V.F.15 Magnetic Annealing of Pt-Alloy Nanostructured Thin Film Catalysts for Enhanced Activity

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Project End Date: October 1, 2015

Overall Objectives

- Explore the potential of high magnetic field annealing to produce highly active surface structures in Pt-alloy oxygen reduction reaction (ORR) catalysts
- Link activity improvements of Pt_3Ni_7 nanostrucutured thin films (NSTF) alloy films measured by rotating disk electrode (RDE) with structural changes measured by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy
- Calculate energetics, geometry and electronic structure from first principles to correlate surface structure with surface reactivity

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

This project is conducting fundamental studies into the effects of magnetic annealing. The technical target is based on RDE-determined mass activity using an as-grown Pt_3Ni_7/NSTF baseline.

- Delivery of best-of-class catalyst via magnetic annealing with 1.5 times the mass activity of baseline

FY 2015 Accomplishments

- Demonstrated magnetic annealing of Pt_3Ni_7/NSTF in a 9 T field at 400°C in Ar and H_2
- Measured specific activity, electrochemical surface area, and mass activity by RDE of both annealed and baseline materials
- Characterized changes in grain size, surface composition, and morphology using XPS, XRD, and scanning transmission electron microscopy (STEM)
- Implemented screened Korringa-Kohn-Rostoker (SKKR) method for advanced density functional theory (DFT) calculations of disordered alloy catalysts

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INTRODUCTION

Replacing a portion of the costly ORR catalyst with transition metals, such as Co or Ni, has not only reduced the overall cost of the electrodes, but has enhanced the initial specific activity through dealloying to form highly active Pt-skin, -shell or -skeleton surface structures. Further, catalyst pretreatments, including dealloying and annealing, can further improve catalyst performance.

In this effort, we explore the effects of high magnetic field annealing as an alternative and innovative approach for tailoring the properties of low precious group metal (PGM) alloy catalysts. This project utilizes unique 9 T magnets in the Advanced Manufacturing Facility at ORNL. Magnetic annealing has been demonstrated in aligning grain growth, modifying surface structures, and even creating new, unexplored structures. This effort explores such possibilities for low PGM alloy cathode catalysts. This work will focus primarily on Pt-transition metal alloys, with an emphasis on 3M's Pt3Ni7/NSTF.

APPROACH

This innovative approach aims to exploit the magnetic properties of these alloys through high magnetic field annealing to modify catalyst surface structures, compositions, and properties under conditions which are both scalable and commercially viable. 3M's Pt_3Ni_7/NSTF has been selected as the primary test structure for these experiments, due to its film-like attributes and high magnetic Ni content. Magnetic annealing (9 T) is performed on thin film samples to establish optimal conditions arising from variables such as field strength, field direction, annealing temperature, annealing time, and environment (H_2 and air).

RDE measurements are used as a screening tool for electrochemical catalyst characterization, and are performed at NREL. These measurements are then compared with structural characterization at ORNL using XRD, XPS, and STEM. As structure-property relationships are unveiled, the data is input into DFT calculations which will identify the source of the activity enhancement and provide guidance for further catalyst design.

RESULTS

The horizontal and vertical magnetics used in this project are shown in Figure 1. A new heating sleeve was designed and fabricated for the horizontal magnetic which allowed for larger sample sizes needed to produce sufficient quantities of material for RDE measurements. The Pt_3Ni_7/NSTF was annealed on the growth substrate in rolled sections of roughly 12 in x 5 in. Following annealing, the NSTF was removed from the substrate and sent as a powder to NREL for RDE analysis. Seven samples were processed and sent to NREL for electrochemical evaluation: two as-grown samples, four specimens annealed at 400°C in Ar or H_2 with and without the magnetic field, and a special sample annealed as a powder at 400°C without the magnet.

