Affiliate, Applied Research Institute (ARI, UIUC)
Specialist in coatings, corrosion and multiscale modeling

Dr. David Ruzic

Professor, Nuclear and Plasma Engineering, UIUC
Specialist in plasma engineering and instrumentation
Inventor of the ECAP and LAPCAP processes

Dr. Dan Krogstad

ARI, UIUC
Coatings, Characterization and Coordination

Dr. Joseph Osborne

Formerly with Boeing Company (~30 years)
Specialist in coating performance,
corrosion protection and coating certification

Dr. Jessica Krogstad

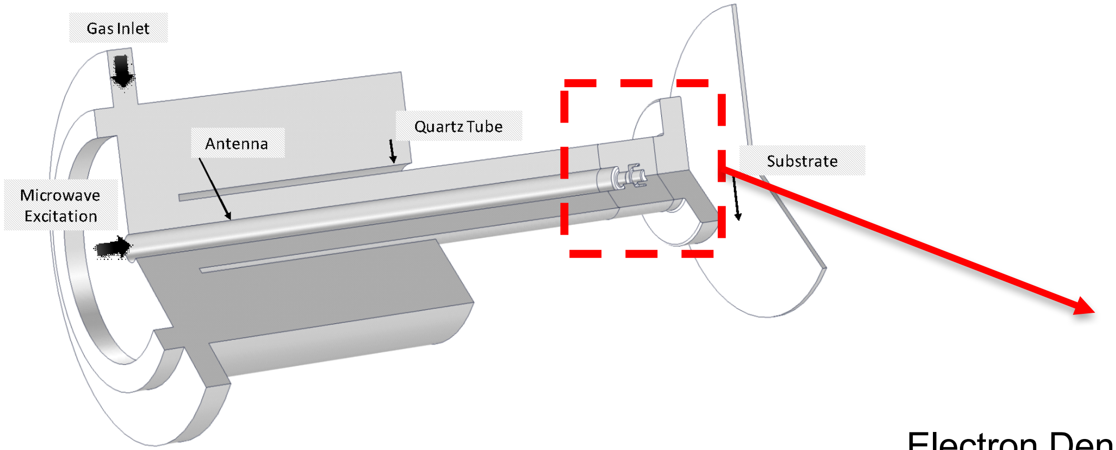
Professor, MatSE, UIUC
Coating optimization and characterization

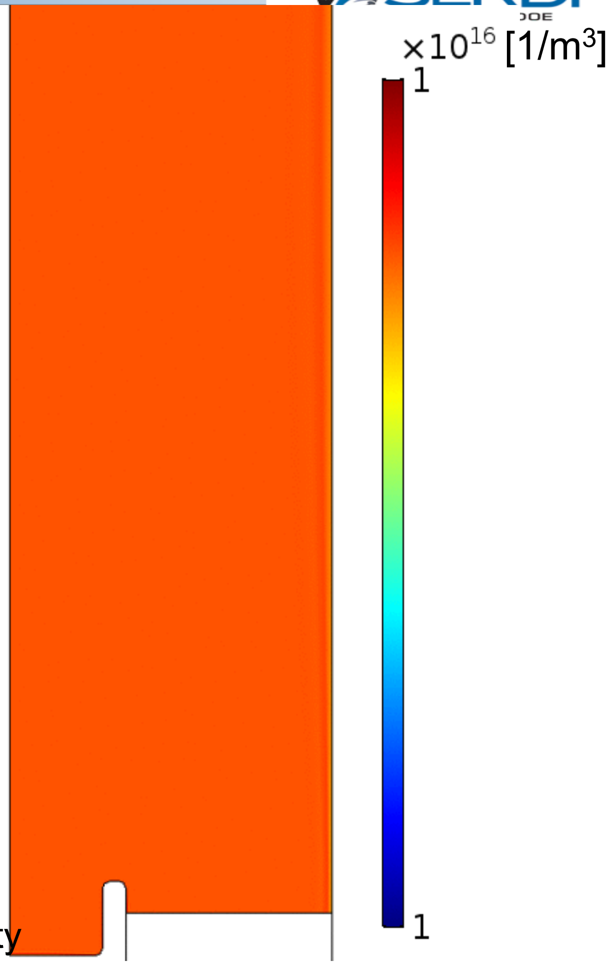
Dr. Brian Jurczyk (Starfire Industries)

