Advanced Low-PGM Cathode Catalysts with Self-Healing Properties for High Performing and Highly Durable MEAs

P.I. Vojislav Stamenkovic

Organization: University of California, Irvine

DOE project award # DE-FOA-0002792

Start Date: October 1, 2023

DOE Hydrogen Program

2024 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID #

FC370

Project Goal

The project will aim to develop and deliver highly-durable and manufacturable fuel cell membrane electrode assemblies (MEAs) with novel low-PGM cathode catalyst, improved mass activity and high current density at high operational potentials as well as extended operational longevity at a reduced cost. The MEA performance will meet the M2FCT 2025 end-of-life target: demonstration of 2.5 kW/gPGM power output (1.07 A/cm^2 current density at 0.7 V; 750 mW/cm2 at 0.7 V) after running a heavy-duty AST equivalent to 25,000 hours.

Outcome of this project will enable technological advancements required for deployment of hydrogen fuel cell powered heavy duty vehicles. The combination of atomic level insight, unique materials development strategies, targeted device integration, and next generation operando diagnostics will yield to greatly improved Membrane Electrode Assembly performance. The project will deliver MEAs with advanced durability, performance and cost, which will have direct impact on the state of the technology, market adoption, and the scientific knowledge.

Overview

Timeline and Budget

- Project Start Date: 10/01/23
- Project End Date: 9/30/26
- Total Project Budget: $4.5M
  - Total DOE Share: $3.6M
  - Total Cost Share: $0.9M
  - Total DOE Funds Spent*: $0
  - Total Cost Share Funds Spent*: $0

* As of 03/01/2024

Barriers

- Barriers and Targets towards highly durable MEAs
  - **Dissolution of Pt catalyst:** mitigation will be done though implementation of physical properties of NP that prevent dissolution.
  - **Carbon support corrosion:** will be addressed by alerted graphitization, adsorption and ion-exchange capacity, porosity and hydro-philicity/phobicity.
  - **Performance improvement:** alloying of P NPs, homogeneous distribution of NPs on carbon support, controlled porosity, surface modifications to attenuate ionomer effect and improve durability.

Partners

UCI

- Project lead (PI): Vojislav Stamenkovic, University of California, Irvine: catalyst design and synthesis
- Co-PIs: Plamen Atanassov and Iryna Zenyuk (UCI): carbon supports and MEA fabrication/testing

