Multiphysics and Multiscale Simulation Methods for Electromagnetic Energy Assisted Fossil Fuel to Hydrogen Conversion

Su Yan [1], Tao Wei [1], Jiefu Chen [2], and Xiaonan Shan [2]

[1] Howard University, Washington, DC 20059; su.yan@howard.edu, tao.wei@howard.edu

[2] University of Houston, Houston, TX 77204; jchen82@central.uh.edu, xshan@central.uh.edu

April 19, 2023

TECHNICAL BACKGROUND & MOTIVATION

- Fossil fuels comprise 80% of current global primary energy demand and the energy system is the source of approximately two thirds of global CO_2 emissions.
- Develop and optimize methods that use electromagnetic (EM) energy to assist fossil fuel to H_2 conversion.
- **Research Questions:**

1. What is the catalyst morphology and how does it affect EM energy deposition during H_2 production?
2. How do physical factors, such as reaction chamber geometry, EM wave intensity and frequency, source material flow velocity, and reaction temperature, affect catalytic active sites?
3. What is the chemical kinetics under different physical inputs and how does it affect H_2 conversion efficiency?
4. How to estimate the throughput, yield, and cost of dehydrogenization?

SIGNIFICANCE OF THE PROJECT RESULTS

- **Research Component:**

  Direct impact on the petrochemical industry by providing theoretically rigorous and technically sound computational approaches to guide low-cost hydrogen generations.

  1. Develop a computational platform to provide fundamental understanding of using alternative energy processes (microwave, radio frequency, plasma and other EM inputs) for low-cost hydrogen production from fossil fuels;
  2. Provide thorough and comprehensive studies on how to improve the H2 conversion efficiency of EM energy assisted approaches using multiphysics and multiscale computation, imaging techniques, and quantum chemistry methods;
  3. Investigate and optimize the H2 production using EM energy and estimate the conversion costs;
  4. Publish on technical journals and conferences to support technology transfer.

SIGNIFICANCE OF THE PROJECT RESULTS

- **Education Component:**

  Education and research opportunities for our African American and other underrepresented minority students.

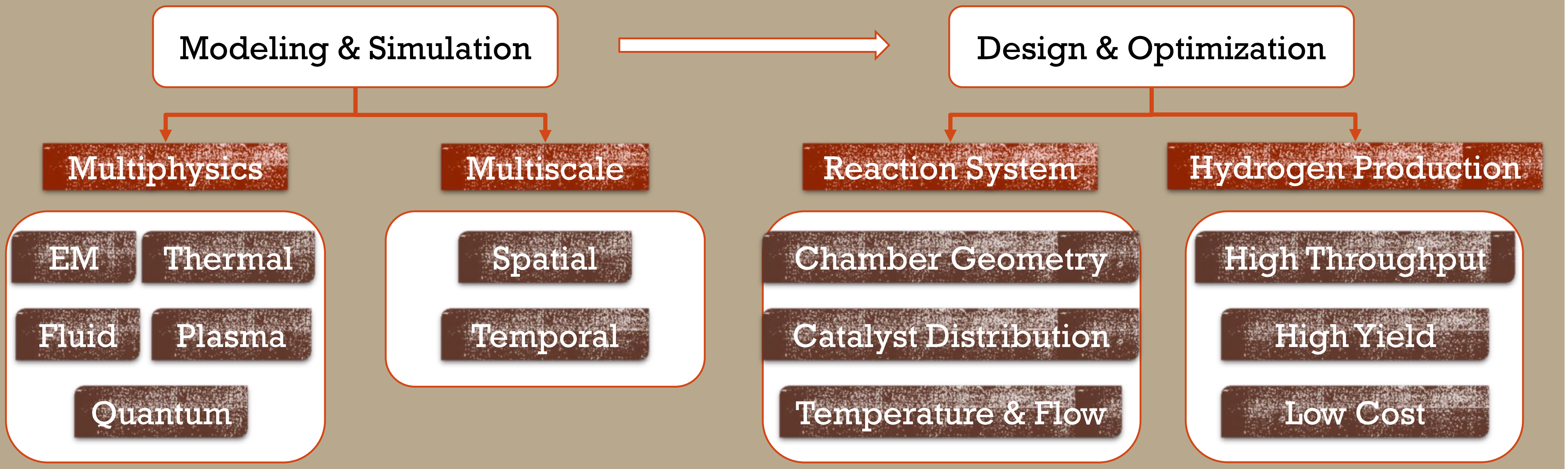
  1. Support one graduate student and multiple undergraduate students in Howard University and one graduate student in the University of Houston;
  2. Provide education and training in an interdisciplinary research team that integrates EM, chemical engineering, computer graphics, material sciences, and computational science and engineering;
  3. Offer an excellent opportunity for our students to be exposed and involved in fossil energy related education and research, and hence, develop their interests and capabilities in creating and executing new research ideas that support the mission of DOE.

PROJECT OBJECTIVES

- **Objective:**

  Develop, implement, validate, and apply multiphysics and multiscale simulation methods for efficient electromagnetic (EM) energy assisted conversion from fossil fuel to low-cost hydrogen.

- **Two Major Thrust Areas:**



SCOPE OF WORK

1. **Understanding 3D structures of catalysts and their supports:**

   Utilize 3D optical imaging and FIB-SEM sectioning and imaging to determine catalyst distribution and support morphology in order to characterize 3D structure;

2. **Characterization of EM hotspots within heterogeneous catalysis:**

   Use computational methods to develop 3D nodal discontinuous Galerkin (NDG) methods for the modeling and simulation of coupled EM-thermal-fluid-plasma problems involving multiscale media;

3. **Multiphysics investigation of EM energy assisted catalytic active sites enhancement:**

   Develop multiscale simulation methods to couple physical with chemical phenomena based on the coupled modeling of the NDG method, reactive forcefield molecular dynamics (ReaxFF MD) simulations, and density functional theory (DFT) simulations;

4. **System design and optimization for high-yield and low-cost hydrogen generation:**

   Use the methods developed above to design an optimized EM-assisted catalytic system for an improved hydrogen conversion efficiency with a lowered cost.

RESEARCH TASKS

Task 1: 3D Geometric Modeling of Catalysts Structure

Obtaining an accurate 3D structure of the catalyst support and distribution help understand EM energy assisted H2 generation process.

- **Subtask 1.1: Optical 3D Imaging**
  1. Use an optical reflection microscope to scan through the catalyst structure;
  2. Image the 3D catalytic nanoparticle morphology and distribution on the substrate.
- **Subtask 1.2: FIB-SEM Sectioning 3D Reconstruction**
  1. Use the focused ion beam -- scanning electron microscope (FIB-SEM) sectioning method to provide the 3D structure of catalyst support and nanoparticle distributions;
  2. The FIB milling ablates the substrate material, which is then imaged and measured by the SEM;
  3. The total 3D structure will be reconstructed using commercial software such as AVIZO.

RESEARCH TASKS

Task 2: Characterization of EM Hotspots Within Heterogeneous Catalysis

Develop hybrid numerical methods to simulate the multiphysical process during H2 generation and characterize EM hotspots within heterogeneous catalysis.

- **Subtask 2.1: Development of Coupled EM-Thermal-Fluid-Plasma Simulation Methods**
  1. Develop a unified simulation platform, based on the high-order nodal discontinuous Galerkin (NDG) method, to solve different physical governing equations, including Maxwell's, heat transfer, electron transport equations;
  2. Develop multiphysical coupling schemes to account for the multiscale issues in space and time.
- **Subtask 2.2: Investigation of EM Hotspots and Heat Generation in Heterogeneous Catalysis**
  1. Investigate and characterize EM hotspots and heat generation by applying the NDG methods developed in Subtask 2.1 to heterogeneous catalysis modeled in Task 1;
  2. Employ two catalyst models: (a) 3D porous structure obtained in Task 1 and (b) homogenized porous material using averaging formulas.

RESEARCH TASKS

Task 3: Multiphysics Investigation of EM Energy Assisted Catalytic Active Sites Enhancement

- **Subtask 3.1: Quantum and Atomistic Simulations of Pd Nanoparticle Catalyzed Reactions**
  1. Perform ReaxFF MD simulations and quantum dynamics simulations (QMD) with DFT of catalyzed reactions of fossil fuel dehydrogenation and coupling to catalysts;
  2. Model chemical reactions at different temperatures, field intensities, and frequencies, using large-scale parallel computations of millions of atoms;
  3. Characterize chemical reactions as a function of heating rate and electric fields of various frequencies and strengths using a combination of atomistic ReaxFF MD and DFT.
- **Subtask 3.2: Development of Coupled Physical-Chemical Simulation Methods**
  1. Develop coupled physical-chemical simulation methods by combining the multiphysics simulation methods in Subtask 2.1 and the ReaxFF MD and DFT methods in Subtask 3.1;
  2. Multiphysics simulations provide physical parameters as the experimental conditions for thermochemical simulations, which provide the materials' EM and thermal parameters as the constitutive relations for multiphysics simulations.

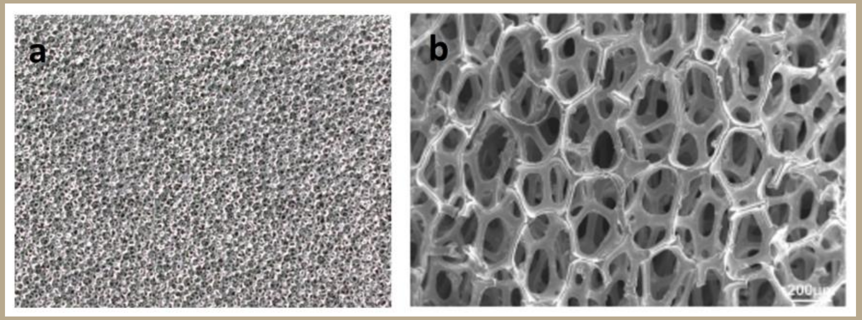
RESEARCH TASKS

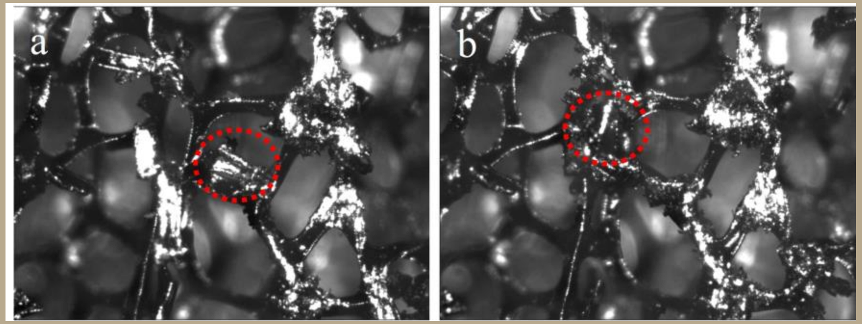
Task 4: System Design and Optimization for High-Yield and Low-Cost Hydrogen Generation

1. Perform system-level design and optimization by collecting and combining the information of 3D morphology of catalyst (Task 1), multiphysics modeling and simulation capabilities (Task 2), and quantum and atomistic modeling and simulation capabilities (Task 3);
2. The conversion efficiency of dehydrogenation of methane will be calculated;
3. Design and optimize the reaction system, including the chamber geometry, catalyst distribution, catalyst support geometry, and temperature and flow control, for an improved hydrogen conversion efficiency with a lowered cost;
4. Apply the simulation methods to optimize the shape of the reaction chamber to achieve a uniform delivery of EM energy throughout the reacting materials and examine the effect of engineered nanoparticles in the local field enhancement to achieve a more efficient EM energy deposition.