As shown in Figure 2a, RDE results show a decline in both specific activity and surface area following annealing both with and without field. Magnetically annealed specimens had a modestly higher mass activity then the field-free annealed specimens. To understand the possible influence of the perylene-red support, which sublimes at these elevated temperatures, Pt_3Ni_7/NSTF was removed from the growth substrate and annealed as a powder. The powder sample showed even lower specific and mass activities. Figures 2b and 2c show the XRD and XPS analysis of the annealed catalysts. XRD showed grain size growth following annealing, with the H_2 annealing leading to a larger grain size. The effect of the magnetic field appears to be a slowing of grain growth, although further experimentation is needed to confirm this result. An increase in C was observed by XPS, indicating perylene-red sublimation with redeposition of C on the NSTF surfaces. More importantly, changes in composition of the surfaces was observed, which would have subsequent effect on the dealloying of the material during RDE, as described later in the report. Consistent with literature reports, annealing led to Pt-rich surfaces. The magnetic field had only a modest effect, showing slightly greater Pt enrichment of the surfaces.

Samples which had been submitted to RDE testing were returned to ORNL for STEM and energy dispersive X-ray spectroscopy (EDS) analysis to understand morphology/composition changes induced by RDE break-in. Such changes are expected based on previous observations with membrane electrode assembly (MEA) samples performed under 3M

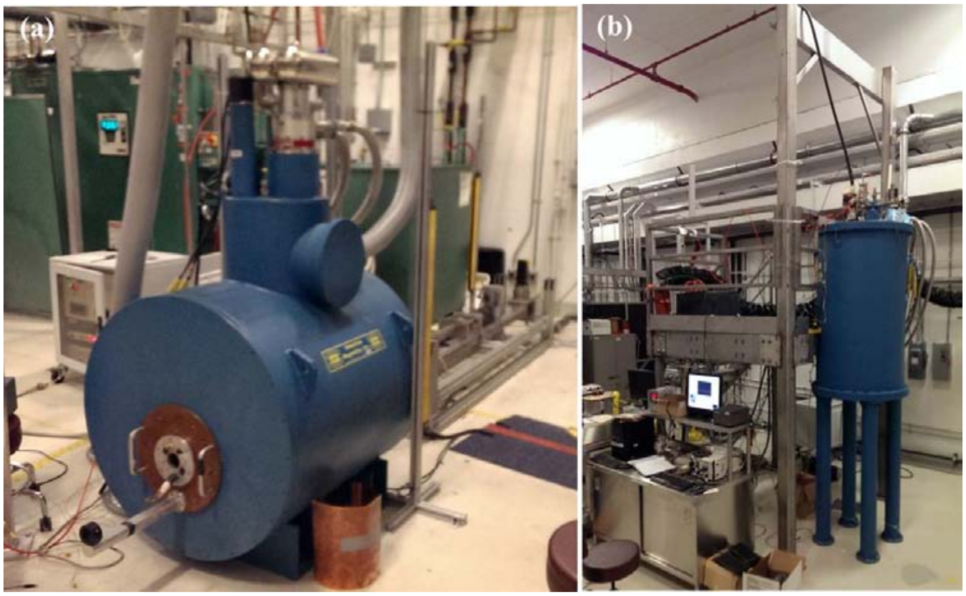


FIGURE 1. a) Horizontal and (b) vertical high field magnets in the Advanced Manufacturing Facility at ORNL

projects. Z-contrast STEM images of five of the post-break-in NSTF whiskers are shown in Figure 3. Annealing affected the degree of Ni dissolution during RDE break-in, which in turn affected Pt-skin and pore formation, key morphological factors controlling electrochemical area (ECA) and specific activity.

Perhaps even more telling was the EDS quantification of the Pt at% (relative to Ni) for each sample. When plotted against ECA, there is a clear correlation between the amount of Ni dissolution (leading to increased Pt content), as shown in Figure 4. Previous XRD and XPS results indicated that the presence of the magnetic field tends to slow grain growth and enhance formation of Pt-rich surface structures during annealing, both of which affect the rate of Ni dissolution. Thus, magnetically annealed samples had slightly higher ECA than the non magnetically annealed counterparts. More ambiguous, however, is the connection between composition and specific activity. While greater Pt at% led to generally

(a) Sample ID	Gas	Process Temp (C°)	Magnet (T)	SA (μA/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

(b)

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

(c)

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

FIGURE 2. (a) RDE measurements of Pt_3Ni_7/NSTF annealed under different conditions. (b) XPS and (c) XRD results from magnetically-annealed sample set

