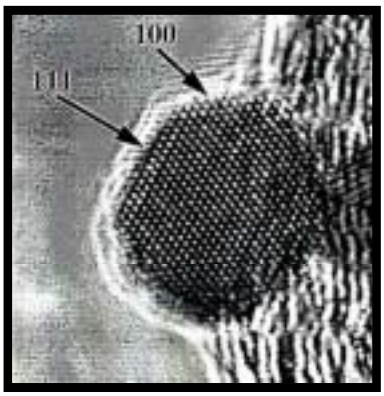
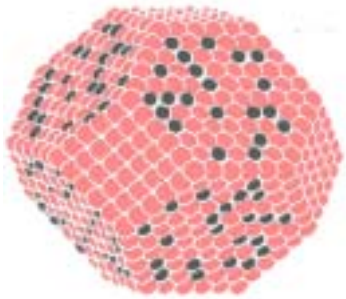
New Electrocatalysts For Fuel Cells





Principal Investigator: Philip N. Ross, Jr.

Staff Scientist: Nenad M. Markovic

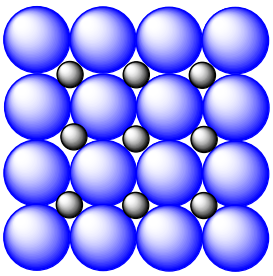
Post Doctoral Fellow: Thomas J. Schmidt
Vojislav Stamenkovic

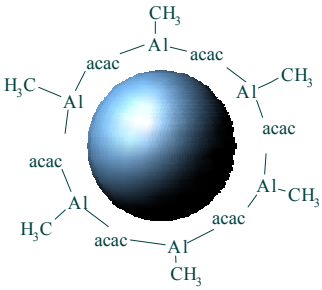
Visiting Scientist: Ursula Paulus
Matthias Arenz
Berislav Blizanac

A research program conducted at the Lawrence Berkeley National Laboratory for the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Advanced Transportation Technologies of the U.S. Department of Energy under contract No. DE-AC03-76SF00098

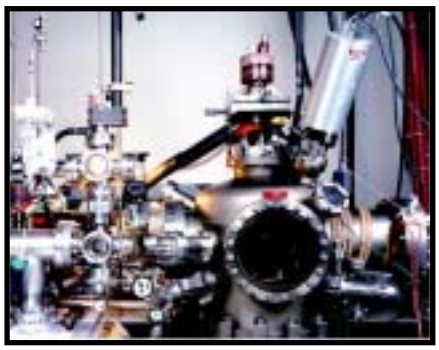
Materials-by-Design Approach

Taylor made surfaces ⟷ synthesis of nanoparticles ⟷ **Fuel cell catalyst**

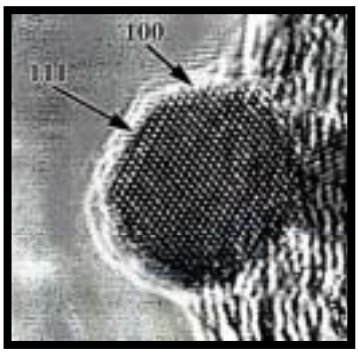




Characterization techniques



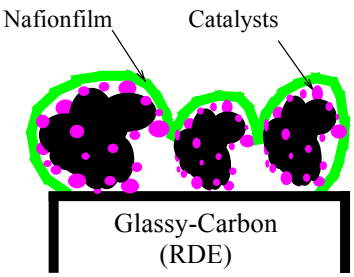
LEIS, XPS, AES, LEED



HRTEM, XRD

Kinetics

HOR, ORR,
CO Tolerance



HOR, ORR,
CO Tolerance

Collaborations

Industry

- GM, Rochester, NY, USA
- Honda, Japan
- E-Tek, New Jersey, NJ, USA
- 3M, Minneapolis, MN, USA

Universities and Institutes

- Max-Planck-Institut fuer Kohlenforschung, Muelheim/Ruhr, Germany
- University of Ulm, Germany
- Paul-Scherrer-Insitut, Villigen, Switzerland
- Universidad d'Alicante, Spain
- Texas Tech University, Lubbock, TX, USA
- University of Eindhoven, Holland
- University of Wales, UK
- University of Bonn, Germany
- University of Liverpool, UK