Drexel UNIVERSITY

Joshua Snyder (Drexel University): surface modifiers

CABOT

Qian Ni (Cabot Corp.): carbon support supplier

IRD Fuel Cells

Madeleine Odgaard (IRD Fuel Cells): MEA fabrication nad testing

Jonathan Braaten (Bosch RTCNA): durability simulations and MEA testing

BOSCH

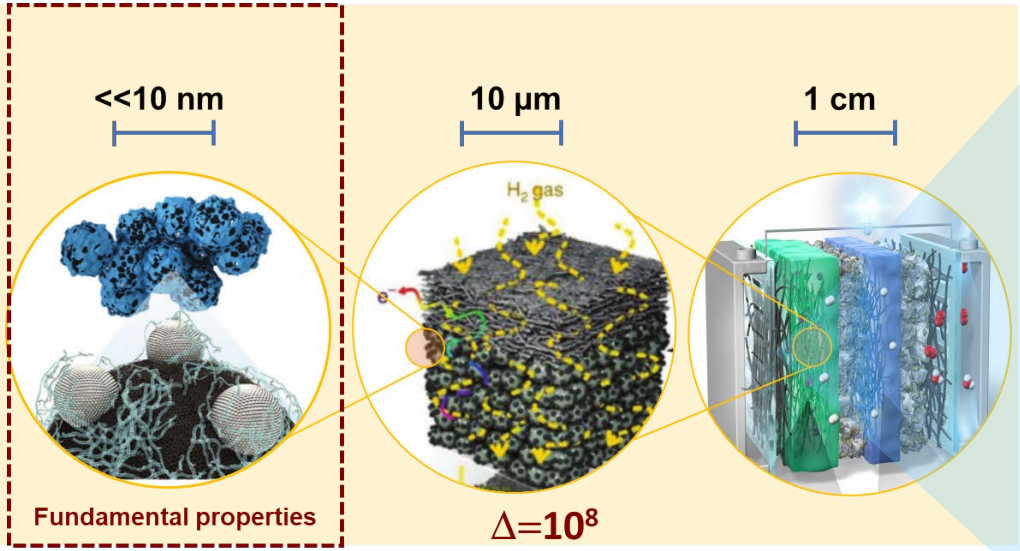
Relevance/Potential Impact

- The overall relevance of this project is reflected through the impact on the DOE EERE Hydrogen Fuel Cell Technologies Office (HFCTO) Program, particularly by addressing critical technical barriers to improve longevity of fuel cells and enable commercialization and the widespread of hydrogen and fuel cell technology targeting medium- and heavy-duty trucks. This will lower greenhouse gas emissions and pollutants diesel engine exhaust, build clean energy infrastructure, strengthen U.S. manufacturing and define pathways to private sector uptake.
- The project has the potential to dramatically reduce dependence on fossil fuels by promoting and enabling sustainable energy resources and creating and maintaining a domestic manufacturing base and workforce for wide deployment of hydrogen technologies, which is in accordance to the DOE Hydrogen Program, Hydrogen Energy Earthshot and U.S. National Clean Hydrogen Strategy and Roadmap.
- Technical targets in this project are line with the DOE Million Mile Fuel Cell Truck Consortia and progress and outcome will be coordinated with consortia.
- The project is addressing main technical barriers for widespread pf hydrogen fuel cell technology and will have impact on the current state-of-the-art by delivering:
  - The highly-durable and manufacturable fuel cell MEAs
  - low-PGM content with novel catalyst structure
  - enhanced mass activity at high operational potentials
  - improved high current density performance
  - extended operational longevity
  - reduced cost

Approach

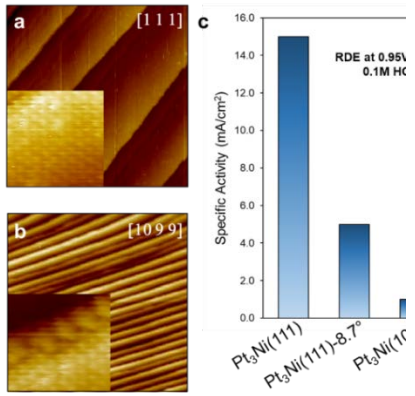
- The project aims to develop robust MEAs for medium- and heavy-duty truck applications with improved durability over the projected lifetime, increased mass activity at high electrode potentials, enhanced performance at high current density, while decreasing PGM content. The approach in achieving these goals relies on utilization of fundamental properties of well-defined two-dimensional (2D) electrochemical interfaces, which will guide rational synthesis of novel fuel cell cathode catalysts, customized characterization tools, implementation of novel carbon supports, interface modification by selected molecular implants, and advanced design and fabrication of MEAs. Uniqueness of this approach is based on the synergy between the nine individual tasks:
  (1) high precision synthesis of nanoparticles with defined control and distribution of atomic structural ensembles and ordered compositional gradient of Pt and transition metal
  (2) design and implementation of advanced carbon-based support materials;
  (3) modifications of catalyst-ionomer interfaces by selected molecular implants;
  (4) advanced component integration strategies;
  (5) advanced electrochemical and structural catalyst characterization;
  (6) electrode component distribution and morphology design;
  (7) electrochemical MEA diagnostics for in-operando AST characterizations;
  (8) feasibility studies for high volume and high throughput roll to roll MEA manufacturing;
  (9) sustainable MEA design aimed for recyclability of membranes and catalyst layers.

Approach

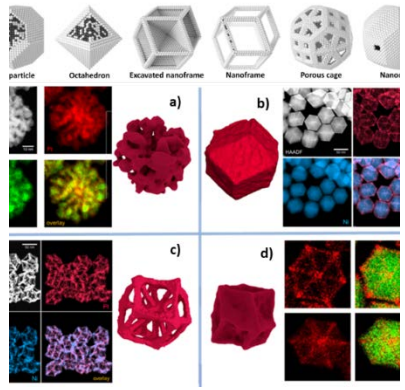


Integrated fundamental science and engineering approach

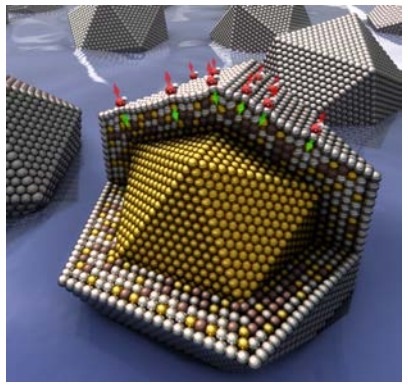
Coupling molecular scale transport and reaction kinetics to screws and bolts