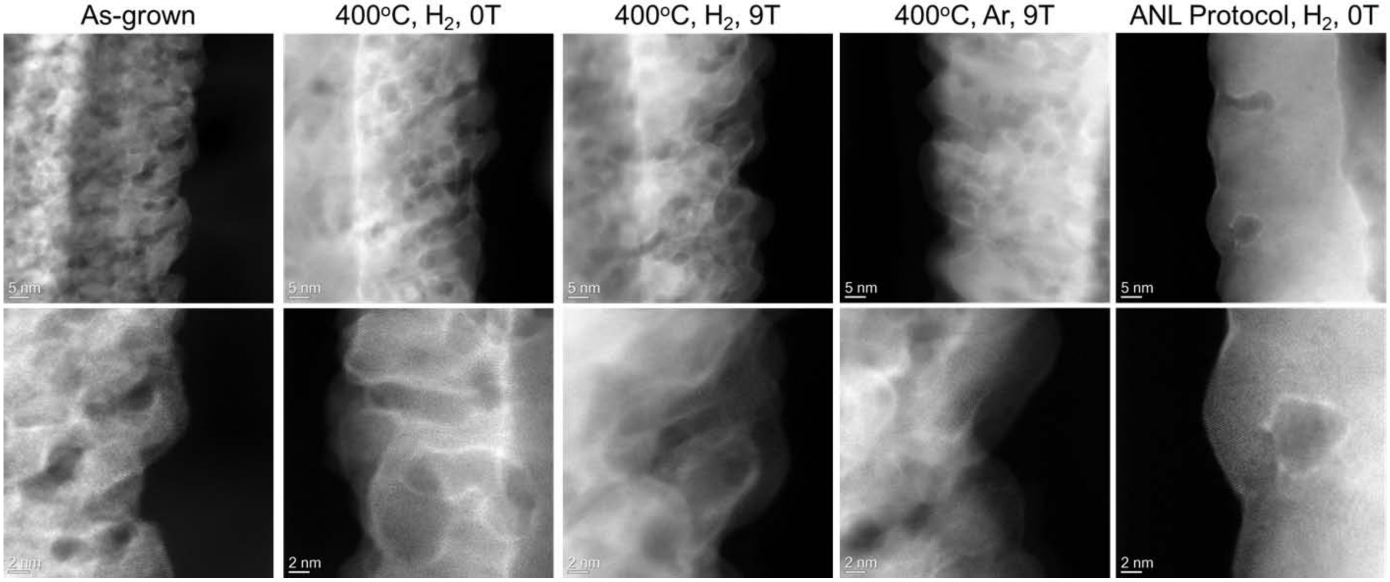


FIGURE 3. Z-contrast STEM images of post-break-in samples for NSTF annealed under different conditions, showing different degrees of pore formation

higher specific activities, the non-magnetically annealed samples (with larger grain sizes) had slightly higher specific activities then their magnetically annealed counterparts. Thus, any increases in ECA from magnetic annealing are being partially countered by drop in specific activity.

We employed a K-space based SKKR method for density functional theory calculations of the Pt-Ni alloys. The SKKR method imposes no periodic boundary conditions for modeling the extended and disordered systems of Pt-Ni alloys. We have calculated electronic structures and ground state magnetism for Pt-Ni and Pt-Co alloys for an entire range of alloying concentrations. Figures 5a and 5b show the electronic structures of Pt$_{0.7}$Ni$_{0.3}$ and Pt$_{0.3}$Ni$_{0.7}$ alloys. Exchange splitting, which gives rise to magnetism, is about

