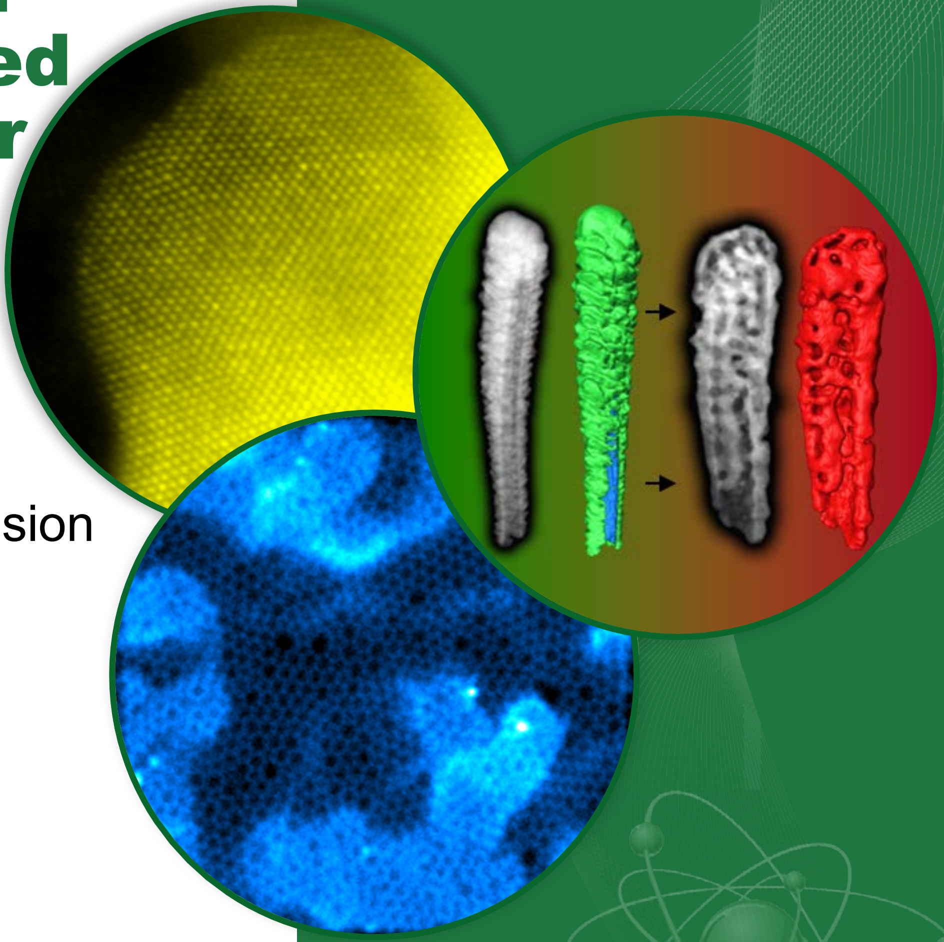
Magnetic Annealing of Pt-alloy Nanostructured Thin Film Catalysts for Enhanced Activity



Project ID: FC121

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2015 DOE Hydrogen and Fuel Cells Program Review

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Overview

Timeline

Project Start: 10/1/2014

Project End: 9/30/2015

Barriers

Durability

Cost

Performance

Budget

Total DOE Funding: $300k

ORNL: $210k

NREL: $90k

Partners/Collaborators

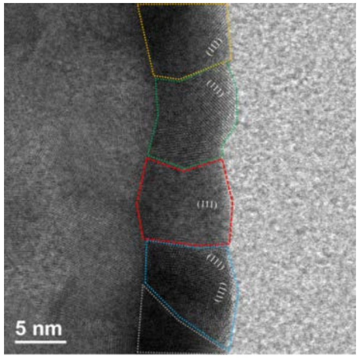
ORNL: Orlando Rios, Craig Bridges, Harry Meyer III, Khorgolkhuu Odbadrakh

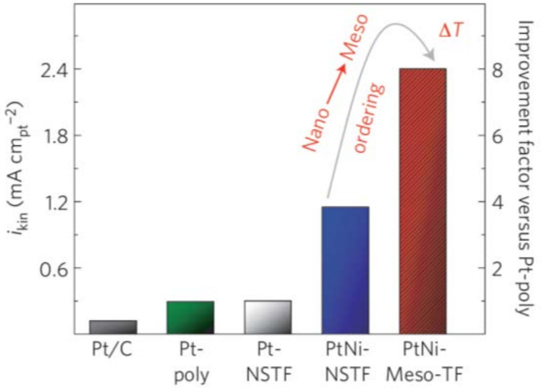
NREL: Shyam Kocha, Jason Zack

3M Company: Andy Steinbach, Dennis van der Vliet

Objective-Relevance

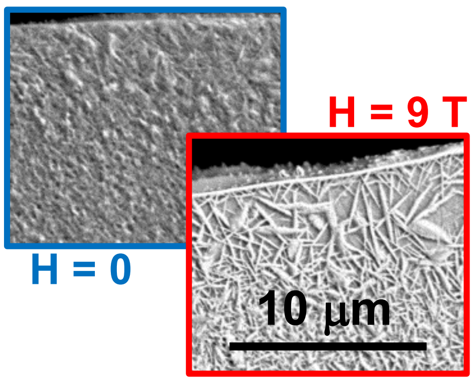
- Explore the potential of high magnetic field annealing to produce highly active surface structures in Pt-alloy oxygen reduction reaction (ORR) catalysts
  - Grain alignment
  - Modification of surface composition
  - Formation of new crystal structures
- Pt_3Ni_7 NSTF as a test structure
  - Ferromagnetic
  - Thin-film like structure
  - High specific activity
  - Further activity gains observed by transformation from nano- to meso-structure



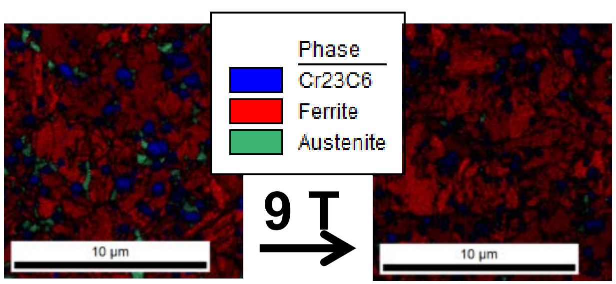


D.F. van der Vliet et al., Nat. Mater. 2012, 11, 1051.