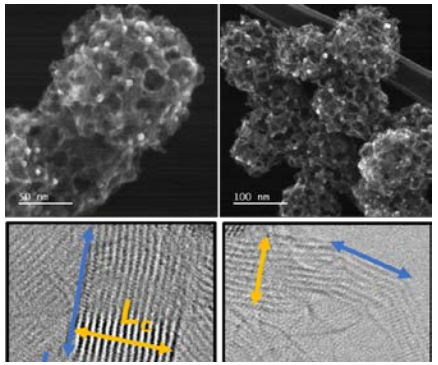
Pt-alloying with transition metals



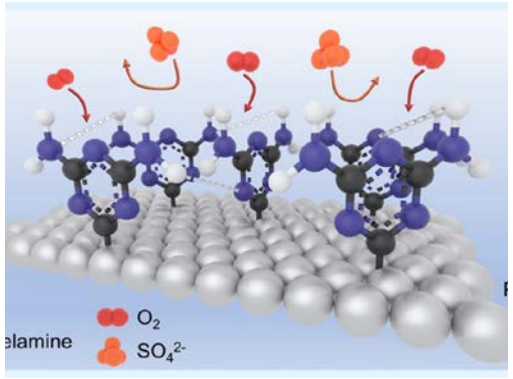
High-precision synthesis of NPs



Self-healing structures



Advanced carbon supports



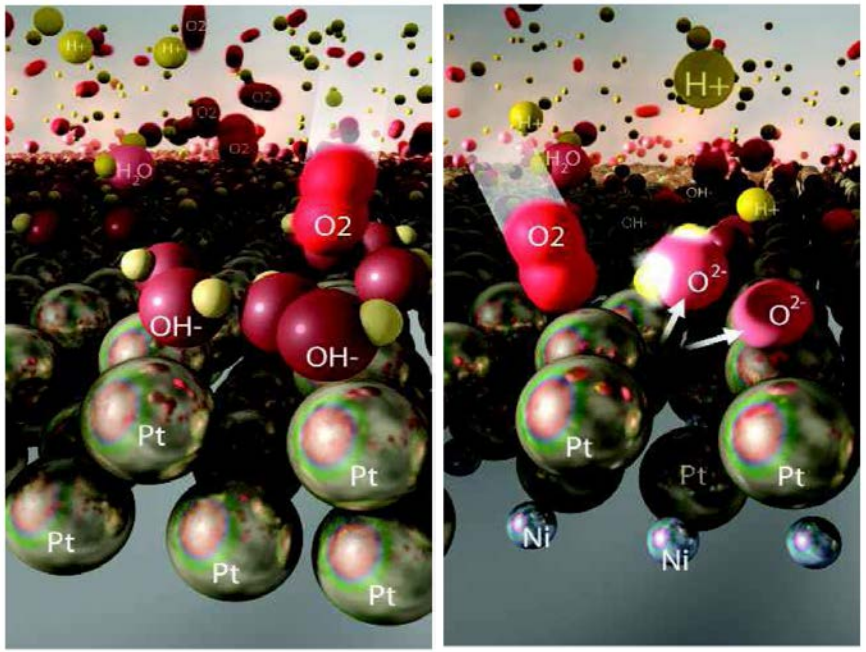
Interface modification

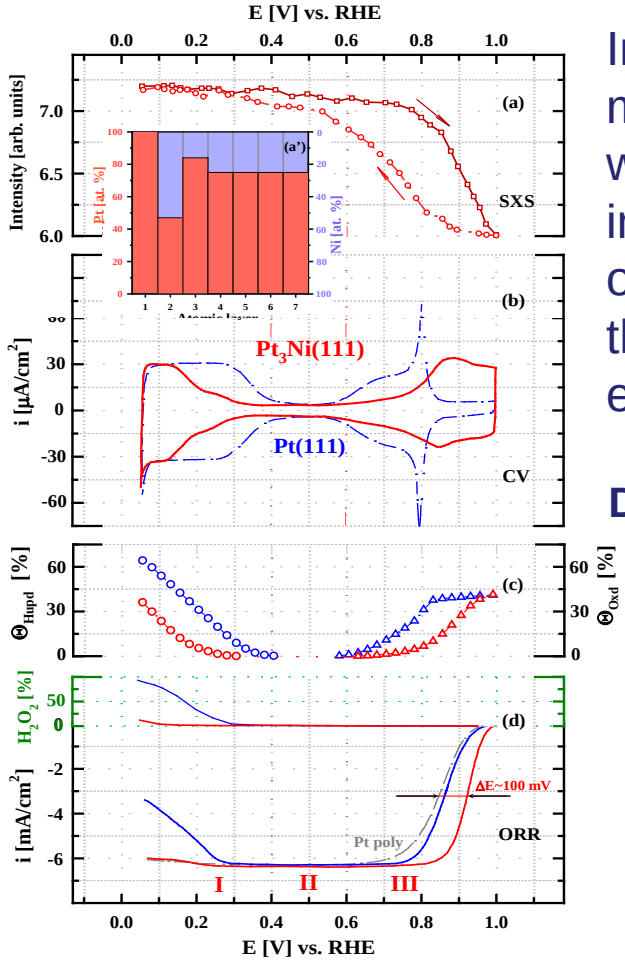
Accomplishments and Progress

(new award: project did not start yet)

- The technical feasibility of the project based on the core synergy between **the four** fundamental discoveries that have been accomplished in our laboratories and will be applied towards novel catalyst design and transferred into high performing MEA electrodes.