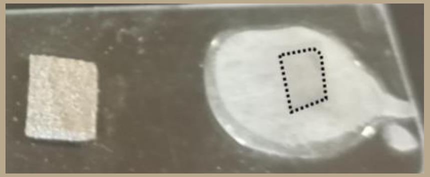
PROJECT STATUS: TASK 1

- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:

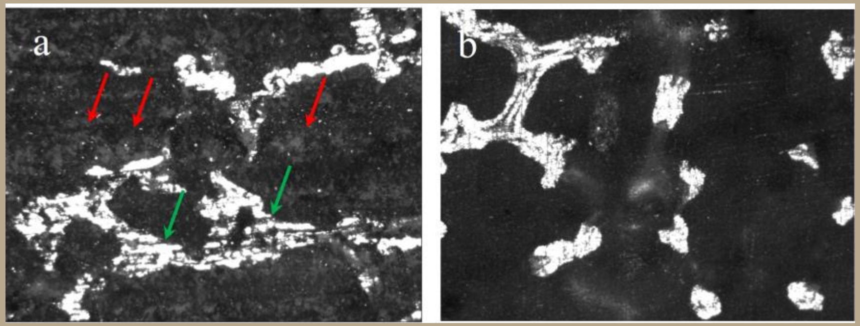




Movement of Ni foam. The red dashed circles indicate the same region before (a) and after (b) the polishing. The structure shape and pattern are totally different.



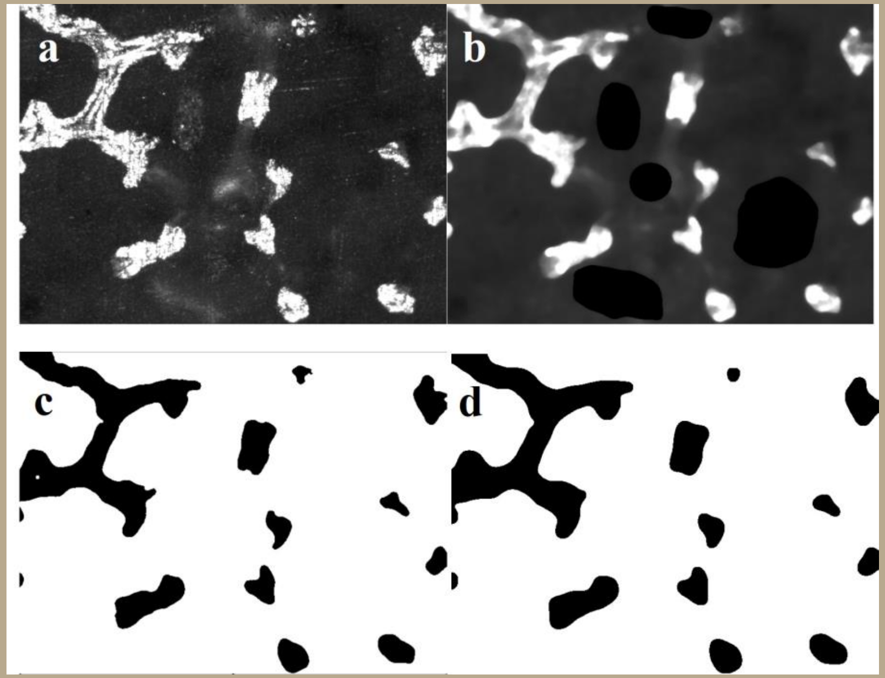
Ni foam with (right) and without (left) epoxy support.



Polished cross-section of Ni foam. (a) Polished in air. (b) Polished in water. Green arrows showed the scratch line, and the red arrows show epoxy residue.

PROJECT STATUS: TASK 1

- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:



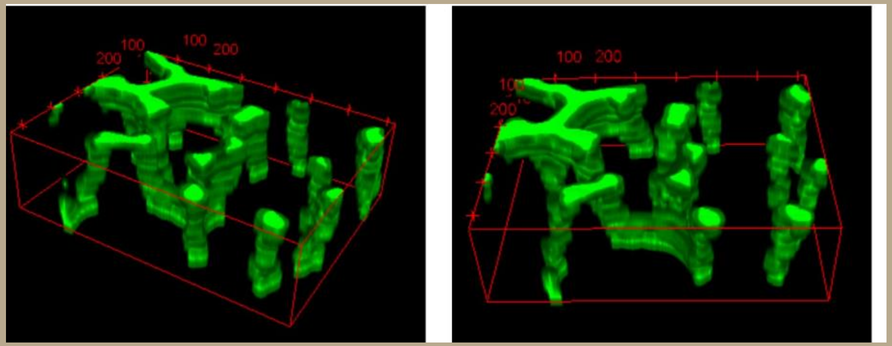
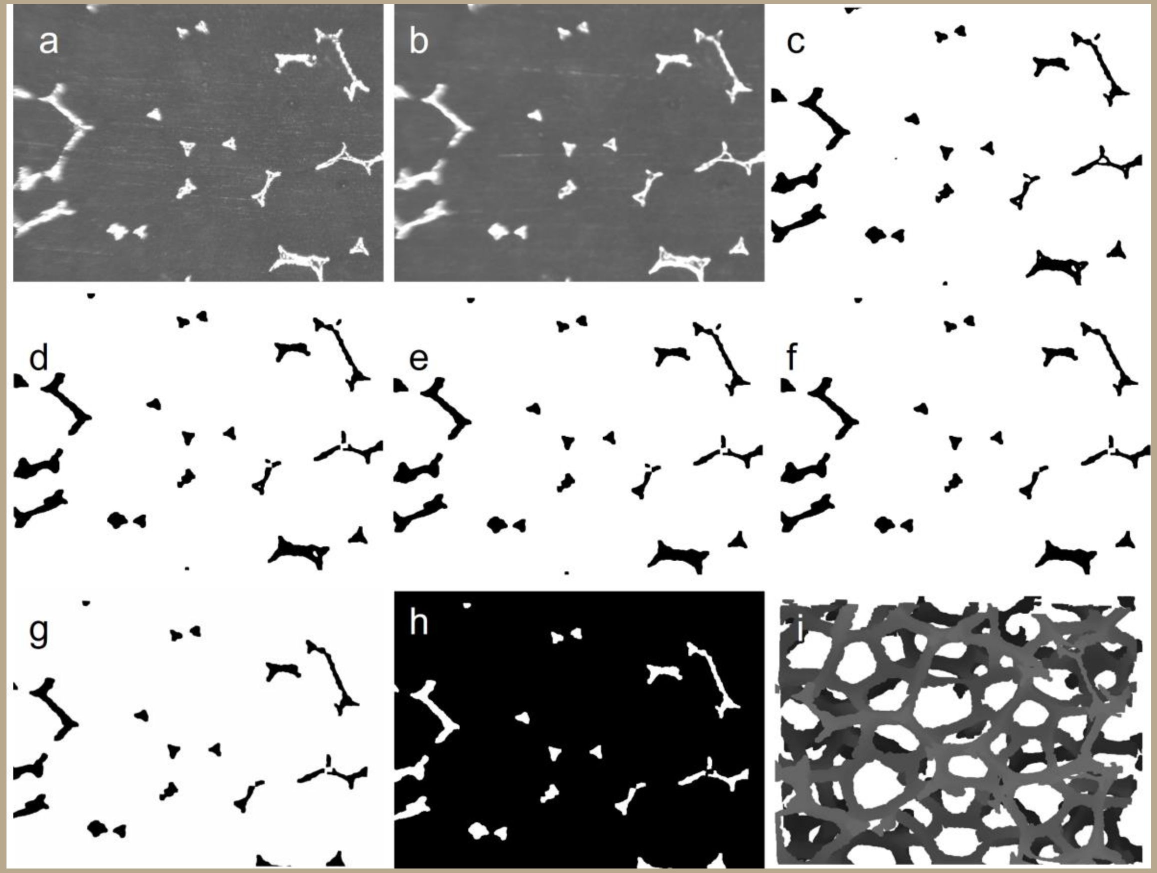


Image segmentation. (a) The raw image of the cross-section of Ni foam. (b) Using median filter to remove the bright particles on the surface. (c) Segmentation by setting a threshold. (d) Remove the small void in the regions using the dilation and erosion.