Small business partner in technology assessment, transfer, and lifecycle cost

Atmospheric Pressure Microwave Plasma

- Microwave Excitations: 2.45[GHz]
- Atmospheric Pressure: 760[torr]
- Deposited Power: 200[W]
- Mass flow: 20[lpm]
- Gas: Argon





Electron Density

Physics Overview

- Plasma
  - Electron drift-diffusion continuity equation
  - Electron energy equation
  - Electron heat source from microwaves
- Electromagnetics
  - Maxwell equations
  - Plasma-EMW electrical conductivity coupling
- Turbulent flow
  - $k - \epsilon$
- Transient heat transfer
  - Energy equation
  - Heat source form plasma reactions

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \boldsymbol{V}) = 0$$

$$\rho \frac{\partial \boldsymbol{V}}{\partial t} + \rho(\boldsymbol{V} \cdot \boldsymbol{\nabla})\boldsymbol{V} = \boldsymbol{\nabla} \cdot \left(-p\hat{\boldsymbol{I}} + \hat{\boldsymbol{\tau}}\right) + \boldsymbol{F}$$

Lorentz Force: $\boldsymbol{F} = \frac{1}{2}\mathcal{R}e\{\sigma\, \boldsymbol{E} \times \boldsymbol{B}^*\}$

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \boldsymbol{V} \cdot \boldsymbol{\nabla}\mathrm{T} = \boldsymbol{\nabla}.\,(\lambda \boldsymbol{\nabla}\mathrm{T}) + \mathrm{Q}$$

$$N_i \frac{\partial}{\partial t}(\ln N_i) + \boldsymbol{\nabla} \cdot [-D_i N_i \boldsymbol{\nabla}(\ln N_i) + N_i \boldsymbol{V}] = S_i$$

Reactive Flow

Faraday's law: $\boldsymbol{\nabla} \times \boldsymbol{E} = -j\omega\mu_0 \boldsymbol{H}$

Ampère's law: $\boldsymbol{\nabla} \times \boldsymbol{H} = -j\omega\epsilon_0\epsilon_{pl}\boldsymbol{E}$

Electric Permittivity: $\epsilon_{pl} = 1 - \frac{\omega_p^2}{\omega(\omega - j\nu_m)}$

Plasma Frequency: $\omega_p = \left(\frac{n_e e^2}{\epsilon_0 m_e}\right)^{1/2}$

Electric Conductivity: $\sigma = \frac{n_e e^2}{m_e}\frac{1}{\nu_m + j\omega}$

Resistive Heating: $Q_h = \frac{1}{2}\mathcal{R}e\{\sigma\, \boldsymbol{E} \cdot \boldsymbol{E}^*\}$

Microwave

Boltzmann: $\frac{\partial}{\partial \epsilon}\left(Wf - D\frac{\partial f}{\partial \epsilon}\right) = S$

$$W = -\gamma\epsilon^2\sigma_\epsilon - 3a\left(\frac{n_e}{N_n}\right)A_1$$

$$D = \frac{\gamma}{3}\left(\frac{E}{N_n}\right)^2\left(\frac{\epsilon}{\sigma_m}\right) + \frac{\gamma k_b T}{q}\epsilon^2\sigma_\epsilon + 2a\left(\frac{n_e}{N_n}\right)\left(A_2 + \epsilon^{\frac{3}{2}}A3\right)$$

$$\frac{\partial n_e}{\partial t} + \boldsymbol{\nabla} \cdot [-n_e(\boldsymbol{\mu_e E}) - \boldsymbol{D_e}\boldsymbol{\nabla}\mathrm{n_e}] = R_e$$