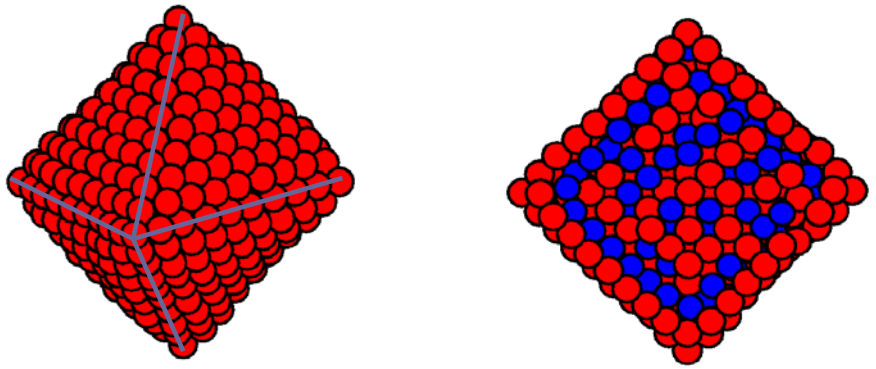
1 *the roles of atomic surface structure and subsurface composition:* Single crystalline PtTM surfaces are the most active materials for the fuel cell cathodic reaction.





Initially we reported a one-order of magnitude enhancement in ORR activity when compared to Pt(111). More recently, improved experimental precision through optimized crystal preparation, have shown the Pt-skinned compositional profile yield even greater activity improvements

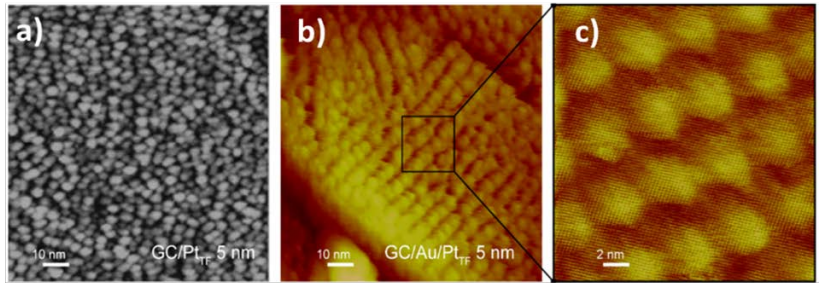
Design principles for Pt-alloy nanoparticles

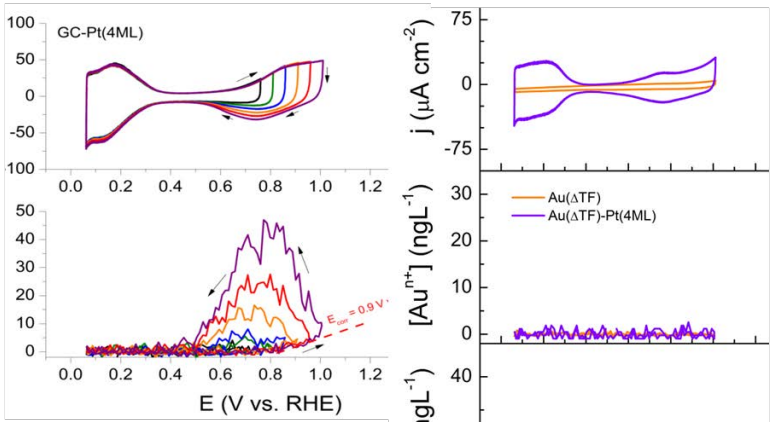


Accomplishments and Progress

(new award: project did not start yet)

2 *the mitigation of Pt dissolution through the incorporation of Au* atoms into the core, subsurface and low-coordinated surface sites. Addition of Au in the near-surface region induces favorable structuring of Pt topmost atoms towards a (111)-surface structure with high-coordination. During the ORR, differences in surface energies between the subsurface Au and surface Pt atoms cause the dissolved Pt atoms to be replaced by Au, passivating and stabilizing the low coordinated vacancies on catalyst surfaces, enabling a self-healing effect.

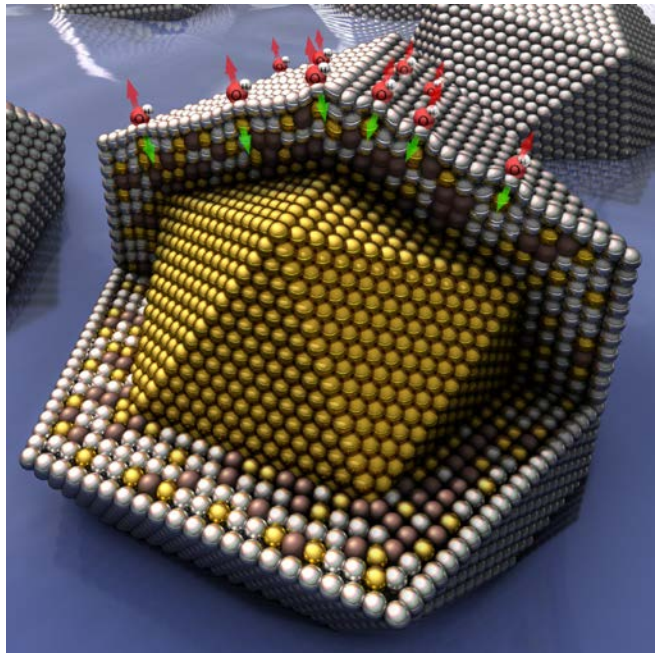




Sputtered thin films of Pt ***(a)*** *and with subsurface Au* ***(b, c)*** *induces surface (111) texturing*