Background: Magnetic Annealing



Crystallizing ferromagnetic alloy in a magnetic field changes grain morphology (SEM).



Processing steel in a 9 Tesla magnetic field minimizes retained austenite.

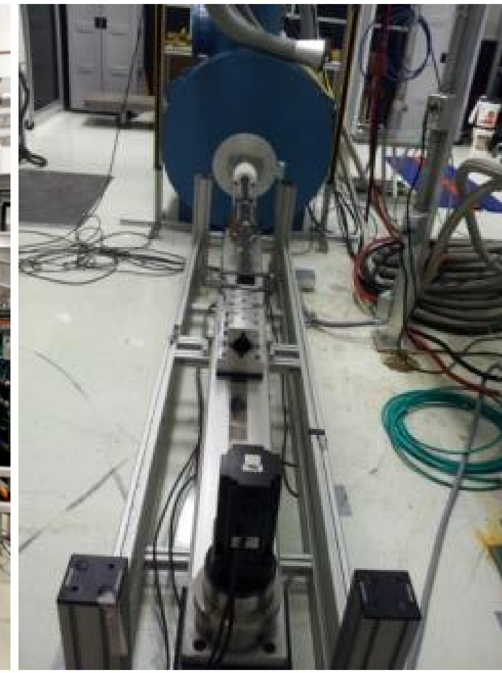
- High Field Magnetic Processing
  - 9T fields produced by superconducting magnets
  - Enables quenching, crystallization, annealing, sintering, compacting, extruding, sonicating at high temperature and field.
- Potential Impacts
  - Particle/grain alignment
  - Facilitate phase transformations
  - More homogeneous microstructures
  - Create new structures/compositions

Background: ORNL Houses World-Class R&D Magnetic Processing Facility

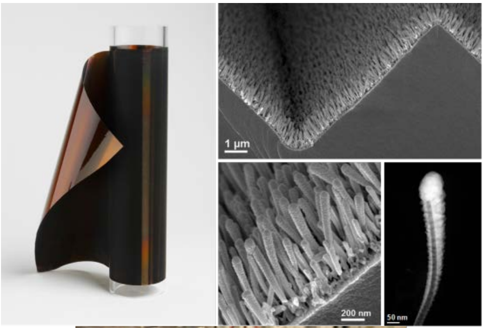
- 5” and 8” diameter bore magnets
- Vertical and horizontal geometries
- 9-inch long uniform field zone
- 0 to 9T magnetic field capability
- Operating temperatures 0°C - 2200°C
- Technology is centered around scalability and energy efficiency

World’s 1st Commercial–Scale Superconducting, High Field Magnet

Continuous-Feed High & ThermoMagnetic Processing



Approach - High Magnetic Field Annealing



Materials Synthesis

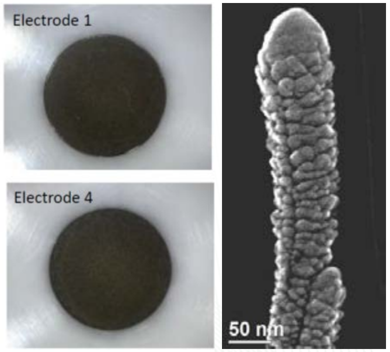
- As-grown Pt_3Ni_7 provided by 3M
- In-house sputtered layers of varying compositions

Annealing in high magnetic field

- Performed on NSTF growth substrate
- Different temperatures and gas environments (H_2, Ar, etc.)

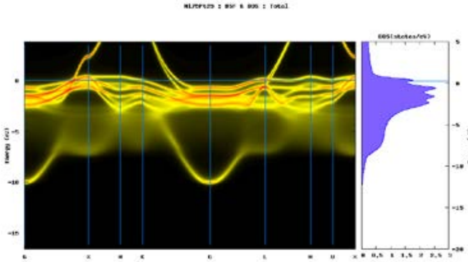
Characterization

- Rotating Disk Electrode (RDE)
- X-ray Photoelectron Spectroscopy (XPS)
- X-ray Diffraction (XRD)
- Transmission Electron Microscopy (TEM)