Future Research 2000

Anode Side

- Optimization of PdAu catalysts
  - Stoichiometry and particle size
- Electrocatalysis on Pd thin metal films
  - Electronic effects
  - Select the most promising substrate for the Pd thin film electrode concept
- Simulation of 'Air-bleed'
  - on FC catalysts under FC conditions

Cathode Side

- Optimization of PtNi and PtCo catalysts
  - Stoichiometry
  - Minimization of Pt amount
  - Pt-skin effects (electronic modification of Pt)
  - Anion effects
- New class of ORR catalysts

Publications (Since 10/2000)

Refereed Journals and Refereed Conference Proceedings:

Markovic, N. M. and P. N. Ross, "Electrocatalysts by Design: From the Tailored Surface to a Commercial Catalyst", *Electrochim. Acta*, 45, 4101, 2000.

Markovic, N. M. and P. N. Ross, "New Electrocatalysts for Fuel Cells: From Model Surfaces to Commercial Catalysts", *CATTECH* 4 (2000) 110.

V. Stamenkovic, N. M Markovic, P. N. Ross, "Structure-relationships in electrocatalysis: Oxygen Reduction and Hydrogen Oxidation Reactions on Pt(111) and Pt(100) in Solution Containing Chloride Ions", *J. Electroanal. Chem.* 500 (2001) 43.

T.J. Schmidt, B. N. Grgur, N.M. Markovic, and P.N. Ross, "Oscillatory Behavior in the Electrochemical Oxidation of Formic Acid on Pt(100): Rotation and Temperature Effects", *J. Electroanal. Chem.* 500 (2001) 43.

C. Saravanan, N.M. Markovic, M. Head-Gordon, P.N. Ross, "Stripping and Bulk COElectro-oxidation at the Pt-Electrode Interface: Dynamic Monte Carlo Simulations", *J. Chem. Phys.* 114 (2001) 6404.

N. M Markovic, T.J. Schmidt, V. Stamenkovic, P.N. Ross, "Oxygen Reduction Reaction on Pt and Pt Bimetallic Surfaces: A Selective Review", *Fuel Cells-From Fundamentals to Systems* 1(2001)105-116.

T.J. Schmidt, V. Stamenkovic, C.A. Lucas, N.M. Markovic, and P.N. Ross, "Surface Processes and Electrocatalysis of the Pt(hkl)/Bi –Solution Interface", *Physical Chemistry Chemical Physics* 3 (2001)3879.

T.J. Schmidt, N.M. Markovic, and P.N. Ross, "Temperature-Dependent Surface Electrochemistry of Pt Single Crystal Surfaces in Alkaline Solution Part I. CO Oxidation", *J.Phys. Chem*, B 105 (2001)12082.

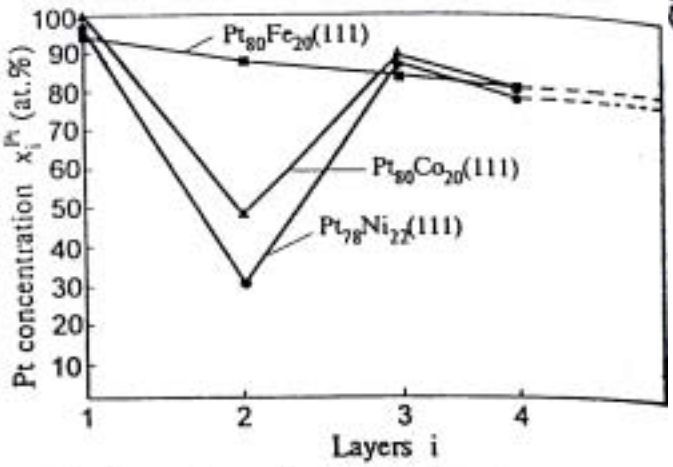
Koper, MTM; Schmidt, TJ; Markovic, NM; Ross, PN. "Potential Oscillations and S-shaped Polarization Curve in the Continuous Electro-oxidation of CO on Pt Single-crystal Electrodes", *J. Phys. Chem. B* 105 (2001) 8381.