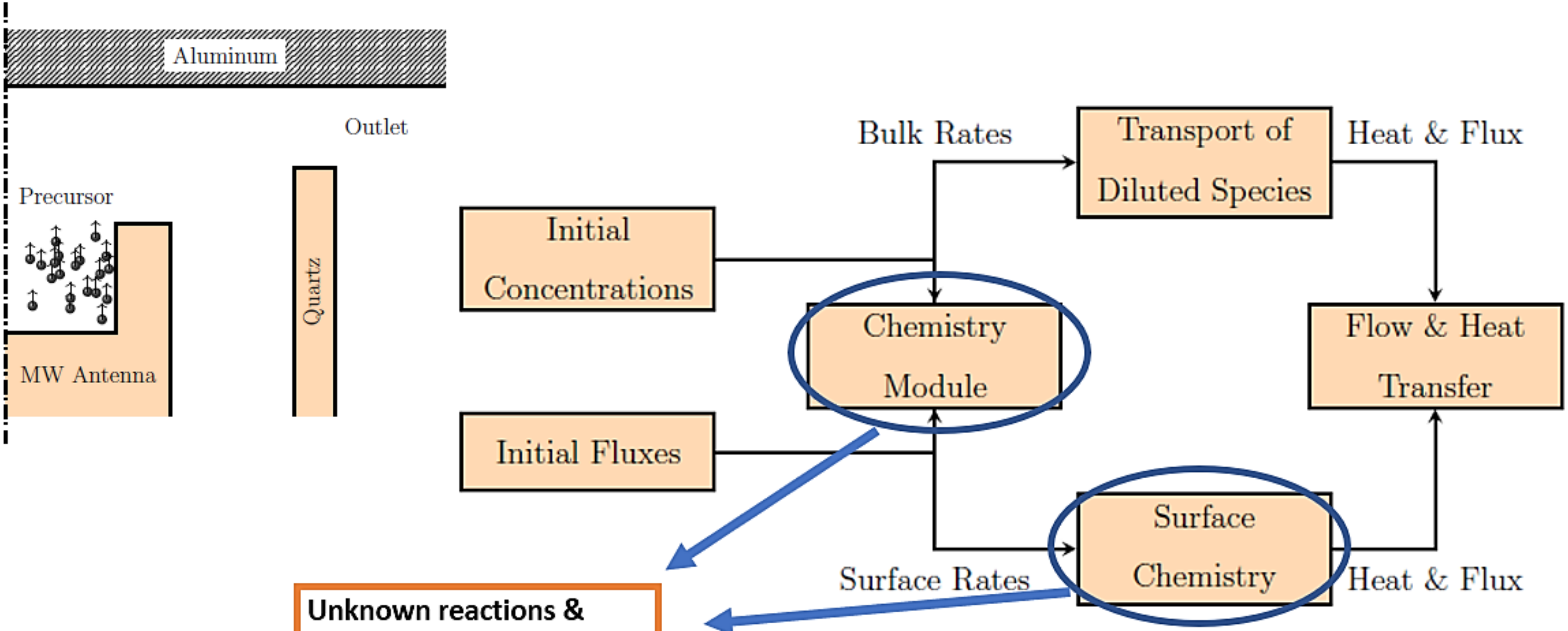
Electron Source: $R_e = \sum x_j k_j N_n n_e$

$$\frac{\partial n_\epsilon}{\partial t} + \boldsymbol{\nabla} \cdot [-n_\epsilon(\boldsymbol{\mu_\epsilon E}) - \boldsymbol{D_\epsilon}\boldsymbol{\nabla}\mathrm{n_\epsilon}] + \boldsymbol{E} \cdot \Gamma_e = R_\epsilon$$

Inelastic Collision energy loss: $R_\epsilon = \sum x_j k_j N_n n_e \Delta\epsilon_j$