DFT Modeling

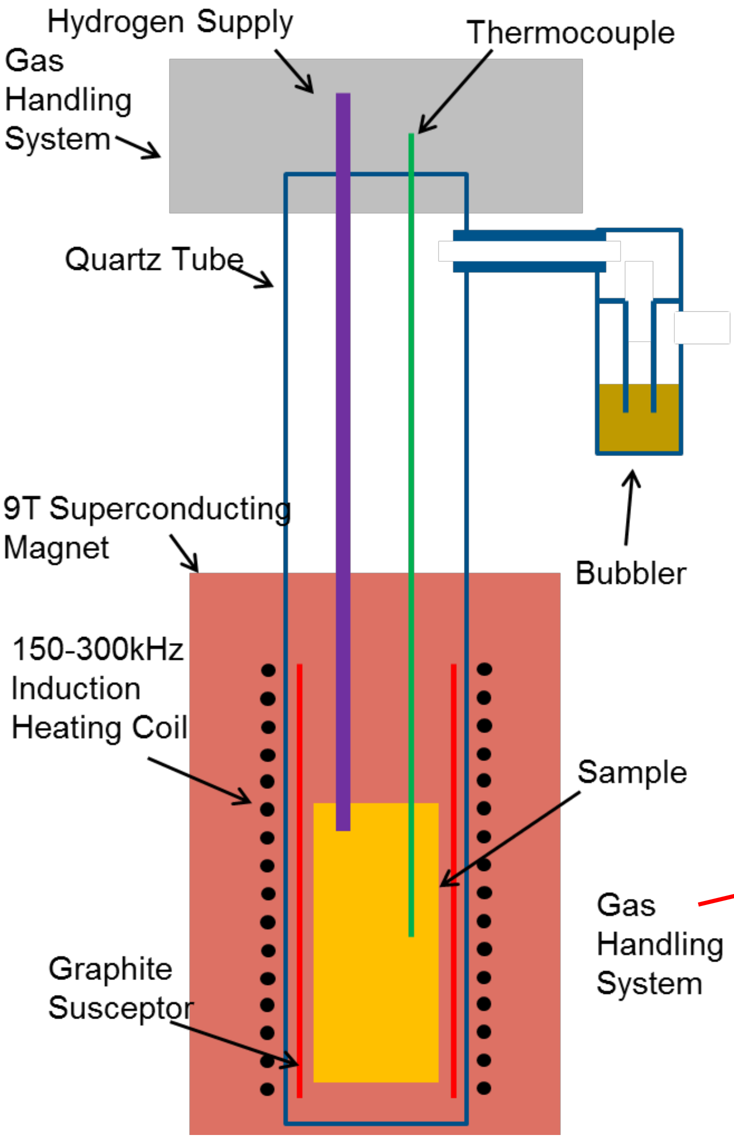
- Multiple Scattering Theory



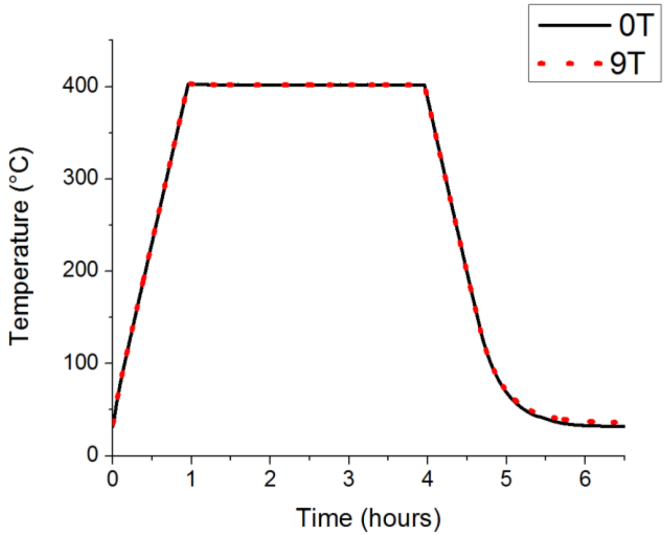
Approach- Milestones

Task #	Project Milestones	Type	Task Completion	
1	Demonstrate magnetic annealing on Pt3Ni7 NSTF-supported catalyst	Quarterly Progress Measure (Regular)	12/31/14	Completed
2	RDE testing demonstrating impact of magnetic annealing on mass/specific activity	Quarterly Progress Measure (Regular)	3/31/15	Completed
3	DFT modeling/microstructural characterization identifying modified morphologies responsible for activity changes	Quarterly Progress Measure (Regular)	6/30/15	Started.
4	Delivery of best-of-class catalyst via magnetic annealing with 1.5 times the mass activity of baseline.	Annual Milestone (Stretch)	9/30/15	Started

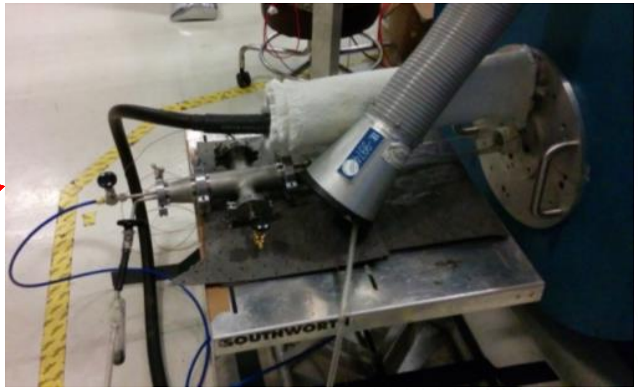
Accomplishment 1: Magnetic Annealing NSTF Roll-good under 100% H_2