Future Directions

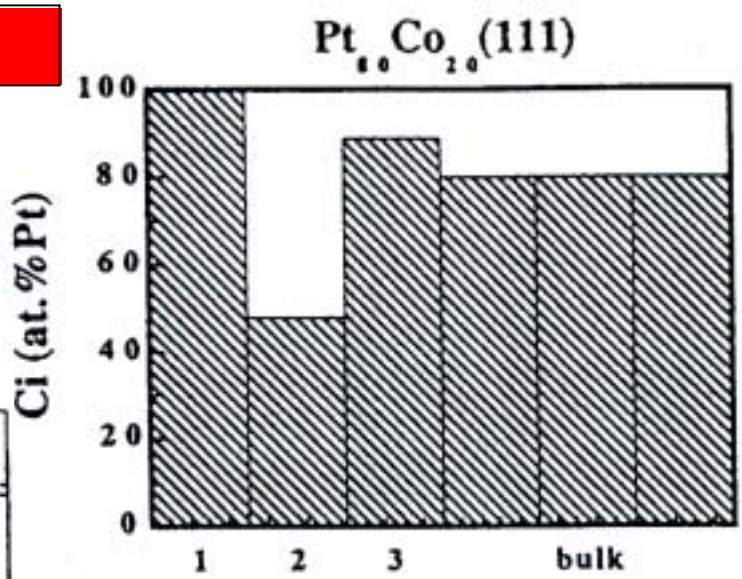
- Unified concept for both anode and cathode catalysts utilizing PGM-based bimetallic nanoparticles with "grape" structure (PGM skin with base metal core) stability of high surface area Pt-bimetallic catalysts
  - Choice of skin and core metals different for anode and cathode
- New synthetic chemistry for nanoparticles with "grape" structure
- Investigation of Re as metal core in PGM "grape" structured nanoparticles
  - Pt and Pd monolayers on Re(0001) model system
  - Re colloidal chemistry
- Optimization of AuPd anode catalyst for HT membranes
- Computational screening of non-PGM catalyst concepts using newly developed (under BES funding) *ab initio* theory of the ORR

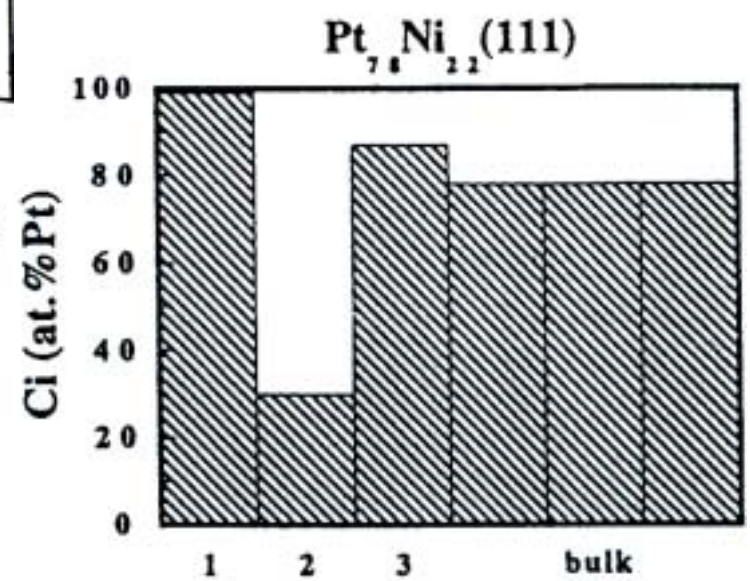
Segregation on Pt_3Ni and Pt_3Co alloys surfaces

Grenoble Group Results



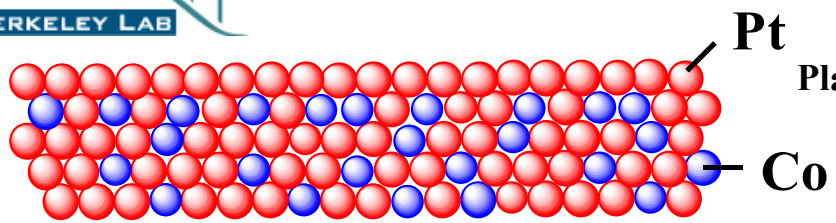
The layer dependence of the Pt surface concentration for Pt–M(111) alloy (M = Fe, Co, Ni).