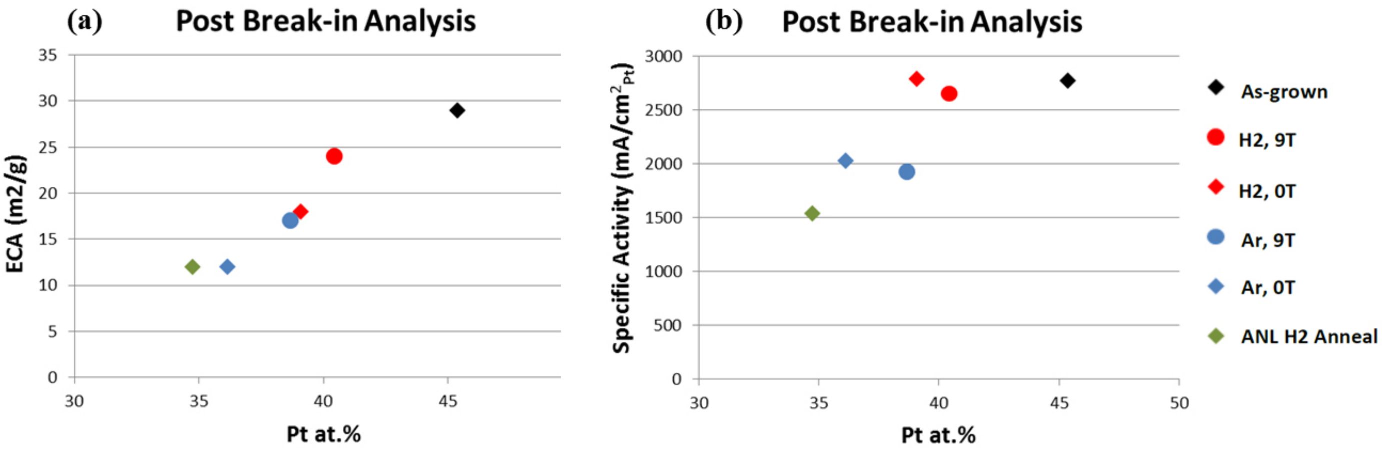
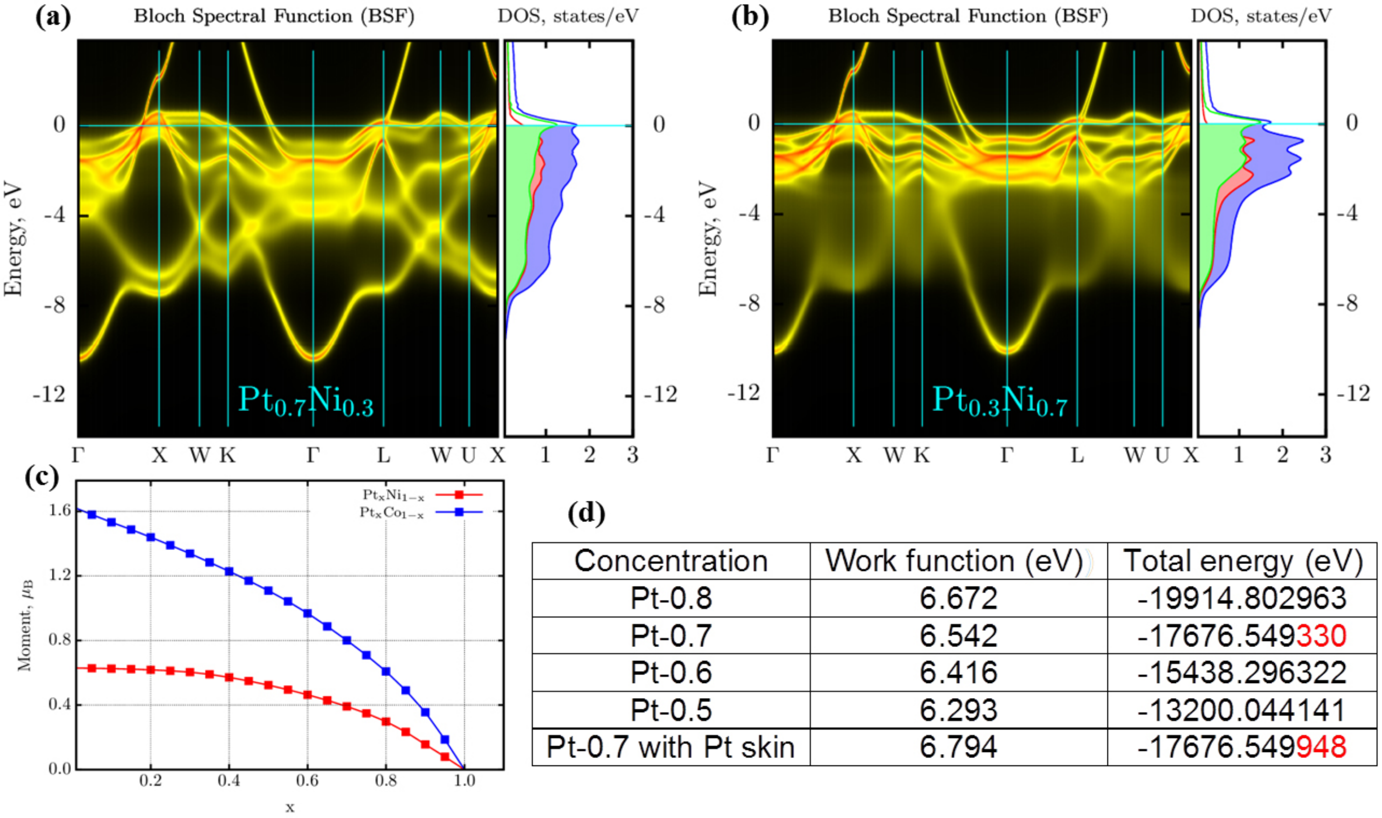