Typical heating curve

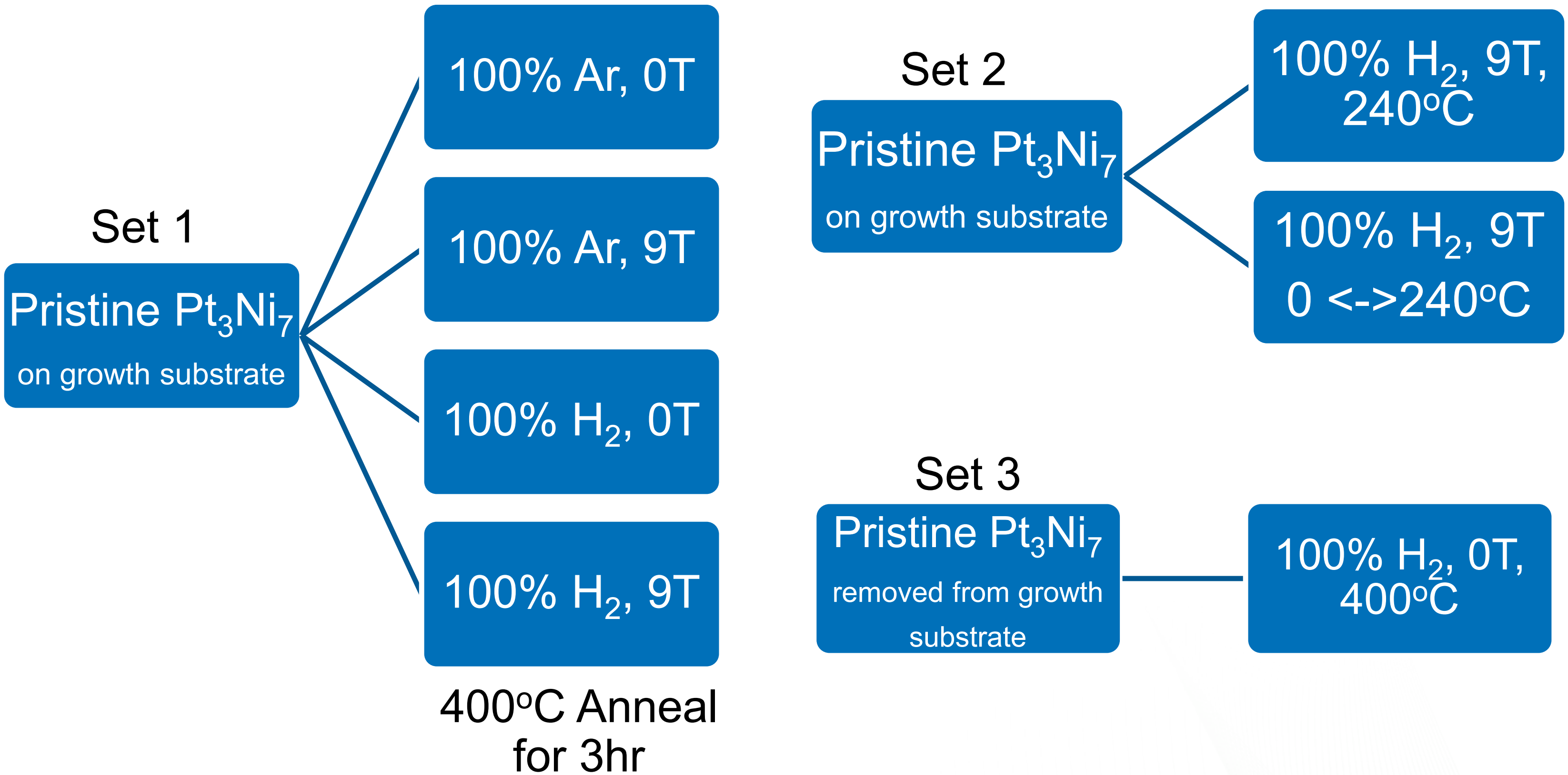


Gas Handling System



Kapton® roll-good stable under Ar and H_2 at 400°C

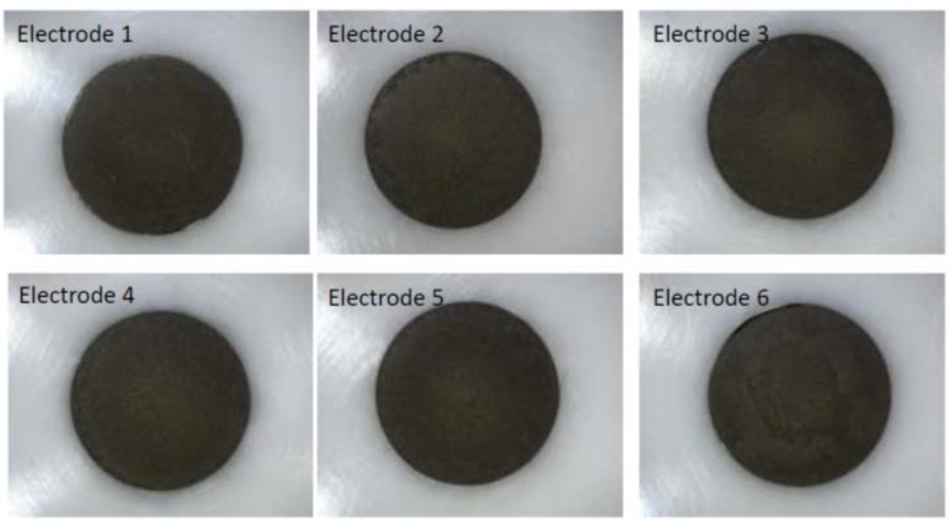
Magnetic Annealing Experiments

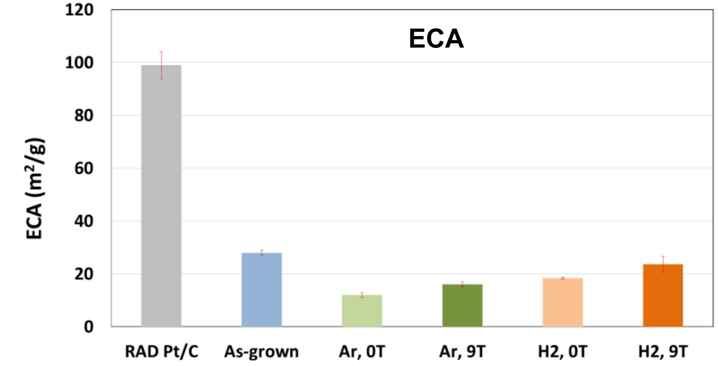


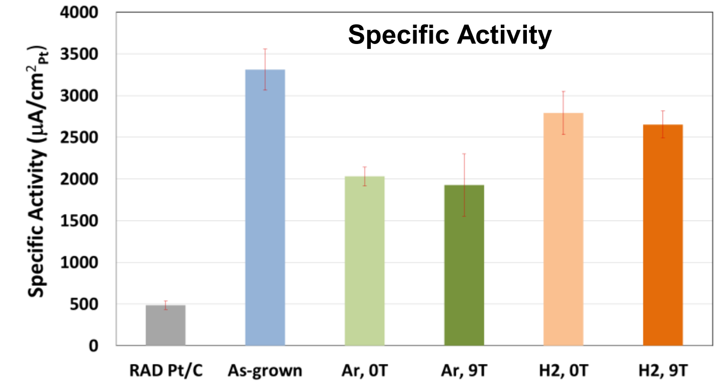
- 3 sample sets produced thus far
- RDE performed on Set 1 and Set 3