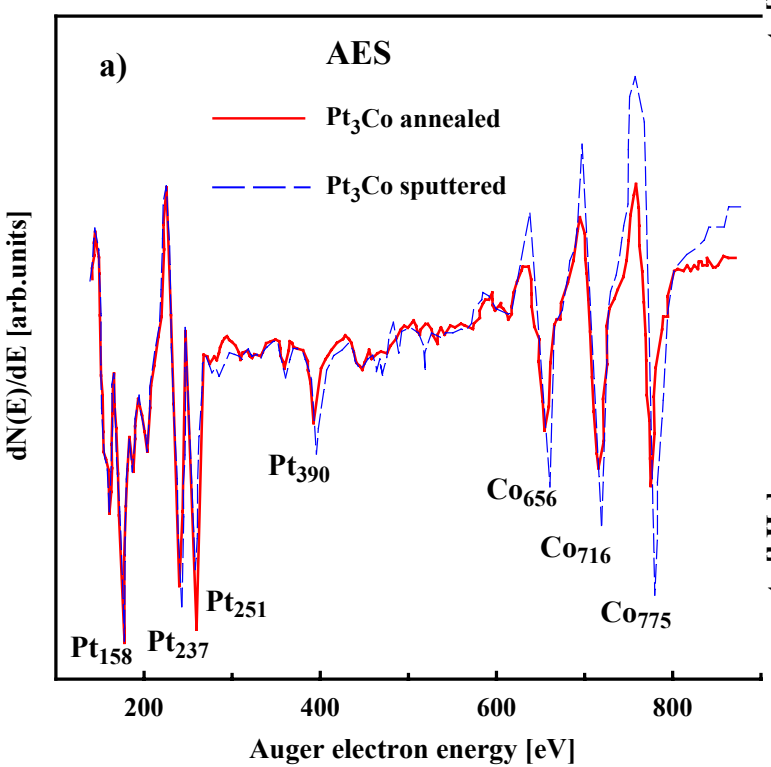


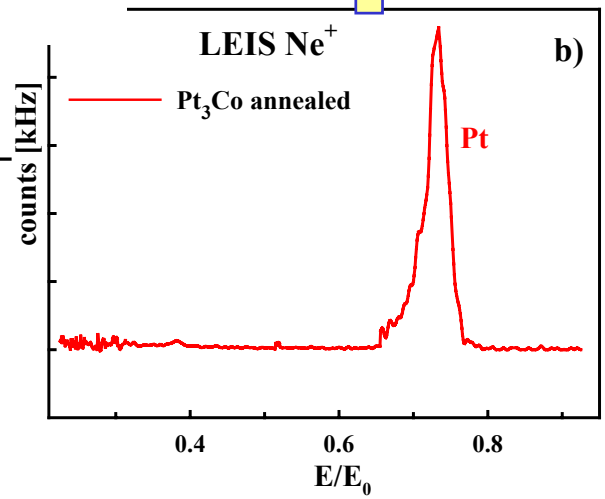
Y.Gauthier, *Surface Review and Letters*, 3(1996)1663