Plasma

Multiscale Chemistry



Initial Concentrations

Initial Fluxes

Bulk Rates

Transport of Diluted Species

Heat & Flux

Chemistry Module

Flow & Heat Transfer

Surface Rates

Surface Chemistry

Heat & Flux

Unknown reactions & required data for Chemkin

Surface cleaning: Nature of the Reactions

- The key mechanisms occurring are
  - Evaporation
  - Thermal Degradation
  - Oxidative Volatility
  - Polymerization
  - Deposit Formation
  - Oxidation
    - Initiation
    - Propagation
    - Branching
    - Termination
- lubricating oils
  - C_nH_{2n-2} to C_nH_{2n-20}
- Pennsylvania oil is generally agreed to be free from unsaturation
  - Pennsylvania oil has been the most studied because of its relatively less complex composition.
  - C_nH_{2n-8} to C_nH_{2n-20}
  - Naphthenes (cycloalkanes $C_nH_{2(n+1-r)}$)
    - n: carbon r: rings
  - Paraffin or iso-paraffin side chains
  - n_C = 0.358 mol. wt. + 7.7 - 0.3 mol. vol.
- Initiation: $ROOH \rightarrow RO_2 + RO + OH$
- Propagation: $RO_2 + RH \rightarrow RO_2H + R$ $R + O_2 \rightarrow RO_2$

$$\overbrace{\hspace{6cm}}^{\text{Primary Free Radical Oxidation}}$$

Initiation:

$$RH \xrightarrow{Q,CAT} R^{\cdot} + H$$

Propagation:

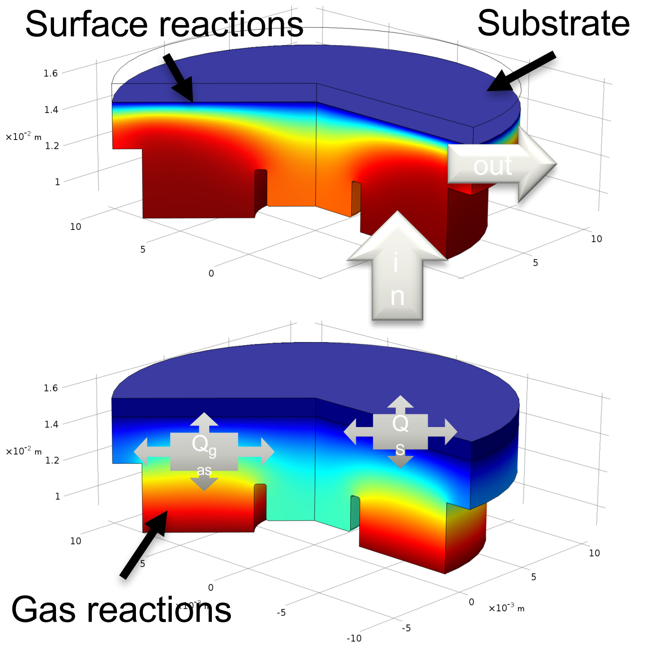
$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$$
$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$$

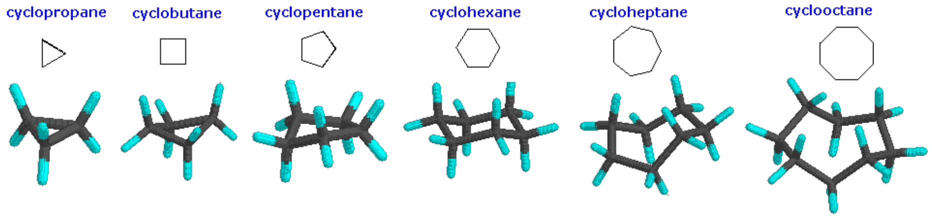
Branching

$$ROOH \longrightarrow RO^{\cdot} + HO^{\cdot}$$
$$RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$$
$$HO^{\cdot} + RH \longrightarrow H_2O + R^{\cdot}$$