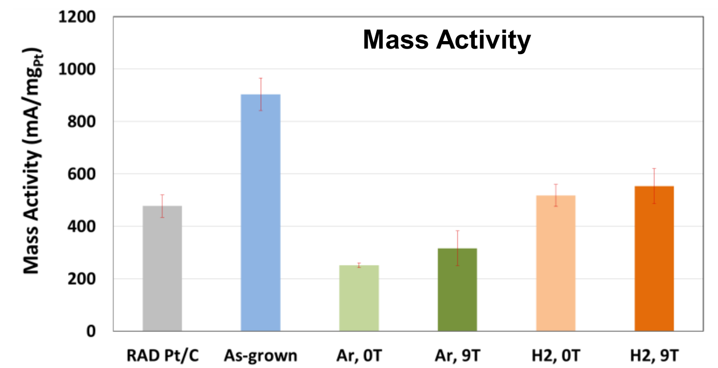
Accomplishment 2: RDE Evaluation

- Standardized RDE Protocol
  - Electrolyte: 0.1 M $HClO_4$
  - Cell Temperature: Room Temp.
  - Break-in: 0.025 – 1.2 V, 0.5 V/s, 100 cycles, N_2
  - CV: 0.025 – 1.0 V, 0.02 V/s, 3 cycles, N_2
  - IV: –0.01 → 1.0 V, 0.02 V/s, 1600 rpm, O_2









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Accomplishment 2: RDE Evaluation

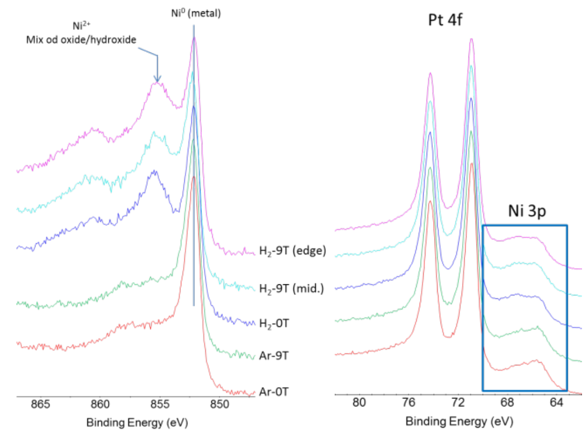
Sample ID	Gas	Process Temp (C°)	Magnet (T)	SA ($\mu A/cm^2_{Pt}$)	MA (mA/mg_{Pt})	ECA (m^2/g_{Pt})
As-Grown	n/a	n/a	n/a	3310	904	28
Ar, 0T	Ar	400	0	2029	251	12
Ar, 9T	Ar	400	9	1927	316	16
H_2, 0T	H_2	400	0	2791	517	18
H2, 9T	H_2	400	9	2653	553	24
Annealed Powder	H_2	400	n/a	1540	186	12
As-Grown Repeat	n/a	n/a	n/a	2774	804	29

- H_2 annealing provides superior activity to annealing in Ar
- Annealing in both Ar and H_2 leads to lower ECA and specific activity than as-grown material
  - Opposite trend of results published in literature on annealing NSTF in H_2
    - D.F. van der Vliet et al., Nat. Mater. 2012, 11, 1051.
- Magnetic field yields higher ECA, lower specific activity
- Extended annealing of powder sample yields even lower activities

Accomplishment 3: XRD and XPS

Surface Composition (at.%)

	Pt	Ni	O	C	Cr	N	Ni/Pt
As Received	9.3	27.8	42.5	20.5	0.0	0.0	3.00
Ar_0T	10.5	12.8	10.0	63.7	0.2	2.8	1.22
Ar_9T	9.0	10.4	10.7	66.9	0.3	2.7	1.15
H2_0T	10.2	21.7	25.0	43.0	0.2	0.0	2.13
H2_9T_mid	10.4	21.5	21.8	45.8	0.5	tr	2.07
H2_9T_edge	11.7	27.5	25.0	35.8	0.0	0.0	2.34



- XPS shows C surface contamination after annealing (perylene-red sublimation)
- Difference in Ni/Pt between Ar and H_2
- Grain size: As-grown-> Ar -> H_2
- Magnetic field yields smaller grains with slightly larger lattice parameter

Sample	Latt. par. (Å)	Grain size (nm)
Pt (lit.)	3.9231	
As-grown Pt_3Ni_7	3.6977	3.8
Ar 9T	3.6894	4.9
Ar 0T	3.6841	5.6
H_2 9T	3.6779	5.9
H_2 0T	3.6736	6.8