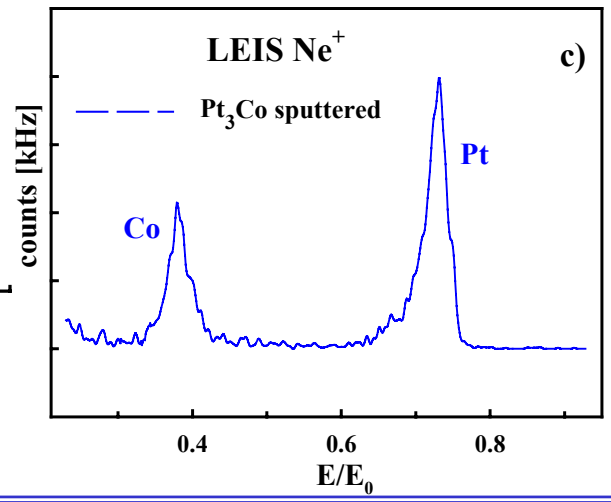
Pt_3Co: AES, LEIS



Platinum 'Skin' on the surface







- **AES:**

  -Co depeleted on the annealed surfaces
  -Pt enrichment?

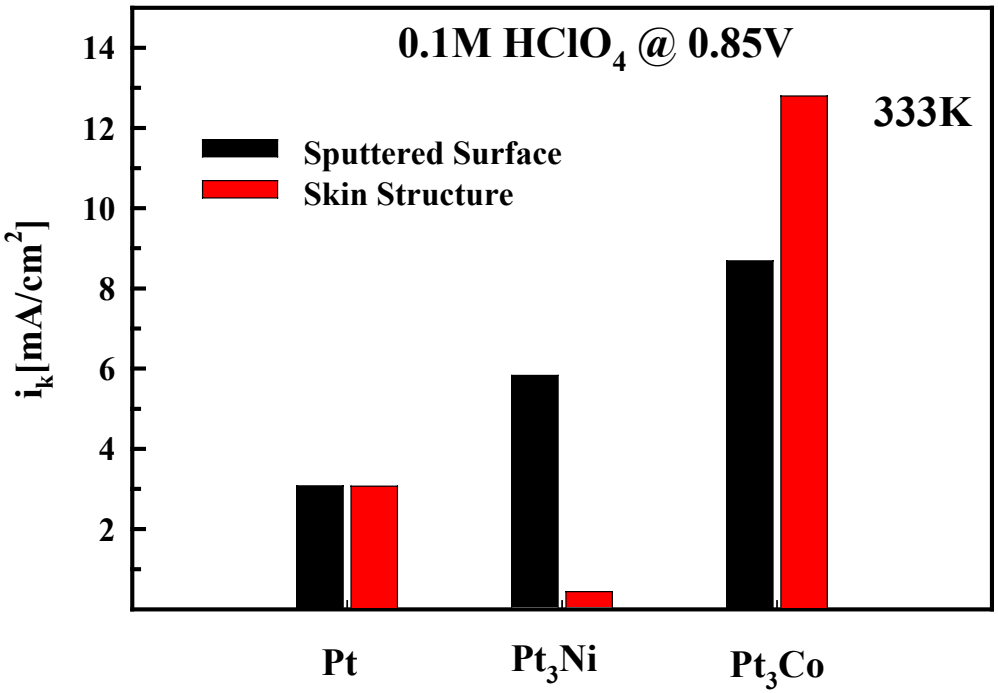
- **LEIS:**

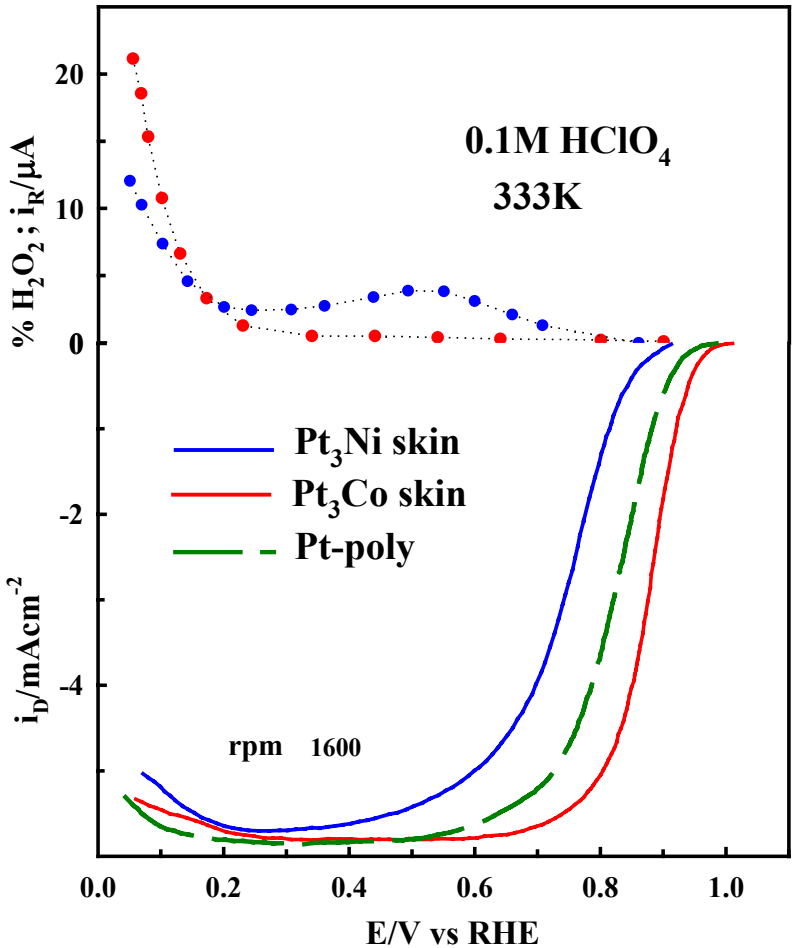
  -Complete Pt enrichment on the annealed surface
  -Bulk composition achieved during in situ sputtering