Termination

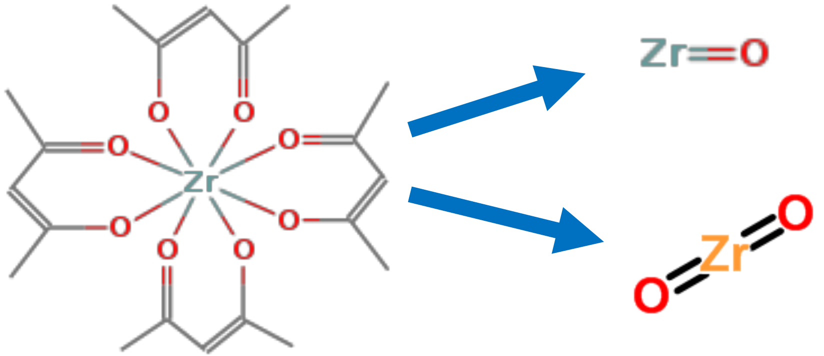
$$\left.\begin{array}{c} R^{\cdot} + R^{\cdot} \\ R^{\cdot} + ROO^{\cdot} \\ ROO^{\cdot} + ROO^{\cdot} \\ RO^{\cdot} + R^{\cdot} \end{array}\right\} \longrightarrow \begin{array}{cc} acids & alcohols \\ aldehydes & ketones \end{array}$$





Reaction Engineering

- In the APP process, Zirconium Acetylacetonate (Zr(C5H7O2)4) first decomposes into a gas phase. The reaction products along with water vapor (H2O) adsorb and react on an Aluminum (Al) substrate to form Zirconium Oxide (ZrO2) layers.