Design principles for Pt-alloy NPs with incorporated Au:

-Transition from 2D to 3D materials: NPs/Carbon
-Utilization of the difference in surface energy
-Induced surface segregation
-Fine tune oxophylicity of the surface atoms
-Materials at different scale
-Ultimate tuning of the structure-function

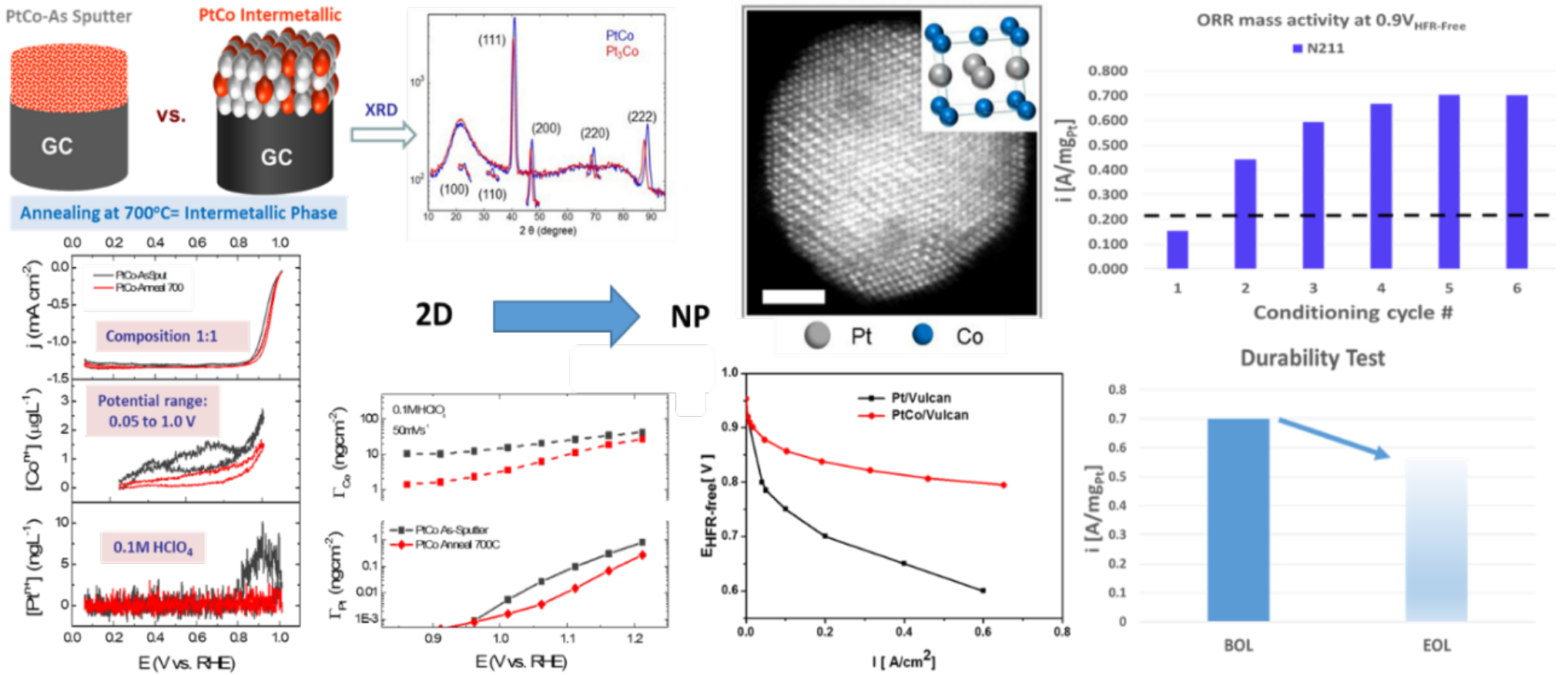


***self-healing*: ELIMINATING DISSOLUTION @ ATOMIC SCALE**

Accomplishments and Progress

(new award: project did not start yet)

3 *the intermetallic structure* further promotes the beneficial effects of Pt-alloys described above, enhancing both specific activity and durability through reinforced formation of a larger fraction of stable (111)-like surfaces. A representative example from our systematic studies of the structure-function properties of PtCo. Utilization of intermetallic structures will be employed across the entire volume of NPs and/or in the NP core, with addition of Au as well as other metals that might mitigate dissolution through a similar mechanism.