Kinetic Enhancement by Skin Effect

- The most active surface at 60°C: Pt_3Co skin

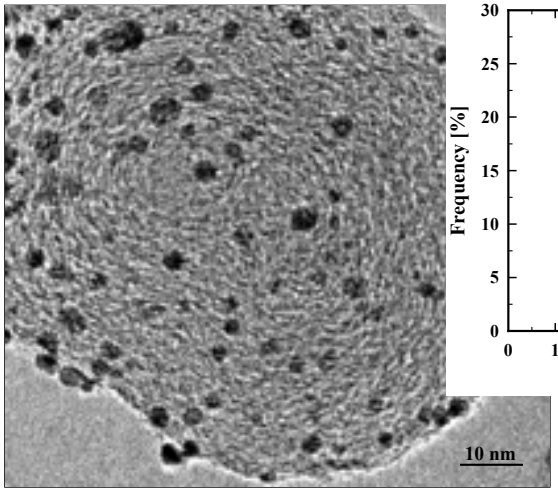
factor: Pt_3Co (s) > Pt_3Co (b) > Pt_3Ni (b) > Pt > Pt_3Ni (s)
4.2 2.8 1.9 1 0.15

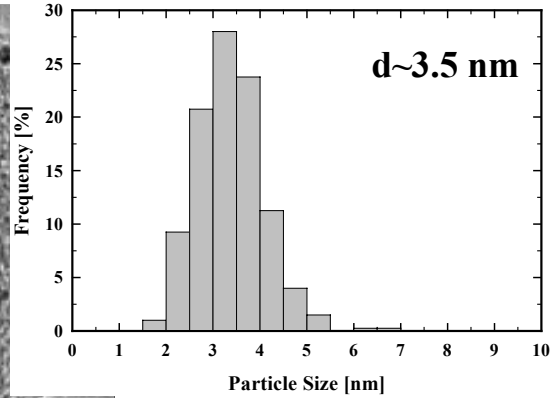




- Skin structure is either more or less active than sputtered structure
- Electronic effects