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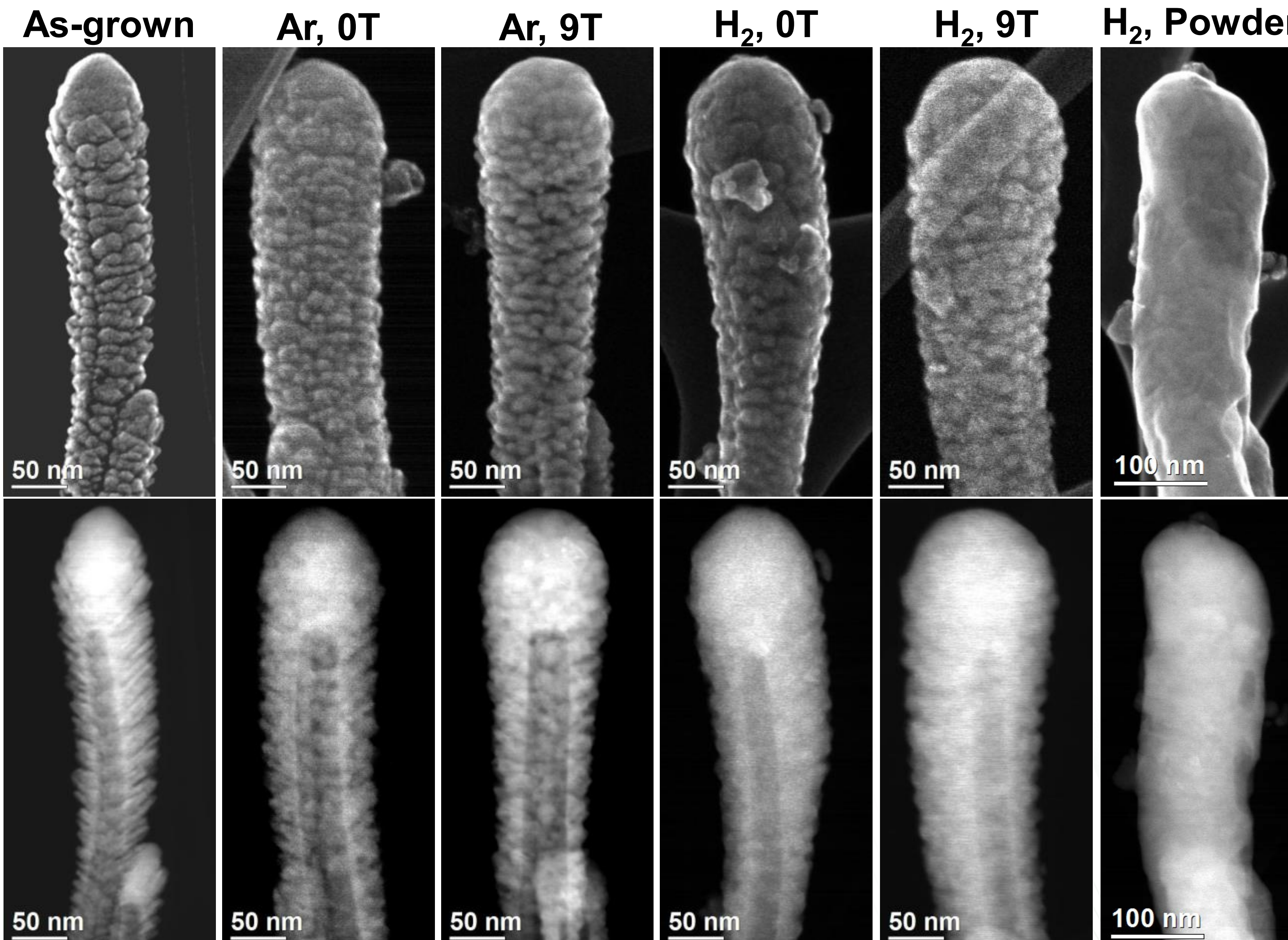
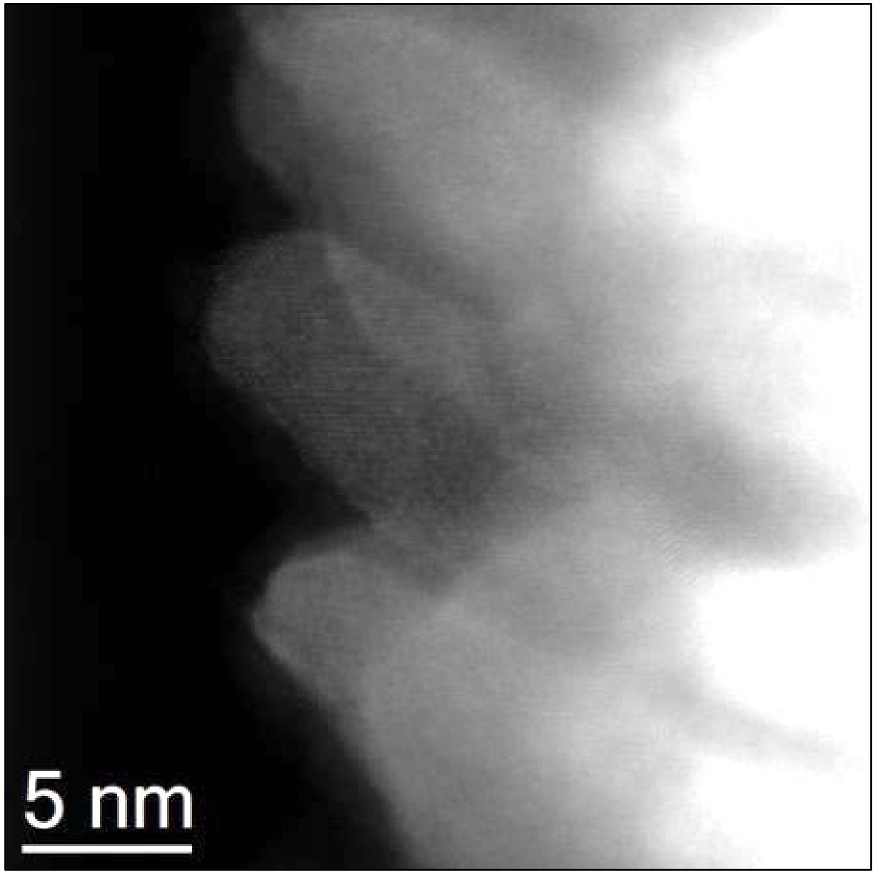
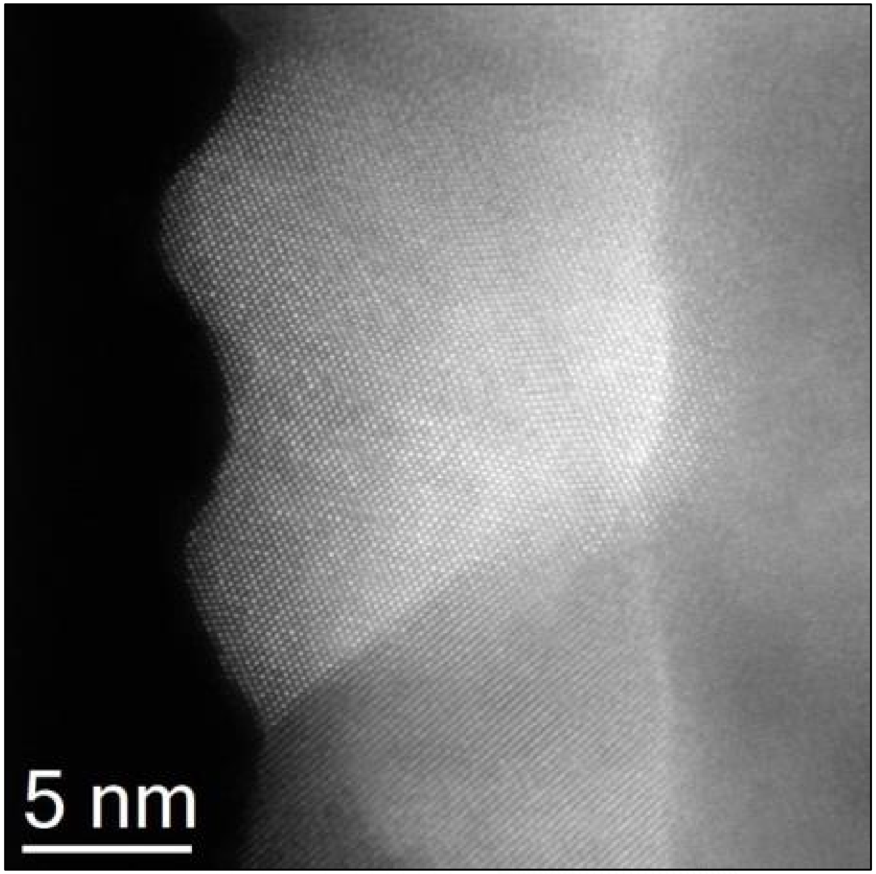
Accomplishment 4: STEM Analysis