1. Gas-phase decomposition reactions

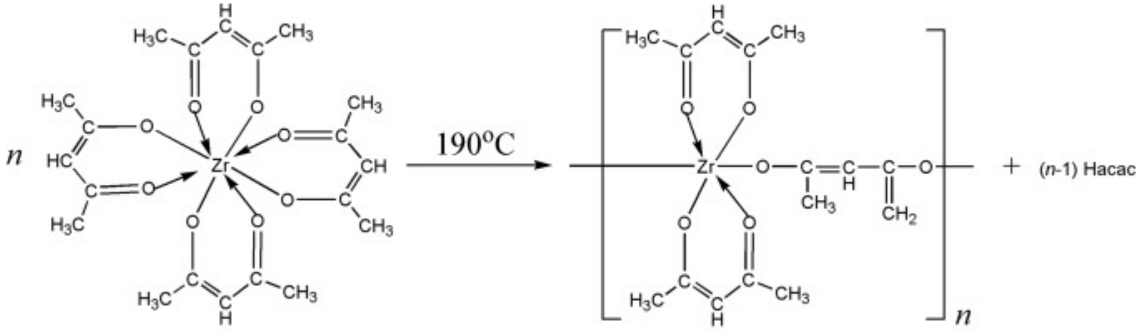
Zr(C5H7O2)4 => Zr(C5H7O2)3 + C5H7O2

Zr(C5H7O2)3 => ZrO(C5H7O2)2 + C5H7O

ZrO(C5H7O2)2 => ZrO(C5H7O2) + C5H7O2

ZrO(C5H7O2) => ZrO2 + C5H7O

ZrO(C5H7O2) => ZrO + C5H7O2

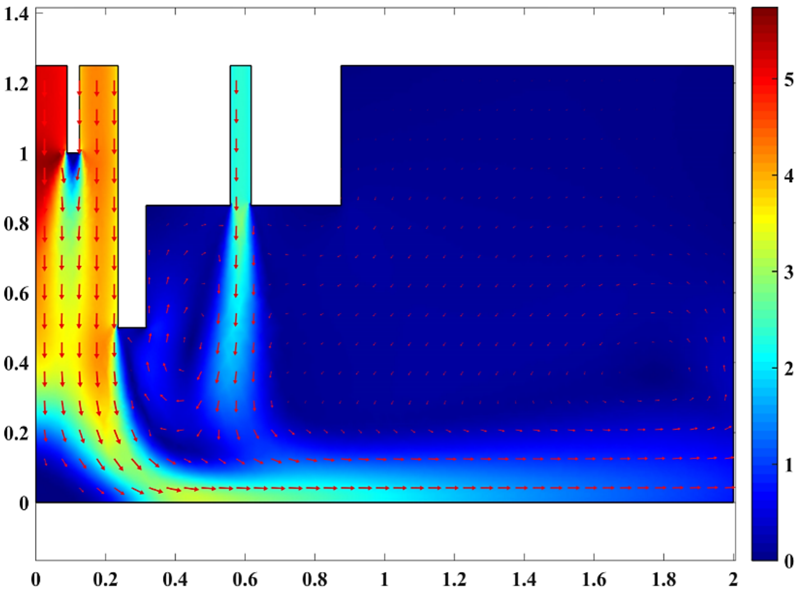


Zr(acac)$_4$

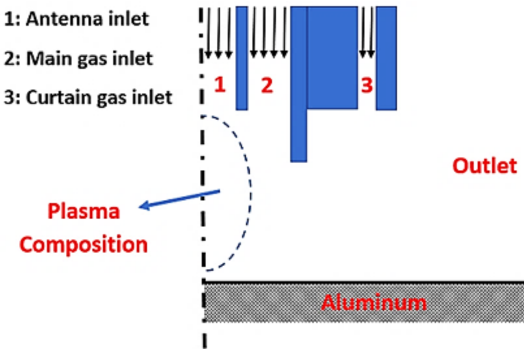
ZrC precursor

ZrO_2: Optimizing Flow Rate and Growth

Curtain gas flow rate = 20 L/min, Velocity magnitude (m/s)

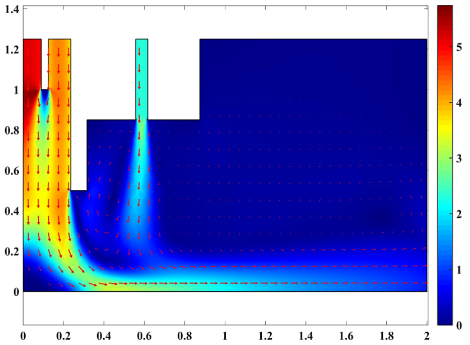


Precursor:
$Zr(AcAc)_4$
U_1 = 5 l/min
U_2 = 20 l/min

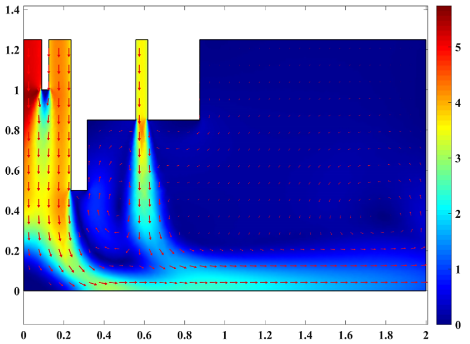


- ❑ Considering the turbulence effects in the models, the flow pattern is smoother at lower gas-curtain flow rate (20 – 40 lpm) almost without eddies.
- ❑ The growth rate of zirconia is higher at lower flow rates due to almost laminar flow pattern which increases the residence time for ZrO and Zr to participate in surface reactions.

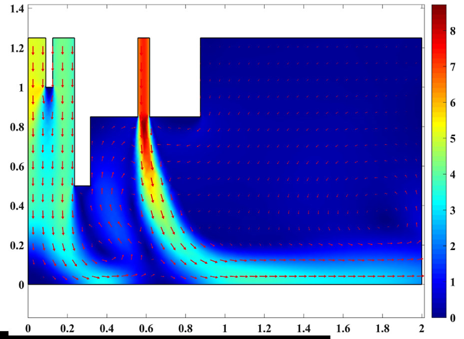
Curtain gas flow rate = 20 L/min, Velocity magnitude (m/s)



