Microplasma-based Synthesis of Nanostructured Pt & Pt Alloy Films

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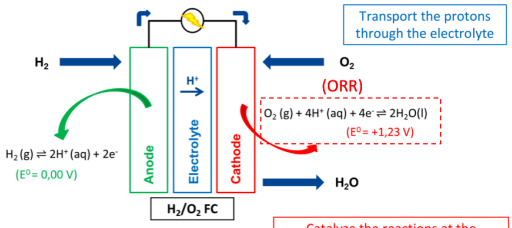
Abstract

Platinum is an excellent catalyst for the oxygen reduction reaction (ORR: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) in a fuel cell, and nanostructured platinum films with particle sizes in the sub-10 nm range are attractive due to their high activity and efficient Pt utilization. In this work, nanostructured Pt and Pt-alloy films and nanoparticles were deposited on doped silicon (Si) and indium tin oxide (ITO) substrates under a variety of conditions using a novel microplasma jet spray deposition technique [1]. Pt precursor (Pt (II) hexafluoroacetylacetonate - Pt(hfac)) was sublimed and fed to the plasma anode capillary tube using an Ar carrier, resulting in aerosolized clusters and nanoparticles that were subsequently spray-deposited on the substrate at pressures from 10-760 torr. The resulting films were characterized using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and atomic force microscopy (AFM).

Nanoparticle Catalysts for Fuel Cells



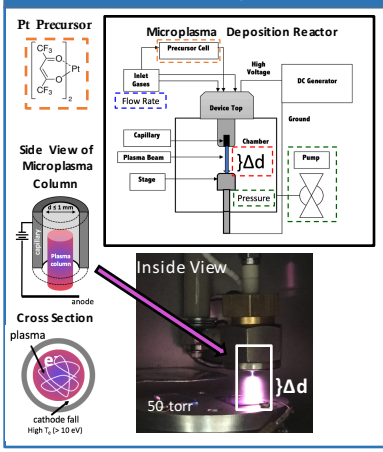
Net reaction (the "redox" reaction):
$2H_2 + O_2 \Rightarrow 2H_2O$
E^o= +1.23V

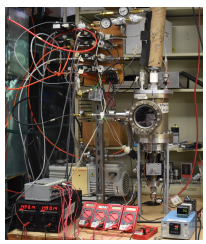
- Fuel cells produce electricity through electrochemical reactions
- $2H_2 + O_2 \rightarrow 2H_2O$
- Fuel cells rely on Pt as a catalyst for oxygen reduction reaction (ORR)
- Platinum is an **expensive** metal → Use Pt more efficiently → Increase surface area [2], alloy Pt with other metals [3]

Project Goals

- Utilize novel methods [1] to deposit Pt nanoparticles for fuel cell catalysts
  → ***Microplasmas***
- Explore how plasma operating parameters affect Pt deposition: pressure, Pt-precursor flux, substrate type, electrical configuration
- Characterize Pt films and nanoparticle morphology
- Electrocatalytic activity testing
- Investigate if Pt can alloyed with Ni
  - Can PtNi be deposited directly and is PtNi catalytically active for ORR?

Microplasma Deposition

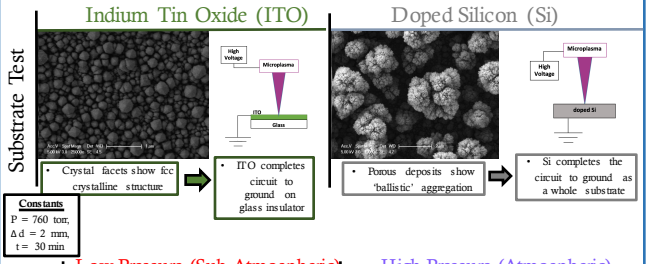


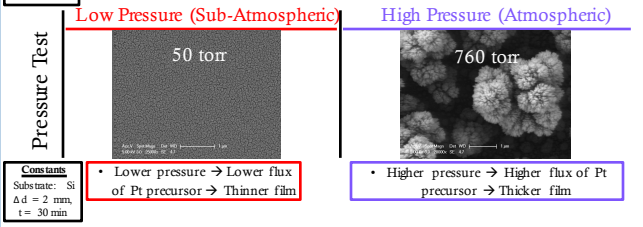


- High voltage (microplasma) discharge struck between capillary and substrate
- **Control Parameters**: gas flow rate, pressure, capillary-stage distance (Δd), precursor cell temperature (for sublimation)

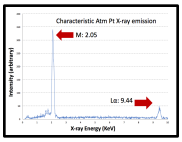
Results

Morphology Tests





Pt Film Composition Analysis

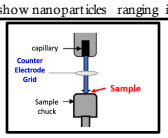


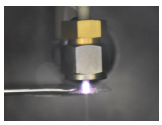
- Energy Dispersive X-ray (EDX)
- Strong signals at 2.05 & 9.44 indicate characteristic x-rays of Pt → Pt heavily abundant

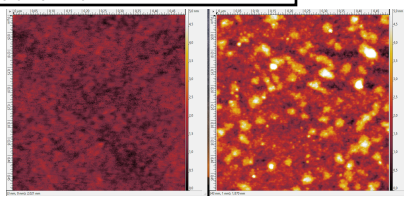
Pt Nanoparticle Synthesis

- The samples grown above are too big for a Pt catalyst → synthesize nanoparticles by increasing capillary-stage distance and by decreasing time
- Conductive counter electrode grid added to apparatus to sustain microplasma circuit at higher pressure
- Samples characterized by Atomic Force Microscope (AFM), yellow/white areas show nanoparticles ranging in size from 4-10 nm

Parameters:
Substrate: Si,
P = 760 torr,
Δd = 10 mm







Si Treated with Inert Argon Microplasma

Si Treated with Precursor Argon Microplasma

Summary

- Deposited diverse range of Pt nanostructures and morphologies
- Pressure and capillary substrate distance had greatest effect on Pt morphology
- Achieved Pt nanoparticles with average size of 4 nm

Next Steps

- PtNi Alloy synthesis → Ni is readily available and less expensive than Pt
- Alloy → catalytically active for ORR?
- Electrocatalytic testing underway

Acknowledgements

Mentors: Joffrey Baneton, Katherine Mackie, Mike Gordon

Funding: GORMAN SCHOLARS PROGRAM

References: [1] TL. Koh, M.J. Gordon *JVST A* **31**, 061312 (2013); [2] Vojislav R. Stamenkovic, et. all *Science* **315**, 5811 (2007); [3] Vojislav Stamenkovic Dr., et. all **118**, 2963-2967 (2006)