PROJECT STATUS: TASK 1

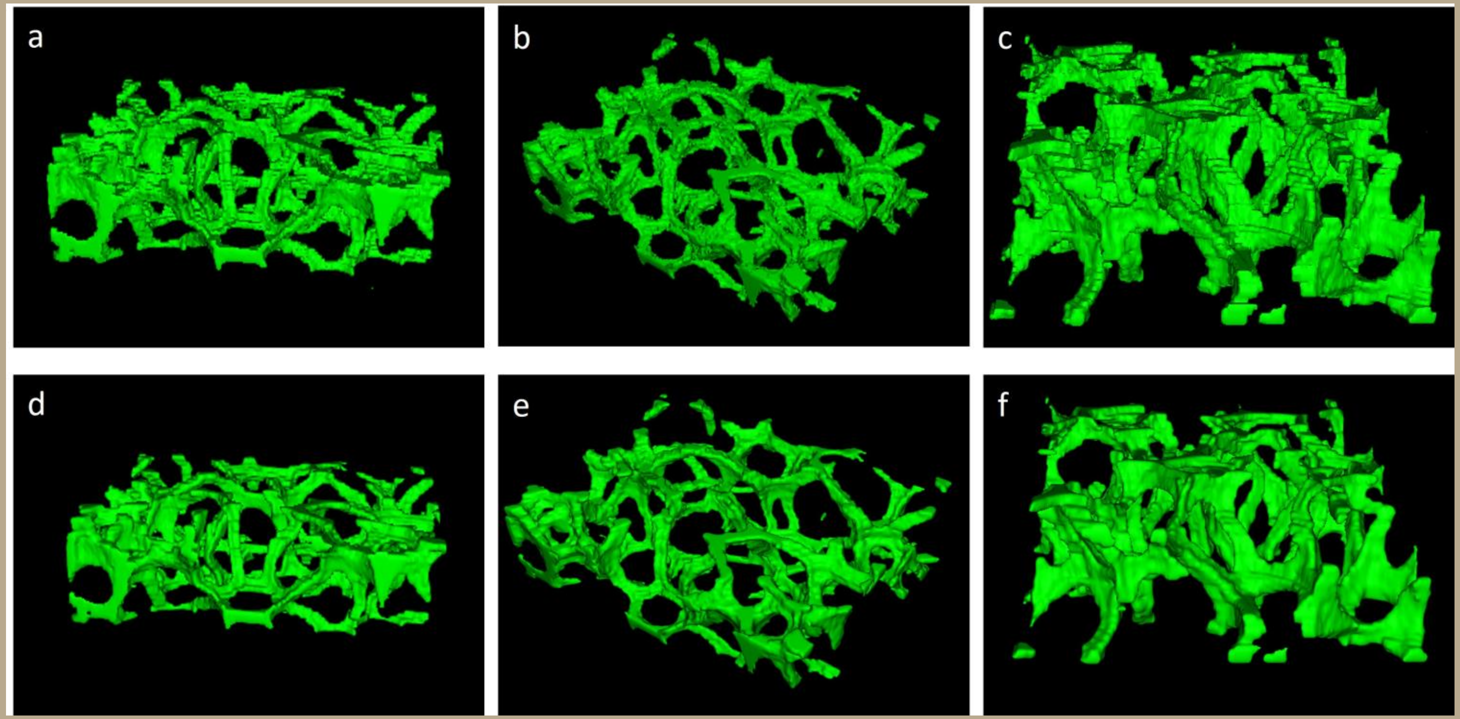
- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:



Modified image segmentation. (a) The raw image of the cross-section of Ni foam. (b) Using median filter to remove the bright particles on the surface. (c) Segmentation by setting a threshold. (d) Using dilate and erode to smooth the boundaries. (e) Fill the holes to remove white area in black part. (f) Remove small particles. (g) Image alignment of adjacent pictures. (h) Switch the color. (i) Build the 3D stack in z direction.

PROJECT STATUS: TASK 1

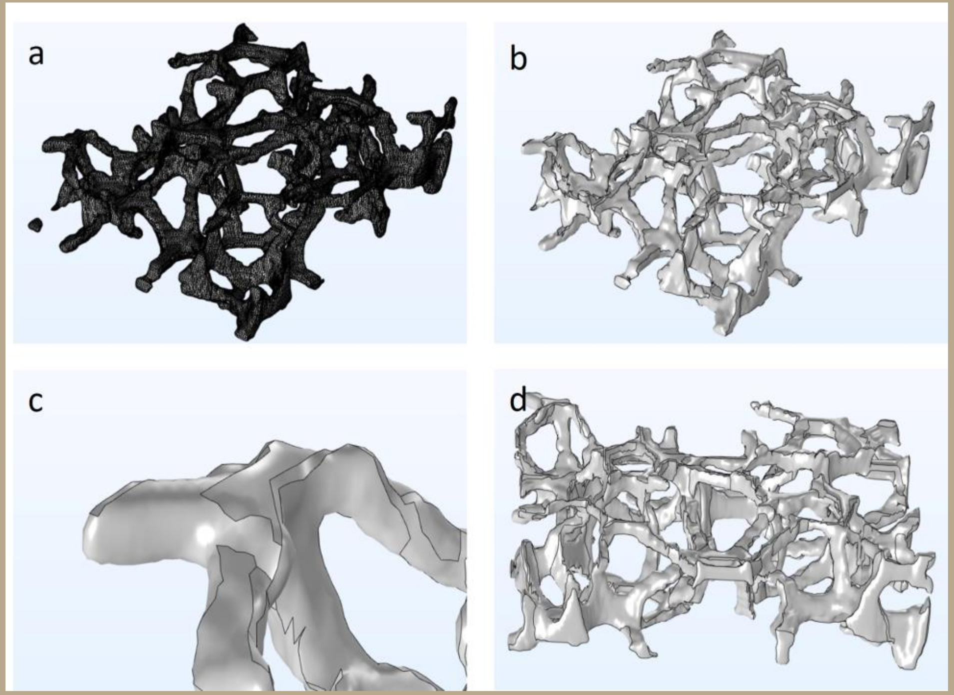
- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:



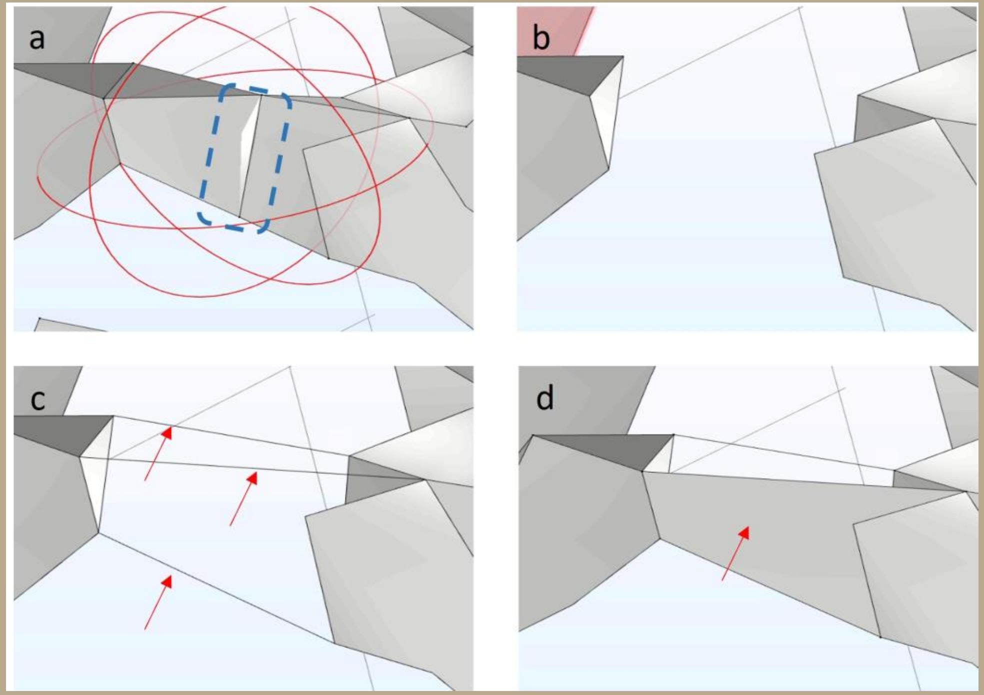
3D reconstructed Ni foam viewing from different angles. a-c before the smooth, and d-f after the smooth. The entire structure is ~ 1.8 mm wide and ~0.5 mm thick.

PROJECT STATUS: TASK 1

- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:



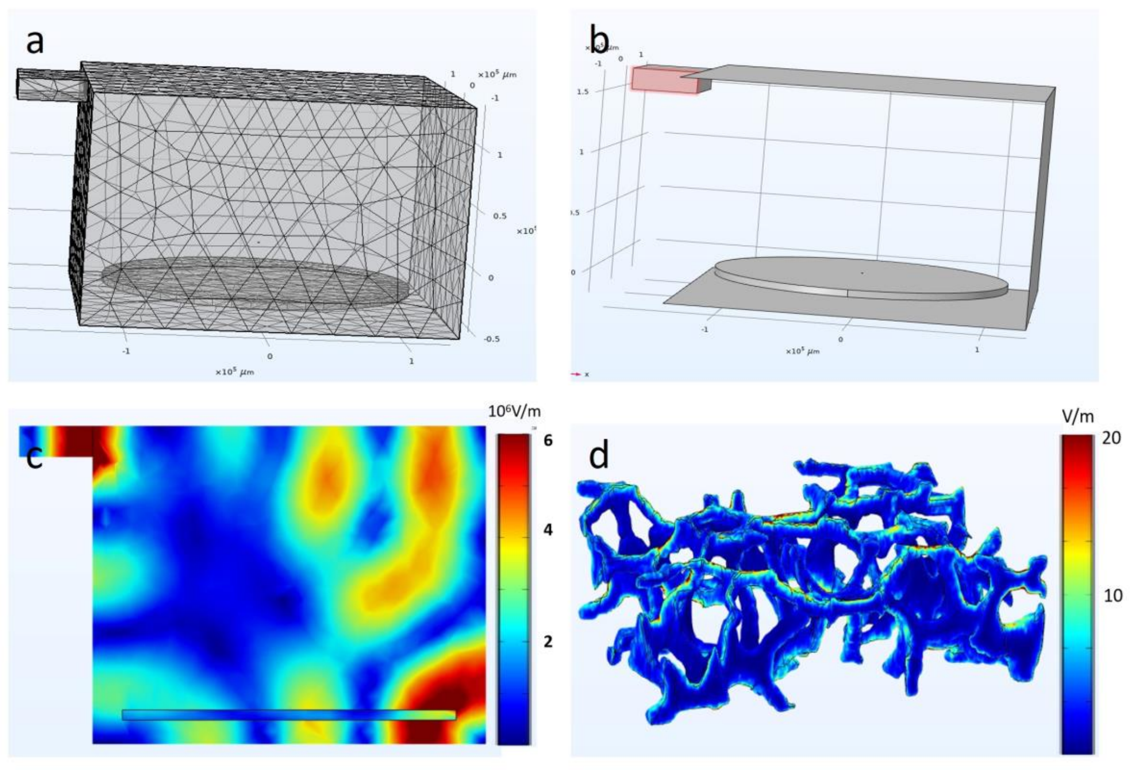
Imported the 3D geometry into the MESHLAB to remove the extra small domains that is caused by the image reconstruction errors Nickel foam. 3D model in COMSOL (a-b) 3D geometry with (a) and without the mesh (b). (c) A zoomed in region. (d) 3D geometry with different angle.