FIGURE 4. Plots of Pt at% after break-in vs (a) ECA and (b) specific activity



Concentration	Work function (eV)	Total energy (eV)
Pt-0.8	6.672	-19914.802963
Pt-0.7	6.542	-17676.549330
Pt-0.6	6.416	-15438.296322
Pt-0.5	6.293	-13200.044141
Pt-0.7 with Pt skin	6.794	-17676.549948

FIGURE 5. Bloch spectral functions (BLS) and density of states (DOS) for (a) Pt$_{0.7}$Ni$_{0.3}$ and (b) Pt$_{0.3}$Ni$_{0.7}$ alloys; (c) Magnetism of Pt-Ni (red) and Pt-Co (blue) alloys at ground state for concentration range from 0.0–1.0; (d) Work function and total energies of Pt-Ni alloy at selected concentrations

the same for both alloys but density of states for $Pt_{0.3}Ni_{0.7}$ alloy are much more pronounced. As a result, $Pt_{0.3}Ni_{0.7}$ alloy has magnetic moment of 0.6 µB per site at T = 0 K while $Pt_{0.7}Ni_{0.3}$ has a moment of 0.39 µB per site. Ground state magnetic moments of Pi-Ni and Pt-Co alloys are shown in Figure 5c for an entire range of alloying concentrations. Pt-Co alloys have more than twice the magnetism of Pt-Ni alloys at all concentrations, suggesting that Pt-Co alloys would respond to magnetic annealing stronger than Pt-Ni alloys.

We have also calculated magnetic ground states for Pt-Ni alloys with surface termination (Figure 5d). The calculations show that $Pt_{0.7}Ni_{0.3}$ alloys with pure Pt skin is energetically favored over pristine $Pt_{0.7}Ni_{0.3}$ surface and lower value of work function. This result suggests that formation of pure Pt skin can be detected through measurement of work functions of samples.

CONCLUSIONS AND FUTURE DIRECTIONS

- Demonstrated magnetic annealing of Pt_3Ni_7/NSTF in a 9 T field at 400°C in Ar and H_2
- Showed magnetic annealing has only modest effect on grain size and surface composition relative to field-free annealing
- Measured specific activity, electrochemical surface area, and mass activity by RDE, which showed, in all cases, annealing leads to a lowering of the mass activity
- Implemented SKKR method for advanced DFT calculations of disordered alloy catalysts, indicating Pt-Co alloys may have greater response to the field

Additional magnetic annealing experiments will be performed at varied temperatures and higher initial Pt concentrations to find the optimal conditions for improving ECA, mass activity, and specific activity. We also plan to begin sputtering Pt-Co alloys onto NSTF to study their behavior under the magnetic field. RDE measurements will add a durability component to test activity of the catalysts over their lifetime.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. D.A. Cullen, “Magnetic Annealing of Pt-alloy Nanostructured Thin Film Catalysts for Enhanced Activity,” Oral Presentation, Fuel Cell Tech Team Meeting, Southfield, MI, April 8, 2015.

2. D.A. Cullen, “Magnetic Annealing of Pt-alloy Nanostructured Thin Film Catalysts for Enhanced Activity,” Poster Presentation, U.S. Department of Energy Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 15–19, 2015.