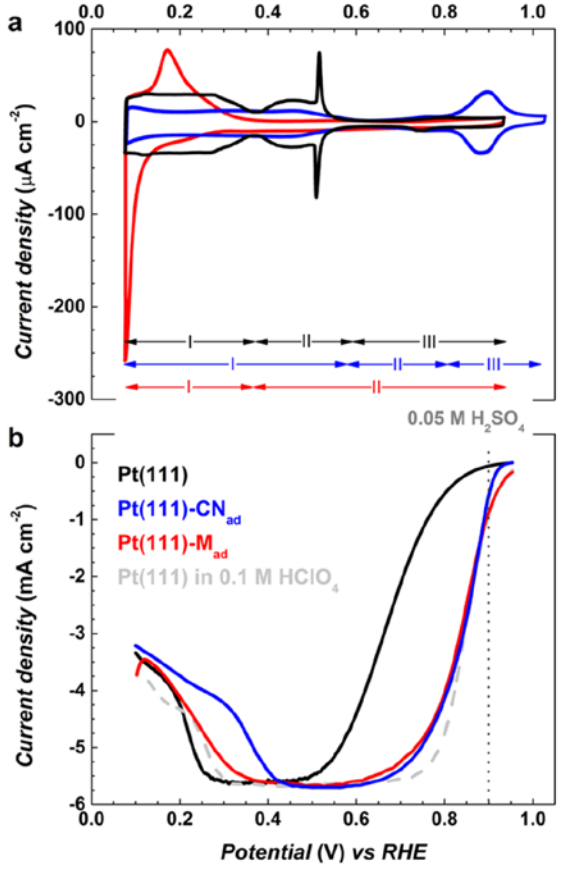


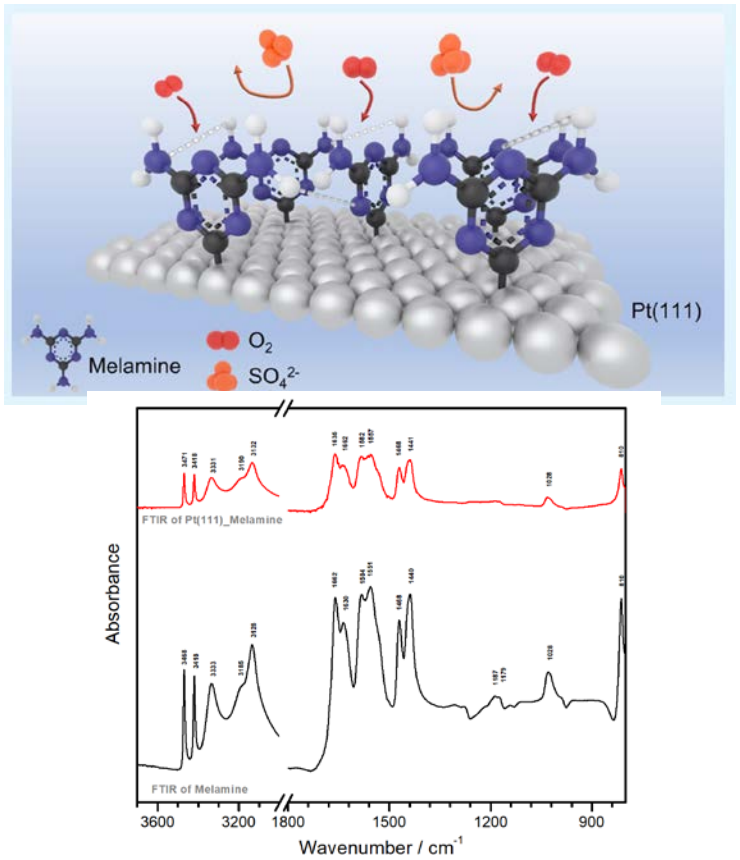
PtCo intermetallic structure: (left) XRD, RDE, and RDE-ICP/MS of as-sputtered vs. intermetallic extended 2D thin film of PtCo; (right) HRTEM and MEA testing of $PtCo_{IM}$/C NPs.

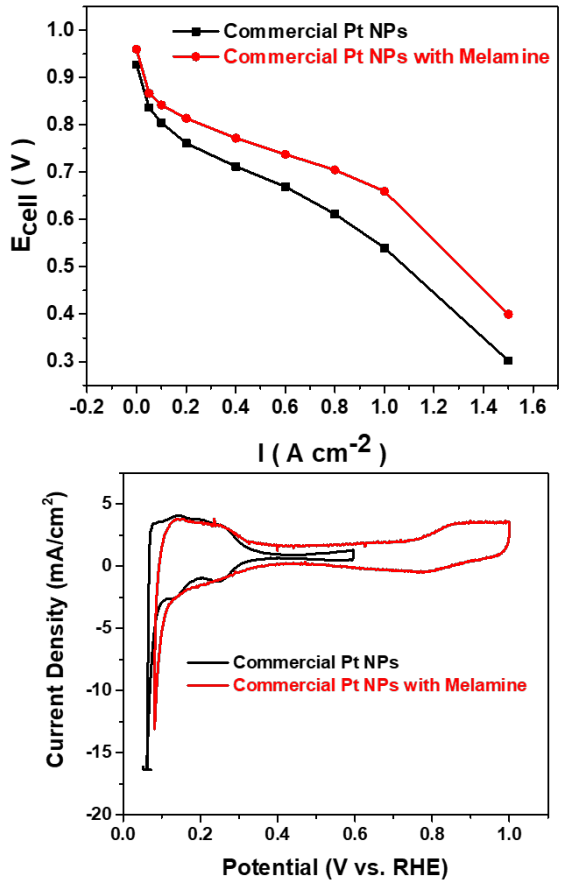
Accomplishments and Progress

(new award: project did not start yet)