Process to remove self-intersecting surfaces and edges. (a) Using balling function to split surface. (b) Delete the intersecting surfaces. (c) Generate new edges. (f) Create new surfaces based on the new edges.

PROJECT STATUS: TASK 1

- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:

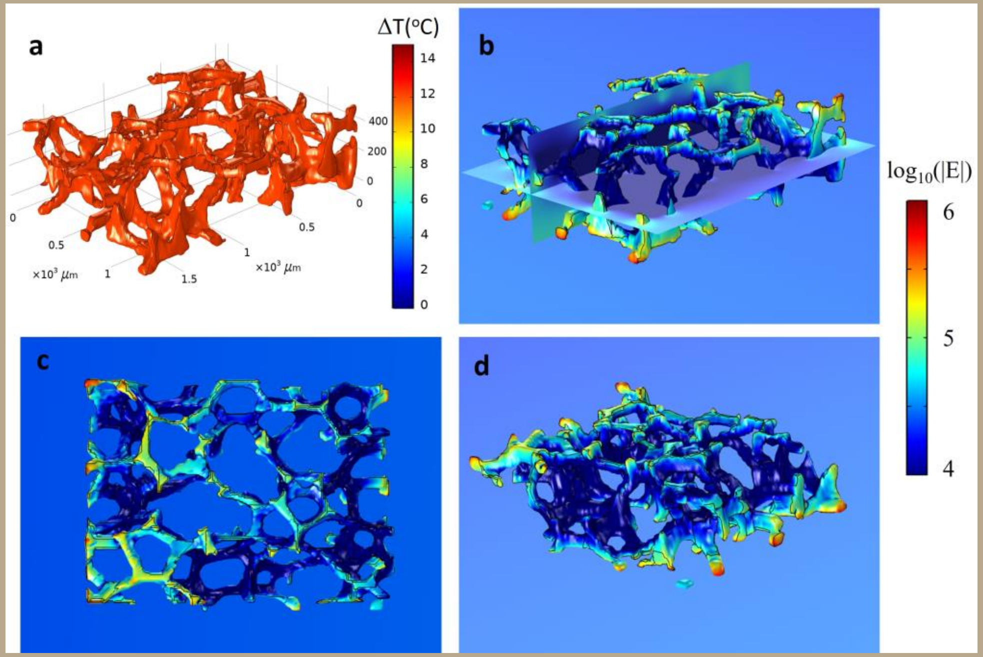


We used the RF module in the COMOSL. The input power of the port is set to 1,000 W, and the frequency is set to 2.45 GHz (**Fig. 1-12 b**). All the boundaries of the microwave is set to impedance boundary. The model includes the waveguide, steel container, glass plate and nickel foam. The rectangular power port (red arrow in Fig. 1-13a) is used to excite the microwave using a transverse electric (TE) boundary condition at 2.45 GHz.

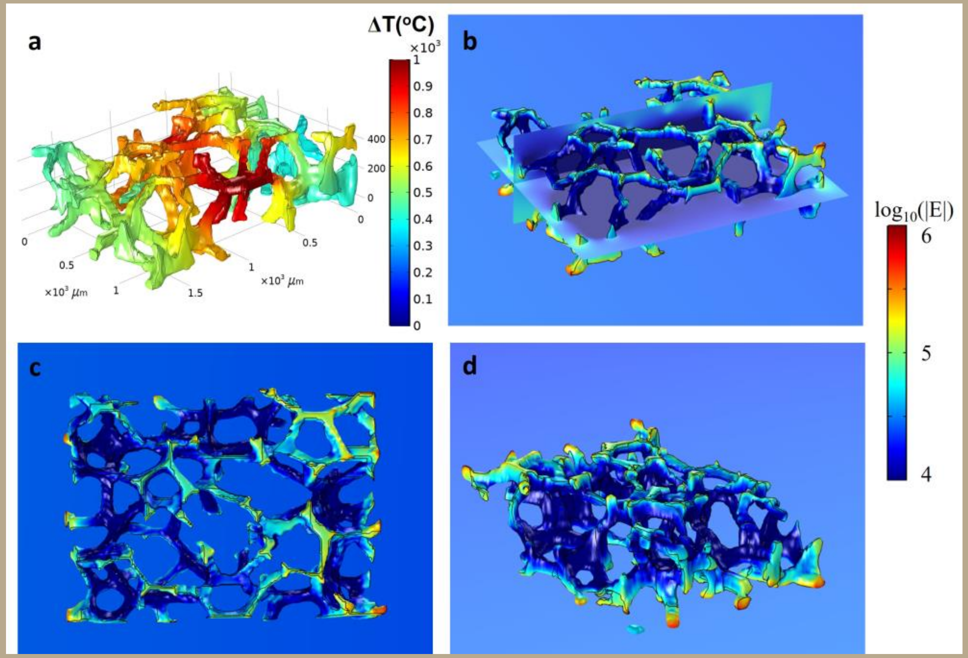
Property	Carbon black	Nickel	Unit
Relative permittivity	62-19j	1	1
Relative permeability	1	3	1
Electrical conductivity	1	2e5	S/cm
Thermal conductivity	0.35	200	W/(m·K)
Density	2000	8900	kg/m^3
Heat capacity	1262	350	J/(kg·K)

PROJECT STATUS: TASK 1

- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:



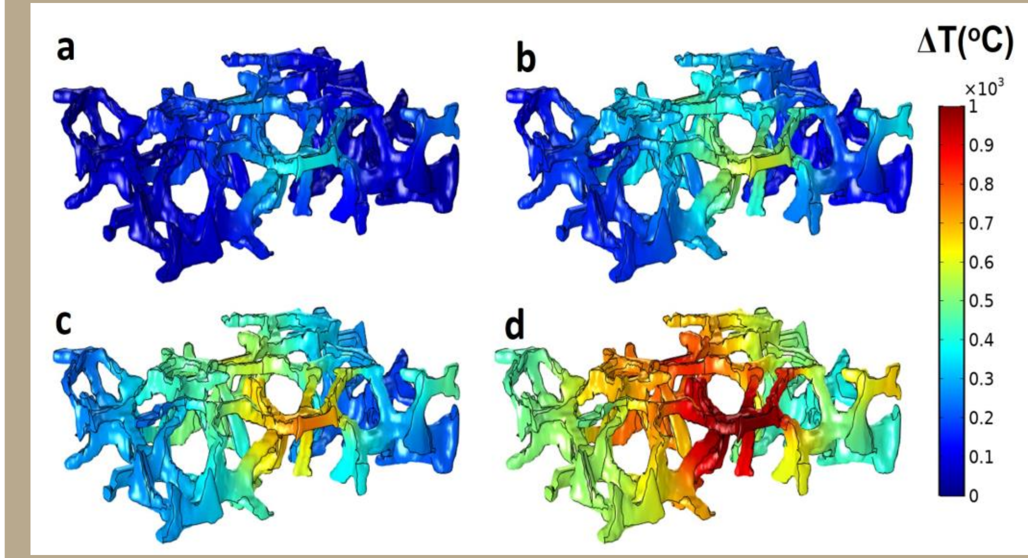
Electric field and temperature distribution on **Ni foam**. (a) Temperature distribution after 5 seconds of microwave heating. (b) The electric field distribution around the 3D Ni foam. (c-d) Electric field distribution at different angles.

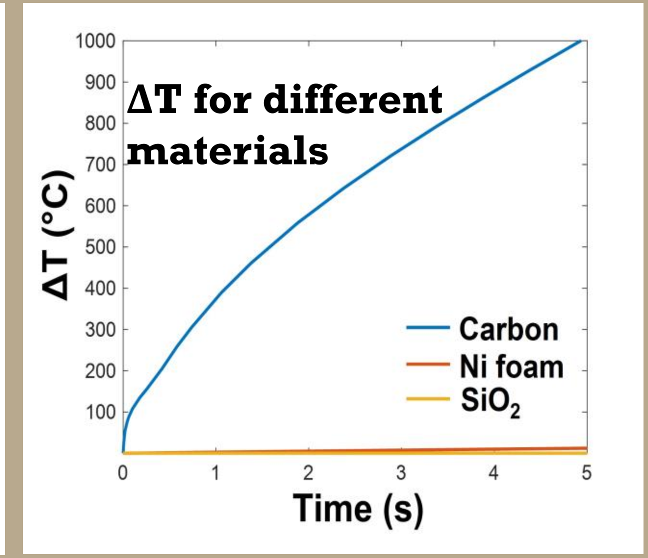


Electric field and temperature distribution on **carbon foam**. (a) Temperature distribution after 5 seconds of microwave heating. (b) The electric field distribution around the 3D Ni foam. (c-d) Electric field distribution at different angles.

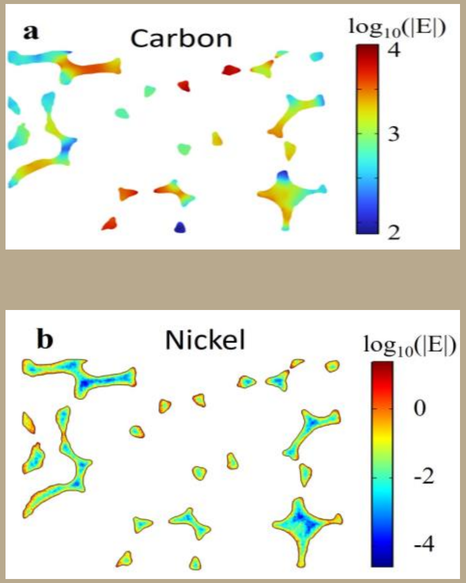
PROJECT STATUS: TASK 1

- Optical 3D Imaging to Obtain Morphology of Catalyst and Study the Localized Chemical Reactions:





Temperature distribution changes over time on carbon foam (a-d), and the heating time for a-d are 1 s, 2 s, 3 s, and 5 s, respectively. (e) Temperature vs time curve.



Electric field distribution across a cross section of the carbon (a) and Ni foam (b). E-field of carbon foam is much bigger than that of Ni foam. The penetration depth of E-field in carbon is much bigger than the Ni foam.