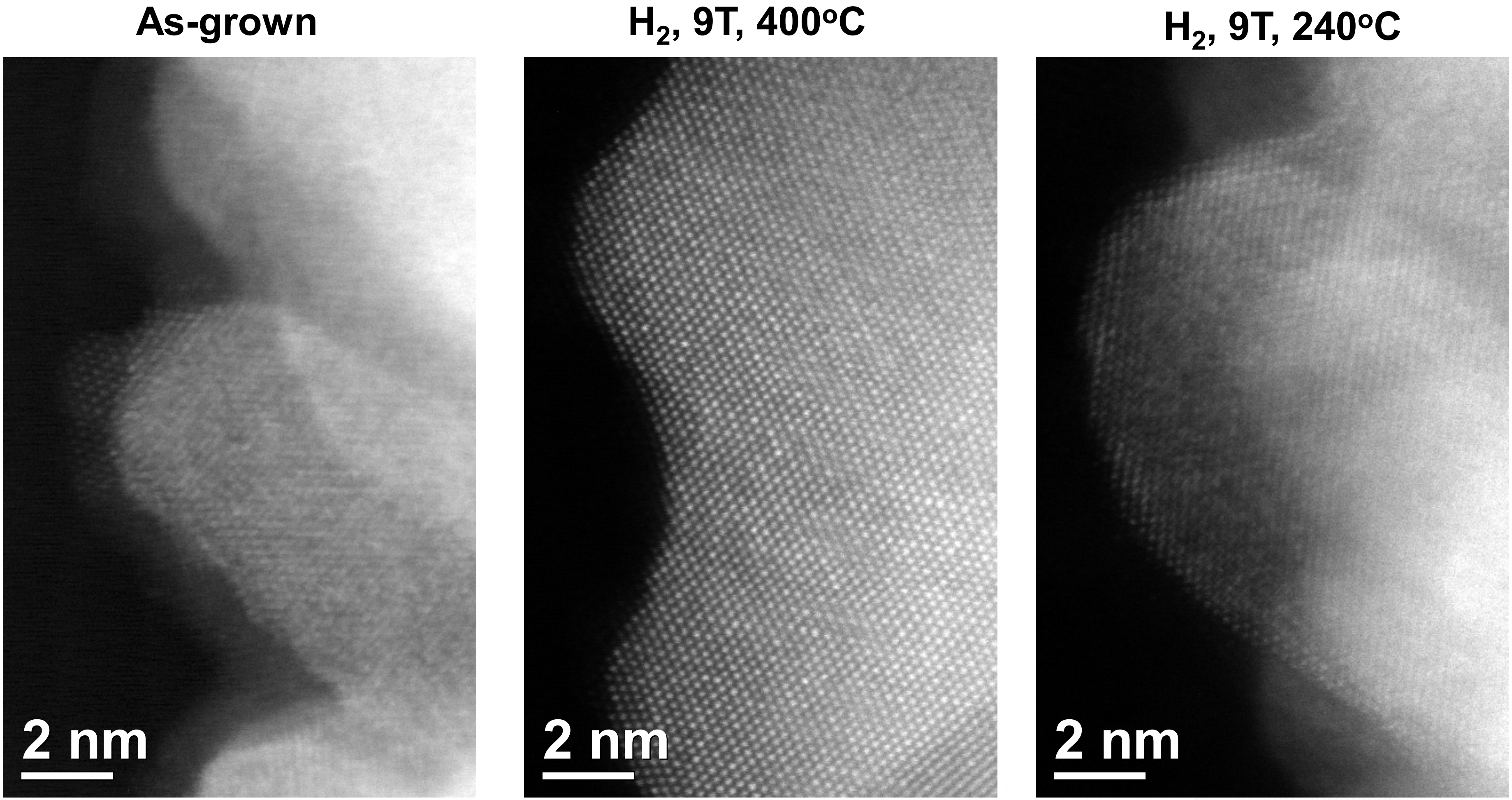
Accomplishment 4: STEM Analysis





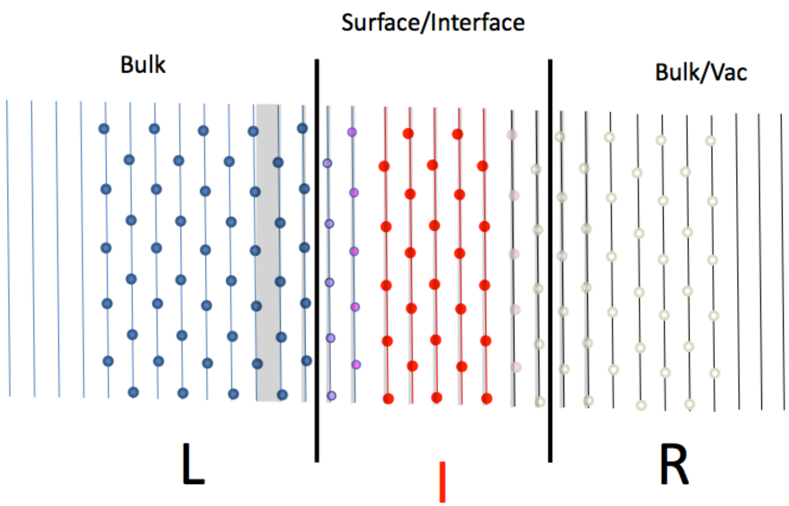
- Increase in grain size with annealing confirmed in STEM
- No modification to surface structure/composition observed following magnetic annealing

Accomplishment 4: STEM Analysis



- Modification to surface structure/composition observed at 240^{o}C, but not at 400^{o}C

Accomplishment 5: SKKR-DFT Modeling

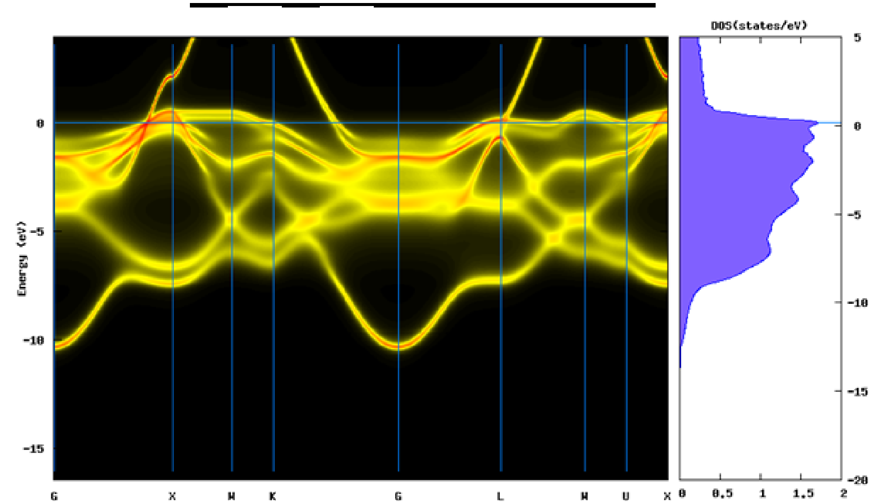


- Screened Korringa-Kohn-Rostoker (SKKR) method better represents disordered systems
  - Coherent potential Approximation(CPA)
  - All Electron Method
  - Fully Relativistic - anisotropy
  - Spin-orbit coupling

Outputs From First Principles Modeling

- Magnetic and electronic structures at ground state
- d-band shift
- Work function with respect to surface composition
- Energetics with respect to composition variations
- Stability with respect to surface/bulk composition
- Magnetic Phase Diagram
- Surface monolayer magnetism
- Magneto-crystalline anisotropy near the surface

$Pt_{0.75}Ni_{0.25}$: BSF and DOS



Collaborations

- National Renewal Energy Laboratory (NREL)
  - Shyam Kocha (co-PI)
    - Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique (FC111)
  - Jason Zack
    - RDE testing

- 3M Company
  - Andy Steinbach
    - Supplier of Pt_3Ni_7 NSTF materials, helpful discussions on project findings and suggestions for future directions
  - Dennis van der Vliet
    - Guidance on H_2 annealing protocols, catalyst removal from growth substrate, and RDE testing of NSTF

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Remaining Challenges and Future Work