4 *the surface modification and fine tuning of electrochemical interfaces through o*ptimization of water, ionomer, and catalyst interactions. Carefully selected spectator molecules limit the degree of ionomer poisoning from physical aggregation and specific adsorption as well as delay the onset of Pt oxidation, enhancing the ORR and catalyst durability. The initial MEA studies of these interfacial modifiers were done with ionic liquids (IL) and melamine molecules. In both cases, the MEAs showed improved activity and durability vs. baseline Pt/C.

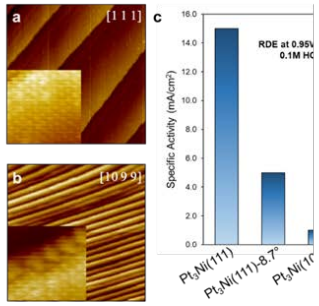




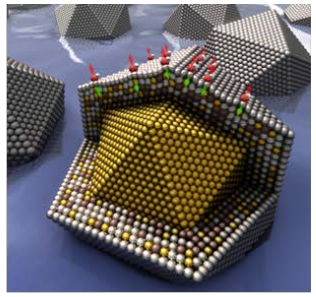


Pt-melamine surface modification: (left) Pt(111) with and w/o melamine (CV and ORR); (center) Raman spectra (right) MEA testing.

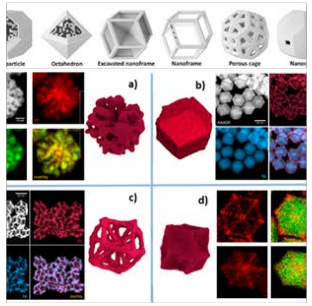
Collaboration and Coordination



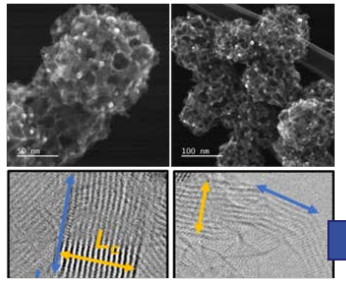
Pt-alloying with transition metals



self-healing structures



high precision synthesis of NPs



advanced carbon supports

UCI University of California, Irvine is a prime institution for the project:

Lead PI: Vojislav Stamenkovic
Co-PIs: Plamen Atanassov and Iryna Zenyuk

The UCI team consists of three faculty members from the Department of Chemical and Biomolecular Engineering that will work on high-precision nanoscale synthesis, and implementation of advanced carbon supports for fabrication and testing of durable MEAs.

IRD IRD Fuel Cells

IRD is a sub institution; industrial partner

Co-PI: Madeleine Odgaard will fabricate and evaluate MEAs.

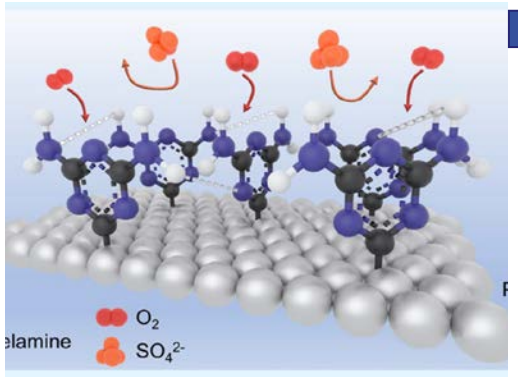
BOSCH

Bosch is a sub institution; industrial partner

Co-PI: Johnathan Braaten will evaluate and validate MEAs.

CABOT Cabot is a sub institution; industrial partner

Co-PI: Qian Ni will work on a series of carbon supports with controlled physical properties

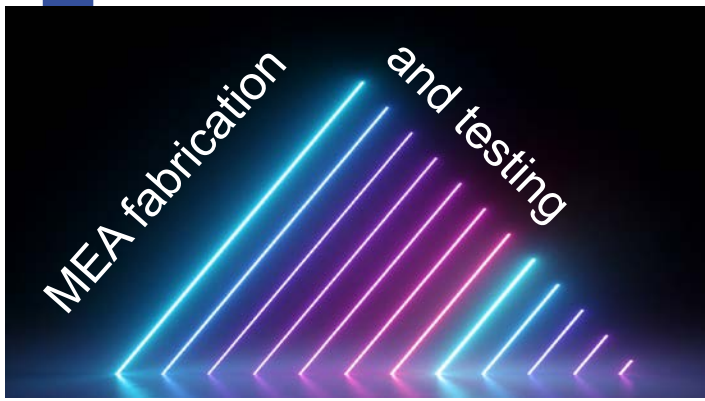


Interface modification

Drexel UNIVERSITY

Drexel University is a sub institution:

Co-PI: Joshua Snyder will implement molecular ensembles in modulating ORR kinetics, mitigating detrimental ionomer interactions and facilitating ionic and gaseous transport in MEA.