PROJECT STATUS: TASK 2

- Numerical Simulation of Multiscale Electromagnetic Problems:
  - Overall large size of the simulation domain: large system to solve;
  - Sub-wavelength geometrical structures cause numerical instability: numerical breakdown;
- An all-frequency stable formulation is proposed, implemented, and validated:
  - All four Maxwell's equations and the current continuity equation are formulated
  - Inhomogeneous Coulomb gauge is enforced.

$$\nabla \times \frac{1}{\mu} \nabla \times \boldsymbol{A} - \omega^2 \tilde{\epsilon} \boldsymbol{A} + \mathrm{j}\omega \tilde{\epsilon} \nabla \phi + \frac{\epsilon_\mathrm{r}}{\mu_0} \nabla \chi = \boldsymbol{J}_\mathrm{imp}$$

$$-\mathrm{j}\omega \nabla \cdot \tilde{\epsilon} \boldsymbol{A} - \nabla \cdot \tilde{\epsilon} \nabla \phi = \rho_\mathrm{imp}$$

$$-\frac{1}{\mu_0} \nabla \cdot \epsilon_\mathrm{r} \boldsymbol{A} + \chi = 0$$

where $\tilde{\epsilon} = \epsilon - \mathrm{j}\sigma/\omega$ denotes the complex permittivity and χ denotes an auxiliary variable introduced to enforce the inhomogeneous Coulomb gauge $\nabla \cdot \epsilon \boldsymbol{A} = 0$.

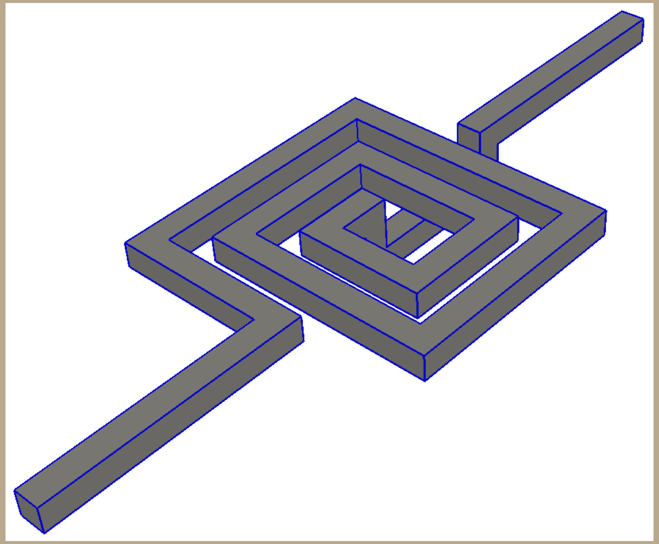
The electric field intensity $\boldsymbol{E}$ and the magnetic flux density $\boldsymbol{B}$ can be recovered as

$$\boldsymbol{E} = -\mathrm{j}\omega \boldsymbol{A} - \nabla \phi$$

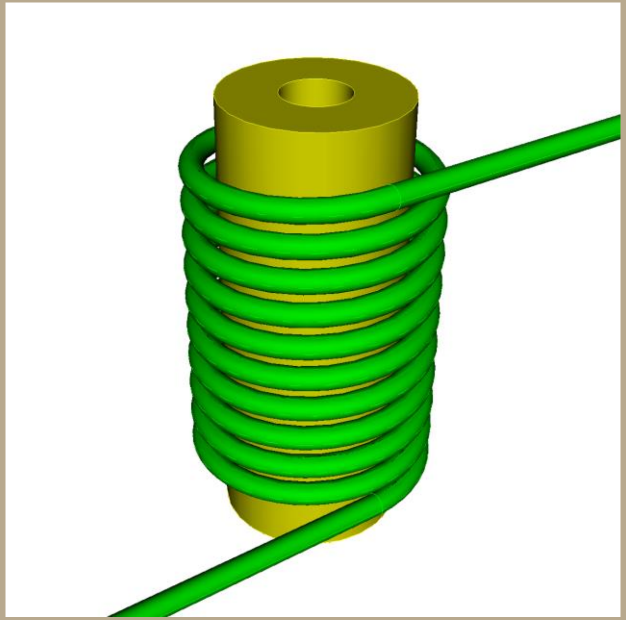
$$\boldsymbol{B} = \nabla \times \boldsymbol{A}$$

PROJECT STATUS: TASK 2

- Validation Examples:
  - Both devices are connected to a 1-V voltage source at different frequencies.
  - Copper conduction wire.
  - Aluminum heating core.



A spiral inductor



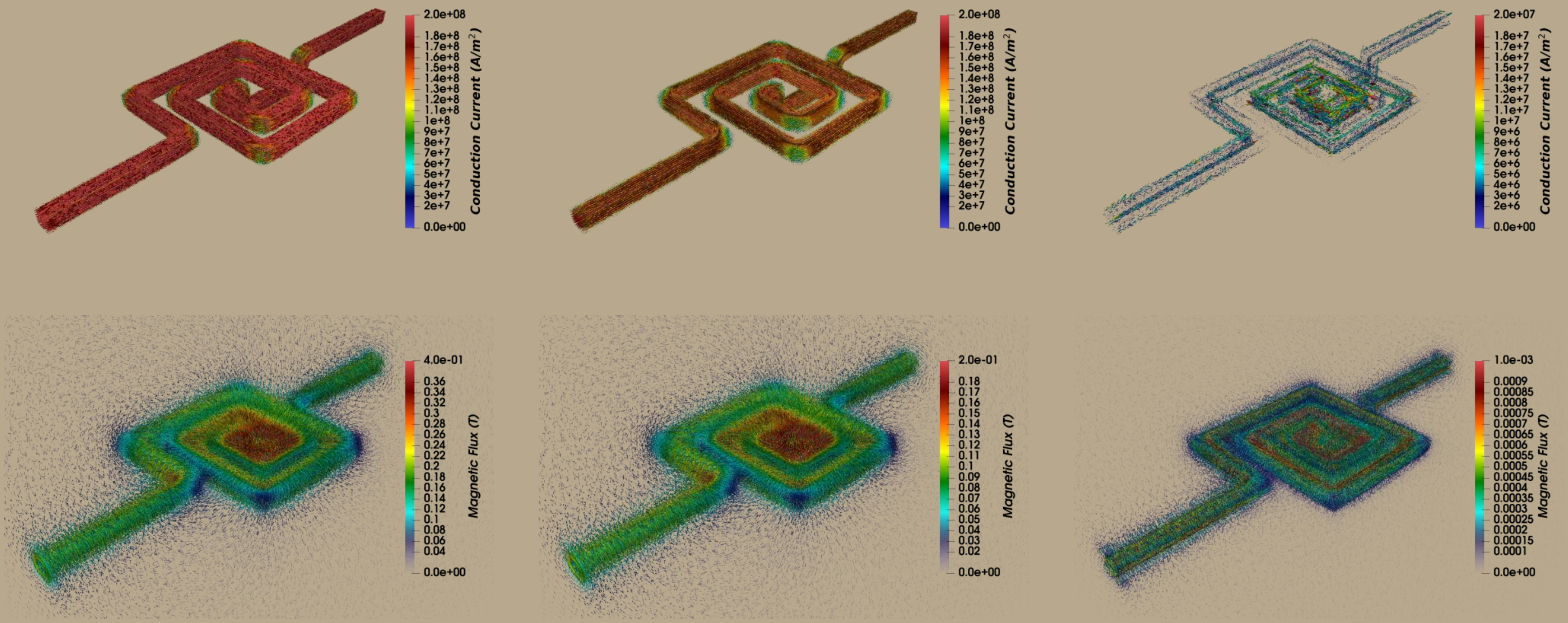
Induction heating

PROJECT STATUS: TASK 2

- A Spiral Inductor:

Current Density

Magnetic Flux



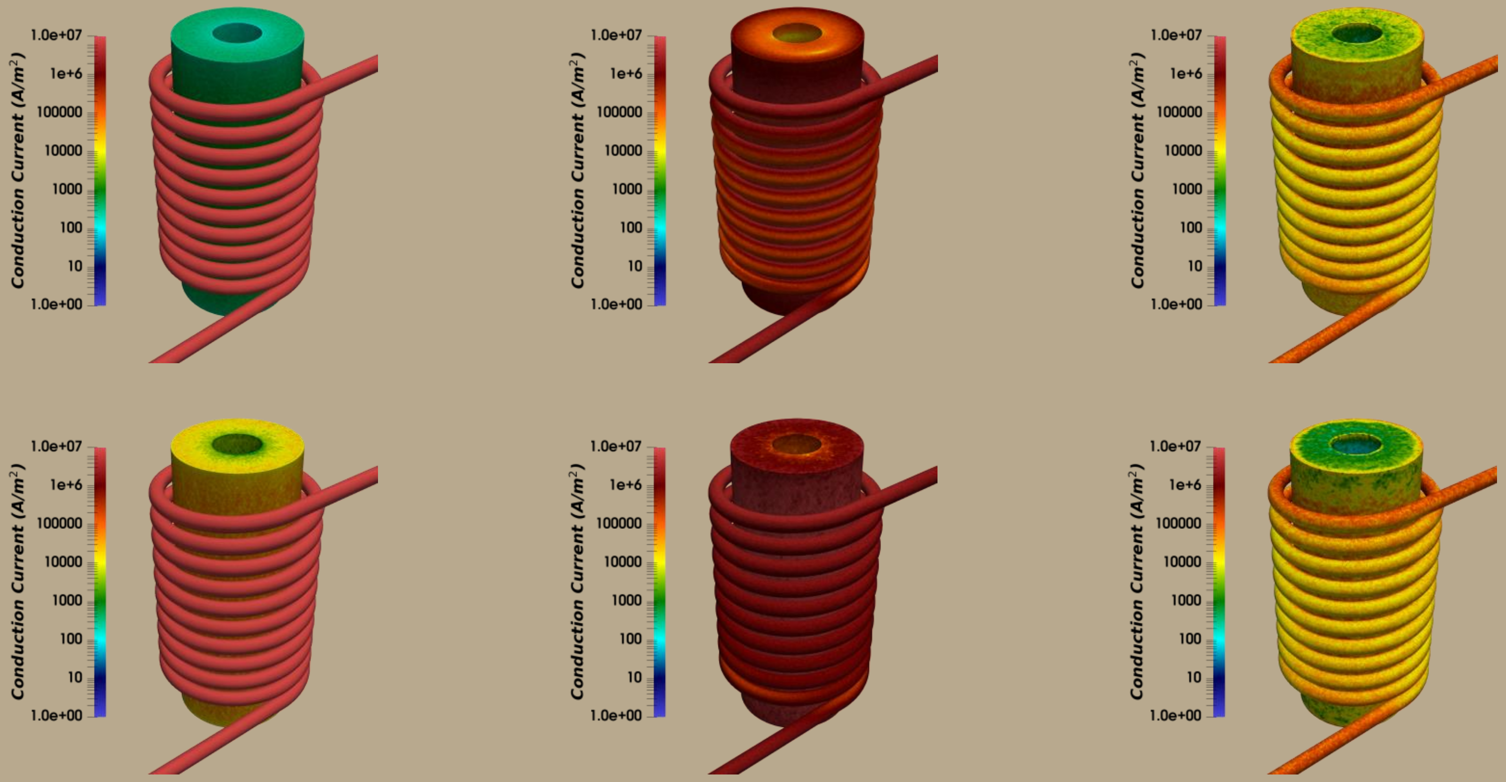
$f = 1$ Hz $\quad f = 1$ kHz $\quad f = 100$ kHz