- Improve magnetic response of NSTF material
  - Modify heating curves (time, max. temperature, etc.)
  - Generate new catalyst compositions ($Pt_{1-x}Ni_x$, $Pt_{1-x}Co_x$)
  - Measure magnetic properties via SQUID
- Characterize post-RDE catalysts
  - Break-in cycles modify composition/structure
  - XRD, XPS, and TEM characterization to be performed after RDE tests
- Durability tests
  - Observe effect of treatments on changes in mass activity, specific activity, and ECA over catalyst lifetime
- Input from Modeling Efforts
  - SKKR-DFT calculations to provide guidance on ideal catalyst compositions and surface structures
- Generate best-of-class catalyst with RDE-determined mass activity exceeding 1.3 A/mg_{Pt}

Summary

- Relevance:
  - Improve performance of alloy cathode catalysts through high field magnetic annealing
- Approach:
  - Study impact of magnetic annealing on Pt_3Ni_7 NSTF model structures, with characterization by RDE, XPS, XRD, and STEM
- Accomplishments:
  - Demonstrated magnetic annealing of Pt_3Ni_7 NSTF in a 9T field at 400^{o}C in Ar and H_2
  - Measured specific activity, electrochemical surface area, and mass activity by RDE
  - Characterized changes in grain size and surface composition using XPS, XRD, and STEM
  - Implemented SKKR method for advanced DFT calculations of disordered alloy catalysts
- Collaborations
  - Worked closely with NREL (RDE testing) and 3M (materials supplier, project guidance)
- Future Work
  - Modify catalyst compositions and annealing protocols to generate new high-performance structures.

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