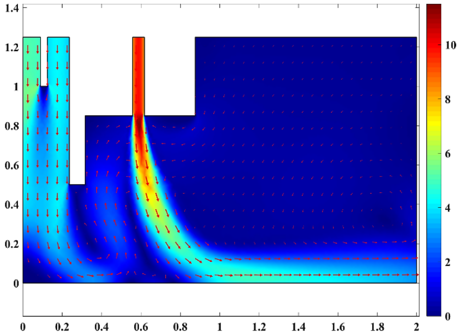
Curtain gas flow rate = 30 L/min, Velocity magnitude (m/s)

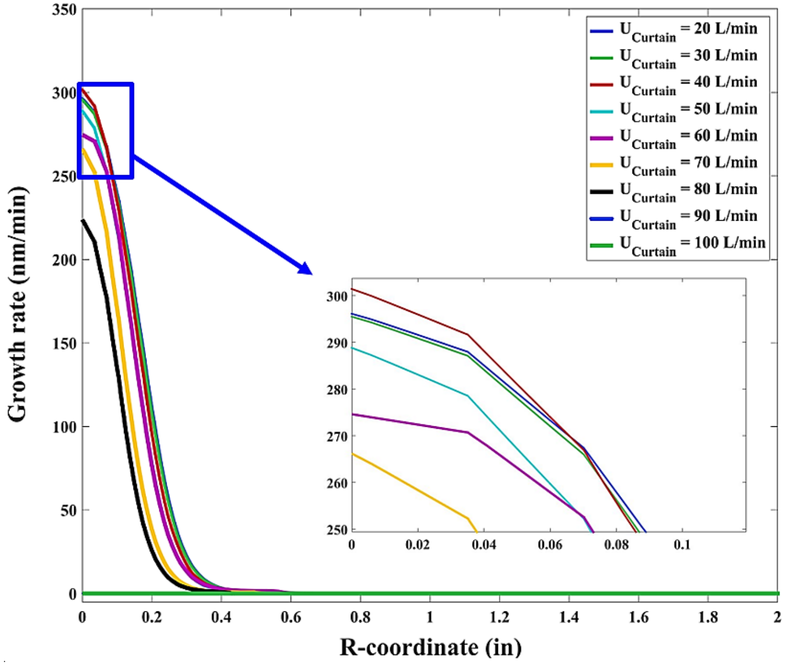


Curtain gas flow rate = 60 L/min, Velocity magnitude (m/s)



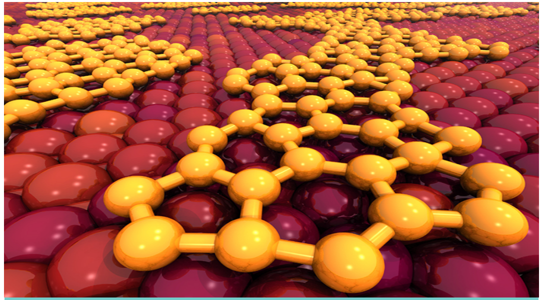
Curtain gas flow rate = 80 L/min, Velocity magnitude (m/s)





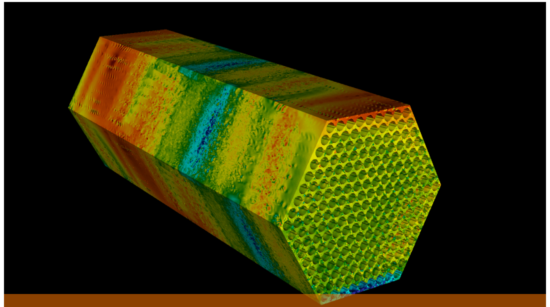
Precursor: $Zr(AcAc)_4$
U_1 = 5 l/min
U_2 = 20 l/min

SUMMARY: PREDICTIVE CONTROL OVER NANOSCALE DOMAINS IN 3D



MULTISCALE LINKS TO MATERIALS PHYSICS AND CHEMISTRY

MESOSCALE MODELS, AI/ML AND PROCESS MODELING



MATERIALS, DEVICE, AND FABRICATION TO PERFORMANCE, RELIABILITY AND AGING

PREDICT → VALIDATE → LEARN AND DECIDE → BUILD