PROJECT STATUS: TASK 2

- Induction Heating:

$\mu_r = 1$

$\mu_r = 1000$



$f = 1$ Hz

$f = 1$ kHz

$f = 100$ kHz

PROJECT STATUS: TASK 2

- Numerical Simulation of Heat Transfer Problems:
  - Equilibrium and transient simulations.
  - Linear and nonlinear materials.
- Heat transfer equation with convective flow:

$$\rho C_P \frac{\partial T}{\partial t} + \rho C_P \boldsymbol{u} \cdot \nabla T = \nabla \cdot (\kappa \nabla T) + q$$

where ρ is the density of the materials, C_P is the specific heat, κ is the thermal conductivity, $\boldsymbol{u}$ is the fluid velocity, and q is the volumetric heat generation. The corresponding boundary conditions associated with the transient thermal analysis includes the Dirichlet boundary condition

$$T = T_d$$

and the air convection boundary

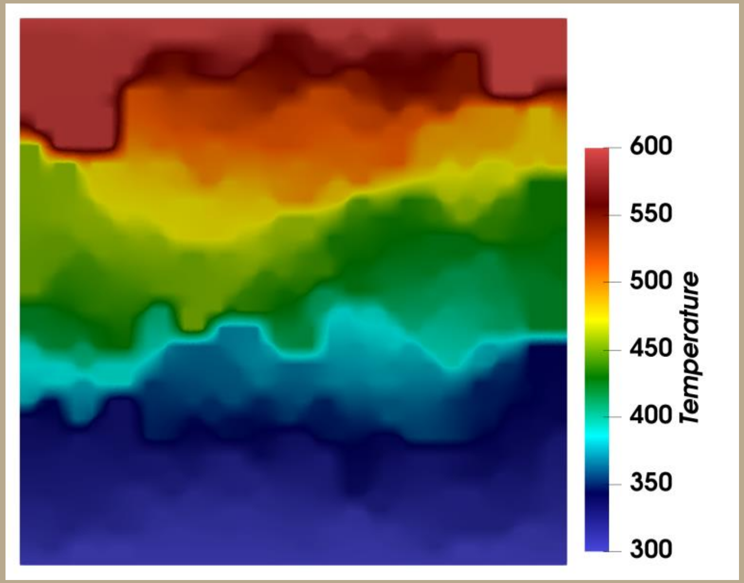
$$\hat{n} \cdot \kappa \nabla T = -h(T - T_a)$$

where h and T_a are the convective heat transfer coefficient and the ambient temperature, respectively.

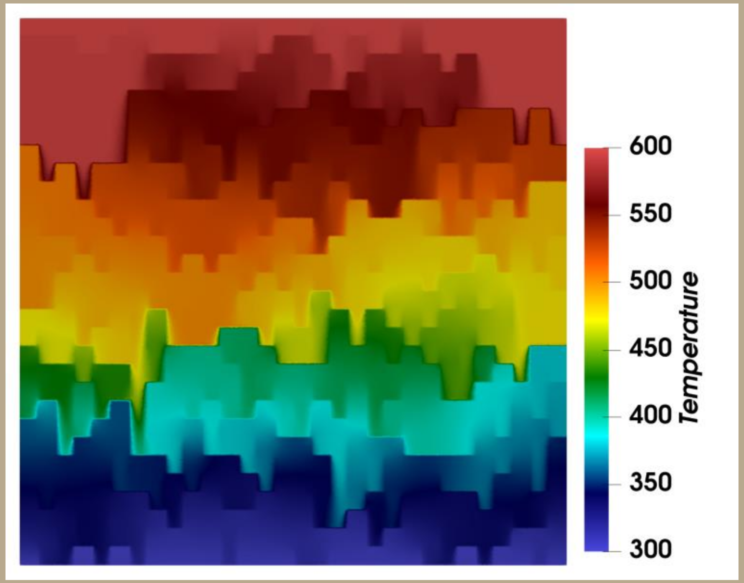
PROJECT STATUS: TASK 2

- Validation Example:
  - Heat transfer in a random checkerboard structure.
  - Dirichlet boundary conditions applied on the top and bottom boundaries.

Geometry of a 30-by-30 random checkerboard



Temperature profile with conductive heat transfer



Temperature profile with conductive and convective heat transfer

PROJECT STATUS: TASK 2

- Numerical Simulation of Multiphysics-Multiscale Electromagnetic-Thermal Problems:
  - All-frequency stable formulation coupled with heat transfer equation.
- Multiphysics Coupling:
  - Electromagnetic power dissipation is converted to heat.
  - The volumetric heat source includes dielectric loss and conduction (Ohmic) loss:

$$q = (\omega\epsilon'' + \sigma)\|\boldsymbol{E}\|^2$$

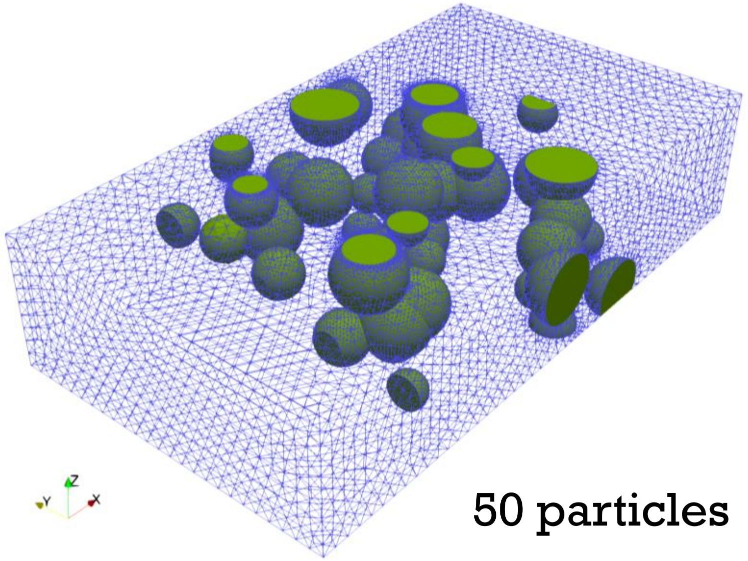
- Multiscale Coupling:
  - EM simulation: frequency domain
  - Thermal simulation: steady state or time domain

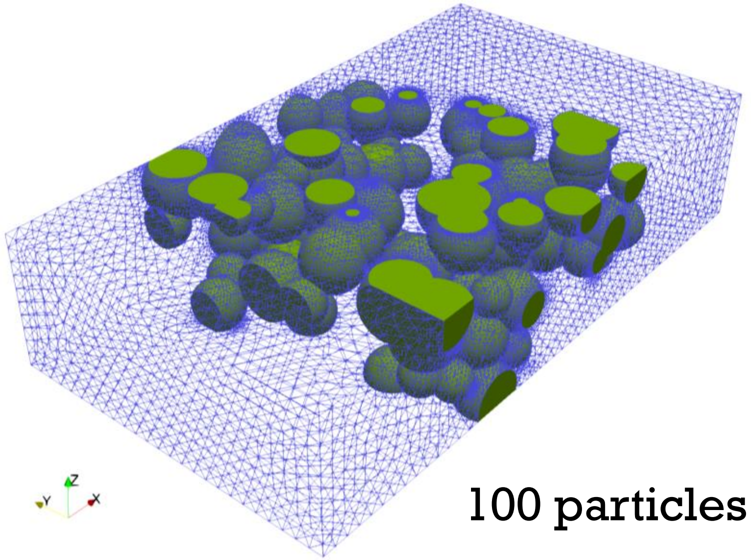
PROJECT STATUS: TASK 2

- Microwave induced thermal effect

Porous material:

- Total size: 1800 um by 1000 um by 400 um
- Particle sizes: 50 to 100 um in radii
- Carbon and nickel particles considered
- Operating frequency: 2.45 GHz
- Microwave intensity: 10 kV/m
- Ambient temperature: 300 K
- Convective cooling at near and far ends
- Thermal insulation at other four walls