FCT MILLION MILE FUEL CELL TRUCK

This project is highly complementary and coordinated with M2FCT Consortium, and utilizes M2FCT's resources in national labs: electron microscopy at ORNL, MEA testing capabilities at NREL and LANL, and X-ray spectroscopy at the beam line at Argonne.

DEIA/Community Benefits Plans and Activities

- The project team members from UCI and sub institutions are committed to enhancing diversity, equity, and inclusion (DEI) and will provide opportunities to inspire, train, and support students and postdoctoral scholars regionally and nationally. UCI is a federally recognized Hispanic-Serving Institution (HSI) and Asian American and Native American Pacific Islander-Serving Institutions (AANAPISI). As a Minority-Serving Institution (MSI), UCI supports a range of offices and programs that focus on DEI from K-12 through to the professorship. The project has detailed DEIA Plan and key elements are listed below:

- overarching goal is to increase the participation and inclusion of underrepresented minority (URM) and female students and faculty. The work will be performed by six project members, of which three are female. To meet this goal, our project objectives are to (O1) Foster K-12 students' interest in STEM, specifically related to engineering and renewable energy; (O2) Create an undergraduate research experience pipeline to industry; and (O3) Create a culture of inclusivity for students and team members from underrepresented groups in engineering.

- the project will have a profound impact on our neighboring, underserved communities. The proposed project focuses on heavy duty trucks operating with fuel cells using hydrogen, resulting in pollution-free operation due to the absence of exhaust fumes leading to significantly better air quality. This benefit is especially relevant for communities suffering under heavy traffic, which are mostly underserved communities in proximity to industrial zones and dense network of freeways in Los Angeles and Orange County.

- UCI Programs that will be utilized: UCI California Alliance for Minority Participation (CAMP), UCI Samueli School of Engineering – Stacey Nicholas Office of Outreach, Access, and Inclusion, UCI and Historically Black Colleges and Universities (UCHBCU), Diverse Educational Community and Doctoral Experience(DECADE) and O2AI staff in partnership with faculty and departmental staff, are heavily involved in identifying and recruiting minority Ph.D. students.

Proposed Future Work

new award: project did not start yet

- FY 2024 and FY 2025:

The two-year workplan breakdown to accomplish the objectives will be executed **simultaneously** in 7 tasks:

Task 1 - Materials Discovery and Innovative Synthesis: 2D materials and modeling guided high-precision synthesis of self-healing nanoparticles with defined size, shape, composition, morphology, and distribution of atomic structural ensembles as well as ordered compositional gradients for Pt-transition metal (TM) alloys;

Task 2 - Durable Catalyst Supports: design and implementation of advanced carbon-based support materials with defined physical properties, pore size, and NP-anchoring sites;

Task 3 - Modified Catalyst-Ionomer Interfaces: modifications of catalyst-ionomer interfaces by selected molecular interfacial modifiers for improved performance and durability;

Task 4 - Advanced Catalyst Characterization: customized structural and electrochemical characterization;

Task 5 | Advanced Component Integration in MEA is aimed at improved durability by i) anchoring NPs to supports; ii) use of molecular interfacial modifiers to decrease oxophilicity of NPs surfaces, and iii) use of molecular interfacial modifiers for carbon support pore filling to increase Pt utilization and reduce dissolution;

Task 6 - Electrode Component Distribution and Morphology Design by identifying weak-spots in electrode component distribution in 3D, novel highly durable electrode morphologies will be designed;

Task 7 - MEA Diagnostics for Accelerated Stress Testing electrochemical MEA diagnostics for in-operando characterizations and accelerated stress testing.

Summary

The outcome of the project will be at least 6 MEAs for independent testing by the M2FCT core lab consortium. The delivered MEAs will meet/exceed the M2FCT 2025 end-of-life target.

The project encompasses a combination of materials development and fabrication scale-up, optimized integration for improved material utilization, advanced performance, and manufacturability, novel in-situ diagnostics to feedback towards materials development and integration tasks, and a focus on recyclability for materials recovery. The overall outcome of the three-year project will be improved MEA durability over the projected lifetime of heavy-duty vehicles, increased mass activity at high electrode potentials, enhanced performance at high current density, and decreased content of PGM.

This will be accomplished by: (1) guided advanced synthesis, informed from well-defined 2D systems, of self-healing cathode catalysts, (2) development and integration of molecular interfacial modifiers to optimizing the catalyst/ionomer interface, (3) development of advanced carbon supports, (4) deployment of advanced in-situ characterization tools, and (5) fabrication and integration of new system components for highly durable MEAs.

Developed materials will be deployed in the MEA cathodes with total PGM loading less than the DOE 2030 target of 0.3 mgPGM/cm2 and meet previously specified performance targets.