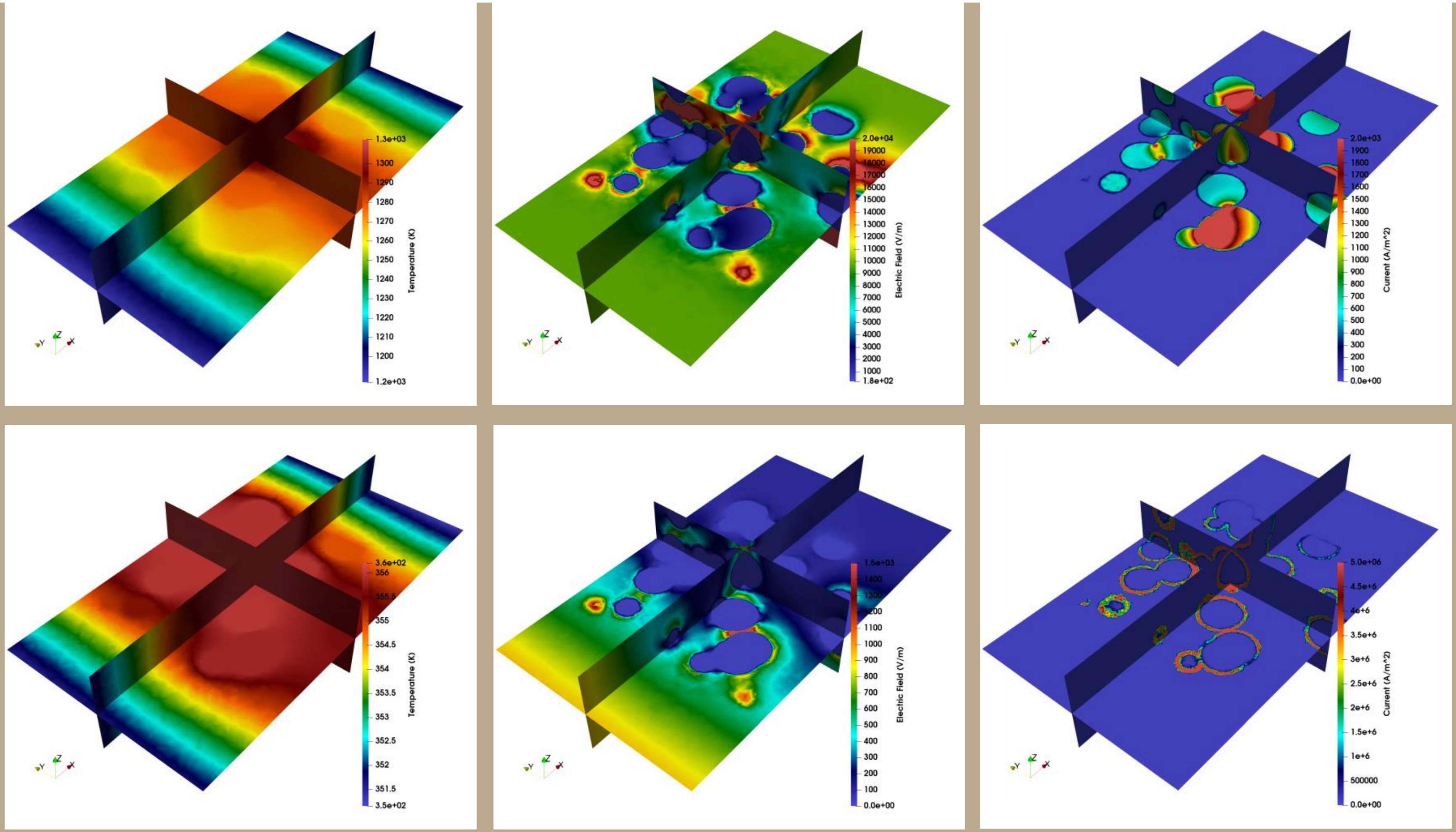


PROJECT STATUS: TASK 2

- 50 Particles

Carbon
(max: 1,300 K)

Nickel
(max: 360 K)



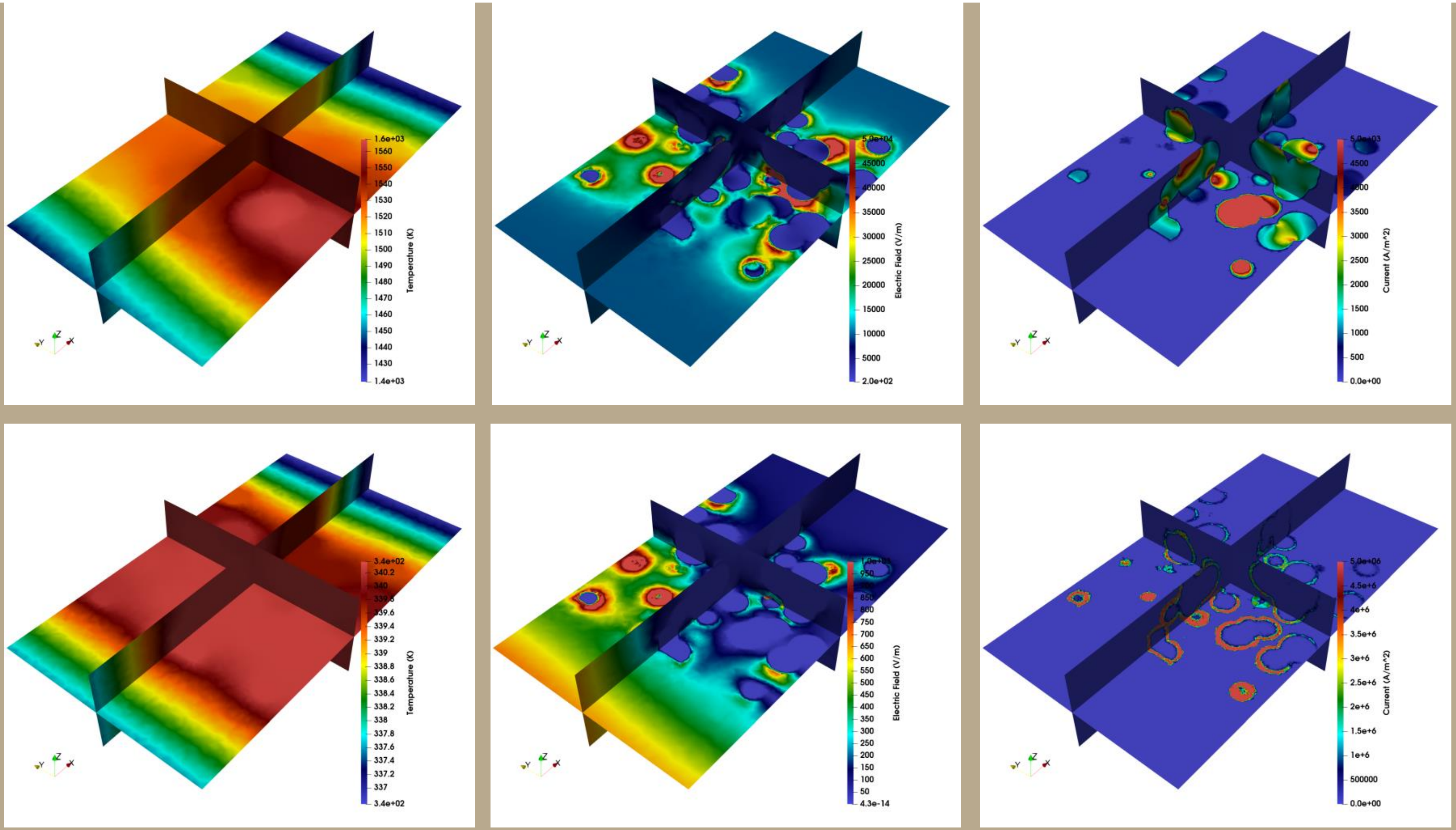
Temperature | Electric Field | Conduction Current

PROJECT STATUS: TASK 2

- 100 Particles

Carbon
(max: 1,600 K)

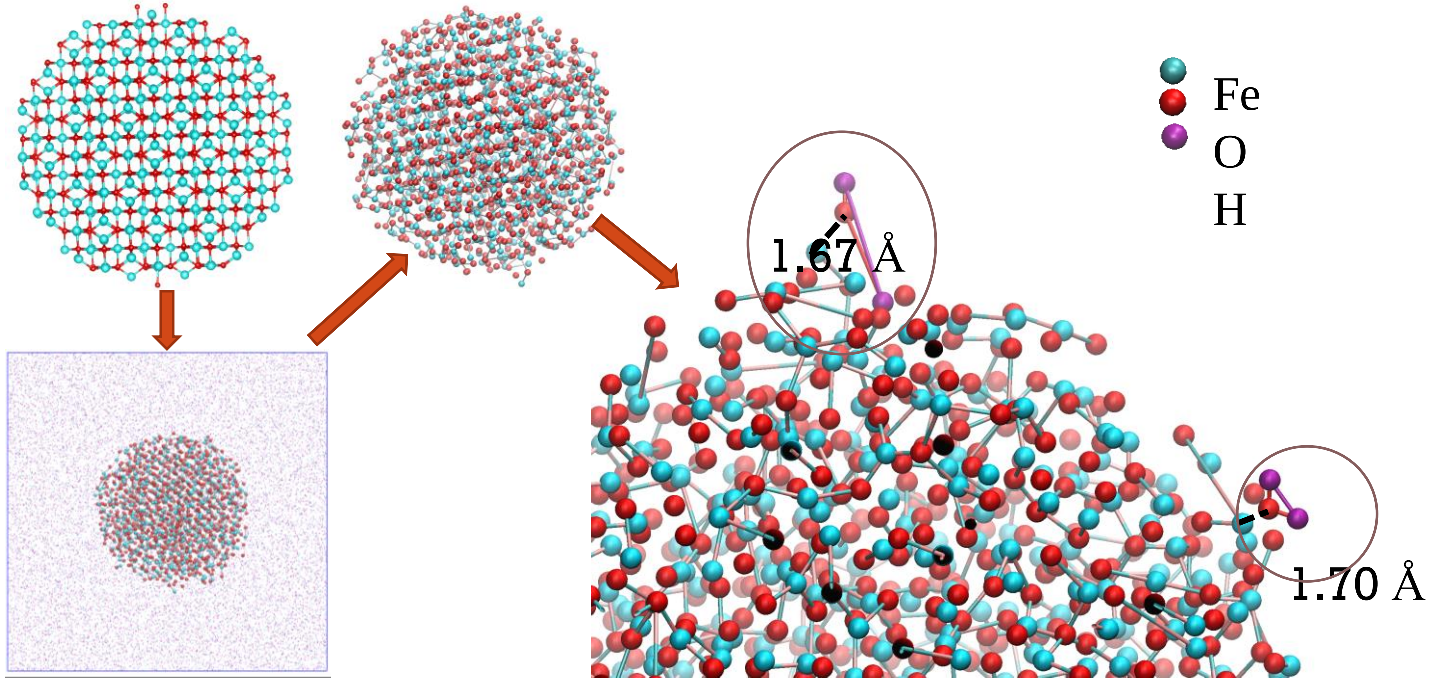
Nickel
(max: 340 K)



Temperature | Electric Field | Conduction Current

PROJECT STATUS: TASK 3

Benchmark of Reactive force field (ReaxFF) molecular dynamics simulation:
γ-Fe_2O_3 (3.2 nm) + 7702 water (800 K)



A demo system about hydrothermal corrosion of a gamma-iron oxide nanoparticle, which was cut directly from the crystal lattice of iron oxide. After solvating the nanoparticle in water at 800 K, the exposed iron atoms are oxidized by neighboring water molecules. At the high temperature, the outer layer of the particle surface become amorphous.

- This will be used to estimate the reaction kinetic parameters of nanoparticles in the project.

STUDENT TRAINING

- **Education and Training:**

Howard:

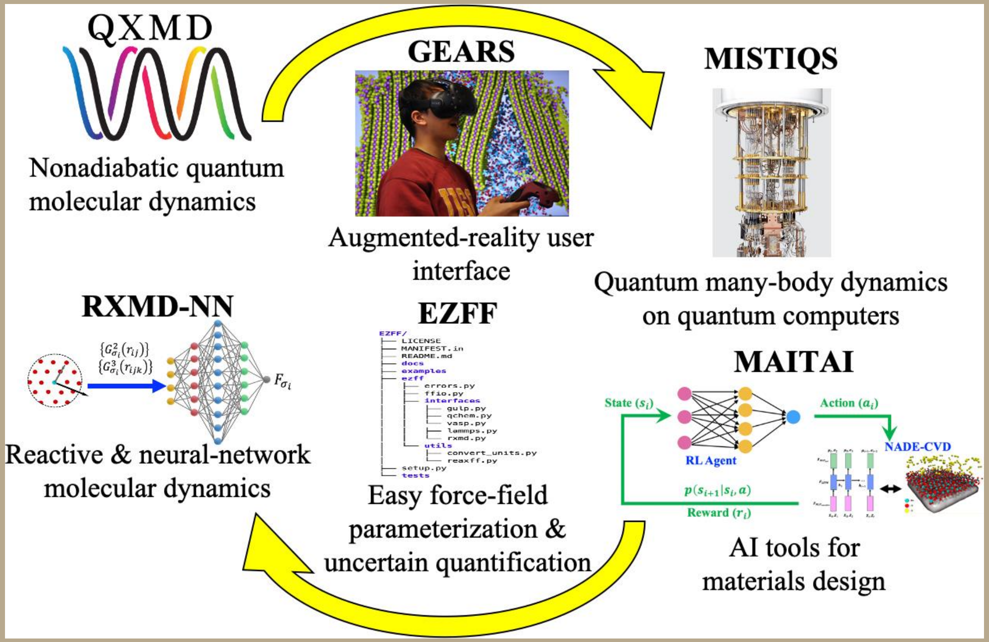
- One Ph.D. student
- Three undergraduate research assistants

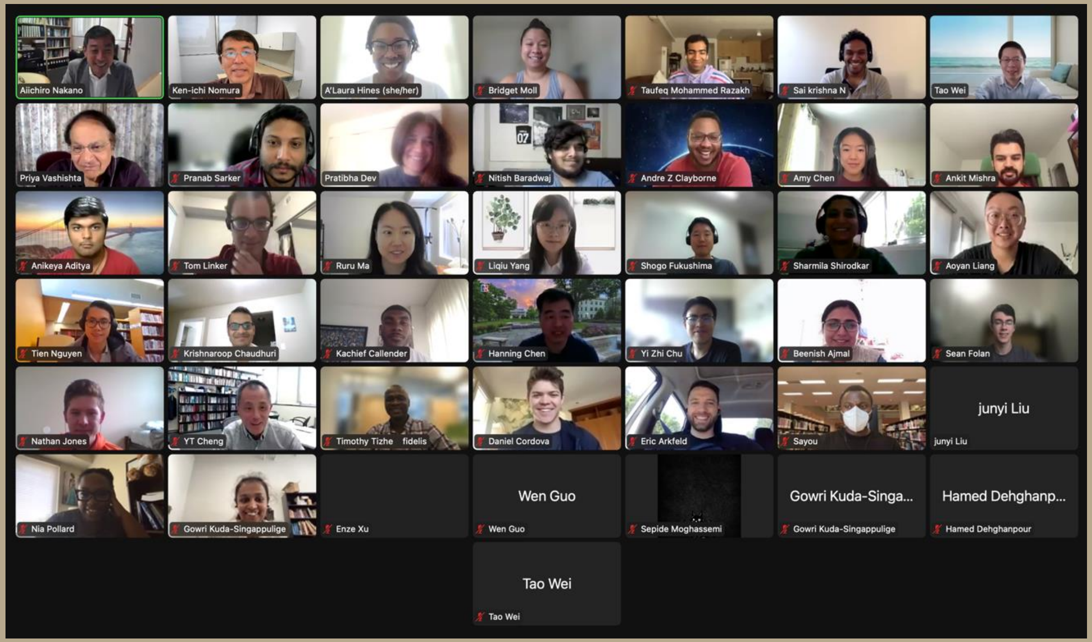
Houston:

- One Ph.D. student
- One high-school student

STUDENT TRAINING

- **Workshop:**
  - **Goal: Train a new generation of materials cyber workforce at the nexus of exascale computing, quantum computing & AI**





CyberMAGICS - Cyber Training on Materials Genome Innovation for Computational Software (2021-2025)
A. Nakano, K. Nomura, P. Vashishta (University of Southern California) and P. Dev, T. Wei (Howard University)

PROJECT OUTCOMES

- **Publication:**

1. Shi, Y. *et al.* Electrochemical Impedance Imaging on Conductive Surfaces. *Anal. Chem.* **93**, 12320-12328 (2021), published, acknowledgement of federal support: yes.
2. Feng, G. *et al.* Probe the Localized Electrochemical Environment Effects and Electrode Reaction Dynamics for Metal Batteries using In Situ 3D Microscopy. *Adv. Energy Mater.*, 2103484 (2021), published, acknowledgement of federal support: yes.
3. Yan, S. A Continuous-Discontinuous Galerkin Method for Electromagnetic Simulations Based on an All-Frequency Stable Formulation, *Progress In Electromagnetics Research M* **106**, 153-165 (2021), published, acknowledgement of federal support: yes.
4. Xu Yang, Jonathan Koonce, Ying-Chau Liu, Guangxia Feng, Yaping Shi, Xiaoliang Li, Mubeen Syed, Xiaonan Shan. Reflection Optical Imaging to Study Oxygen Evolution Reactions, Journal of the Electrochemical Society, 2022, 169, 057507, published, acknowledgement of federal support: yes.
5. Su Yan and A. O. Idubor, “Parameter identification for symmetrical Prandtl-Ishlinskii hysteresis model using Gauss-Newton method,” in Proc. IEEE Antennas Propag. Symp., Portland, OR, USA, July 2023, accepted, acknowledgement of federal support: yes.
6. M. Mekonnen and Su Yan, “Comparative investigation of iterative solutions of the all- frequency stable formulation and its vector-potential-only variation,” in Proc. IEEE Antennas Propag. Symp., Portland, OR, USA, July 2023. accepted, acknowledgement of federal support: yes.
7. M. Mekonnen and Su Yan, “An efficient solution of low-frequency magnetic problems with volt- age sources using all-frequency stable formulation,” in 2023 IEEE MTT-S International Conference on Numerical Electromagnetic and Multiphysics Modeling and Optimization, Winnipeg, Canada, June 2023. accepted, acknowledgement of federal support: yes.

NEXT STEPS

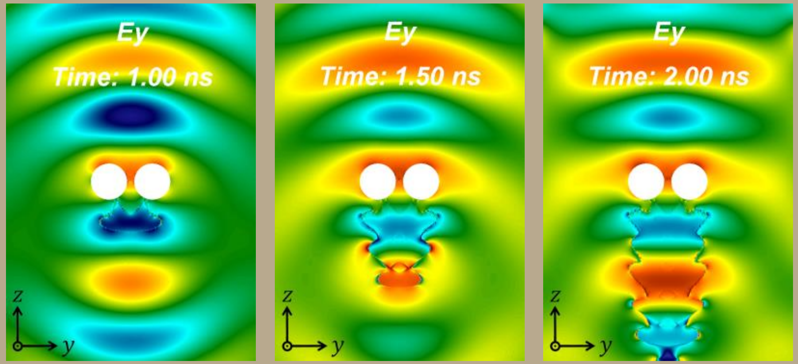
- Perform multiphysics EM—plasma co-simulation to investigate the generation of micro-plasma and its effect on the hydrogen generation reaction.
- Develop coupled physical-chemical simulation methods.
- System design and optimization.

NEXT STEPS

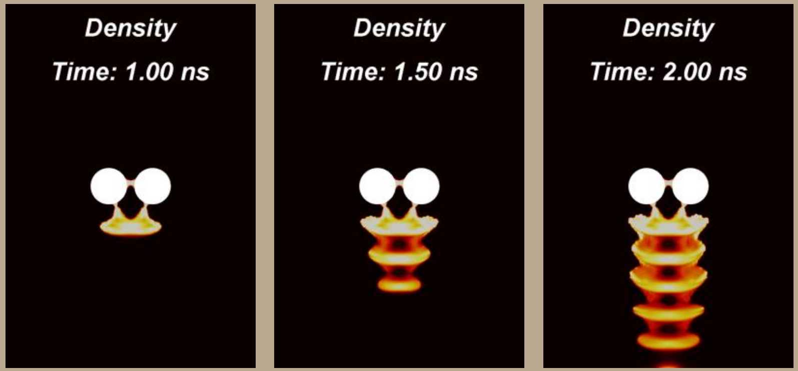
- Multiphysical EM—Plasma Co-Simulation:

Air breakdown and plasma filamentary array generation during high-power microwave operation

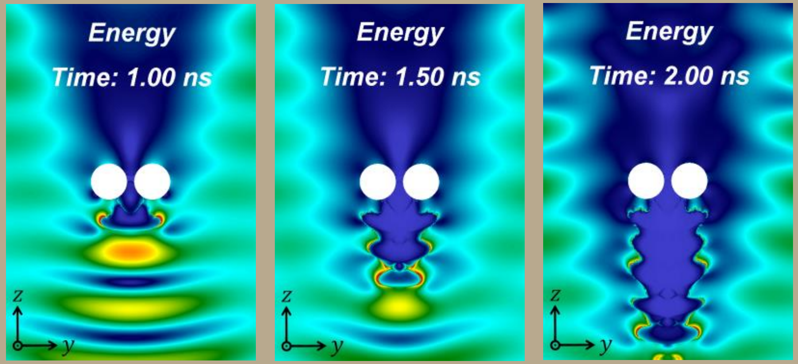
Electric Field



Plasma Density



Plasma Energy



Yan, et al., IEEE JMMCT, 2019, 4, 76

Thank You!
All Questions Are Welcome!

Multiphysics and Multiscale Simulation Methods for Electromagnetic Energy Assisted Fossil Fuel to Hydrogen Conversion

Su Yan [1], Tao Wei [1], Jiefu Chen [2], and Xiaonan Shan [2]

[1] Howard University, Washington, DC 20059; su.yan@howard.edu, tao.wei@howard.edu

[2] University of Houston, Houston, TX 77204; jchen82@central.uh.edu, xshan@central.uh.edu