Characterization of Pt/Vulcan Catalyst

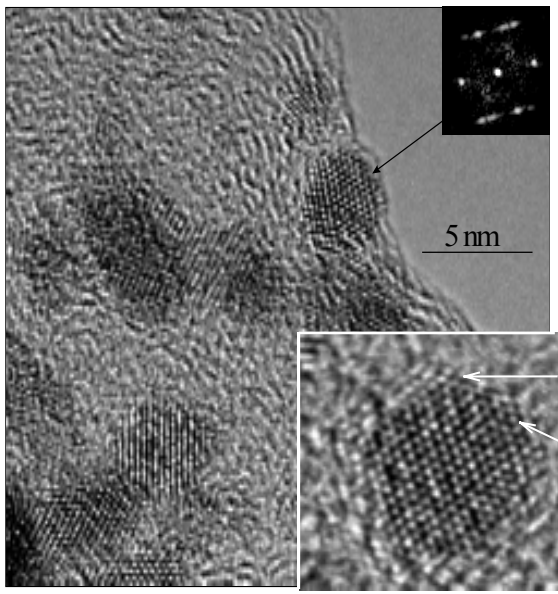




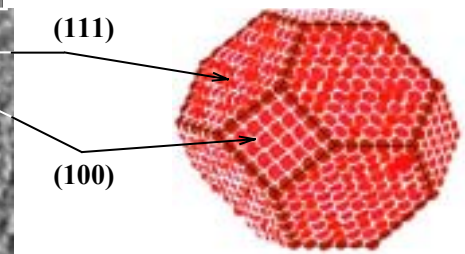
low magnification

- Transmision electron microscopy

- The particle size effects:
  Correlation between the ORR on Pt(hkl) and exposed facets on Pt/C catalysts at fuel cells relevant conditions

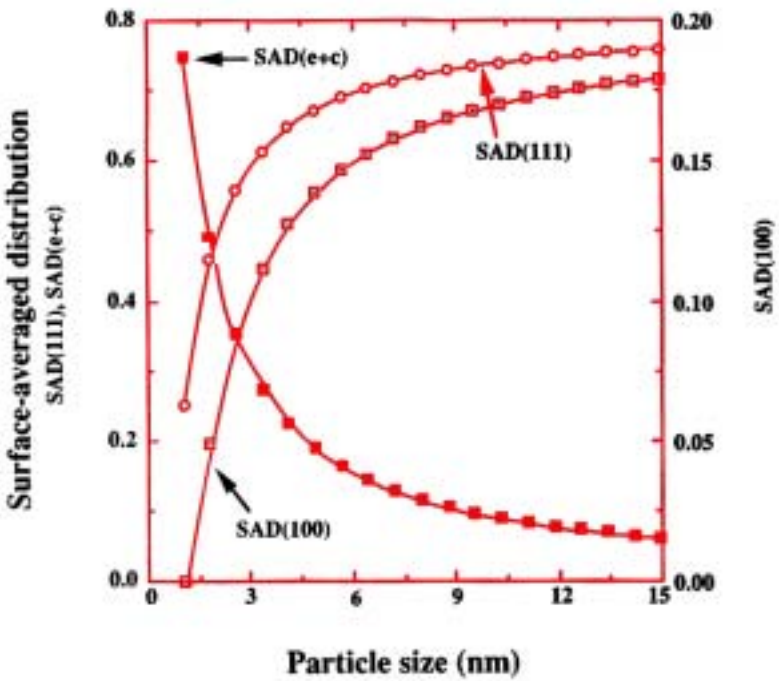


high magnification

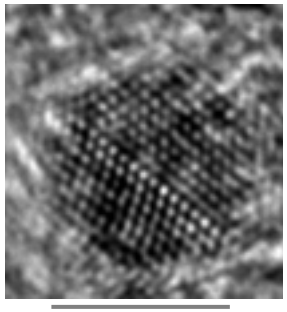


- Mainly cubo-octahedral particles with (111) and (100) facets

Particle size effect

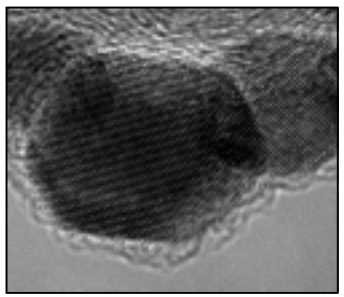


10 % Pt/Vulcan

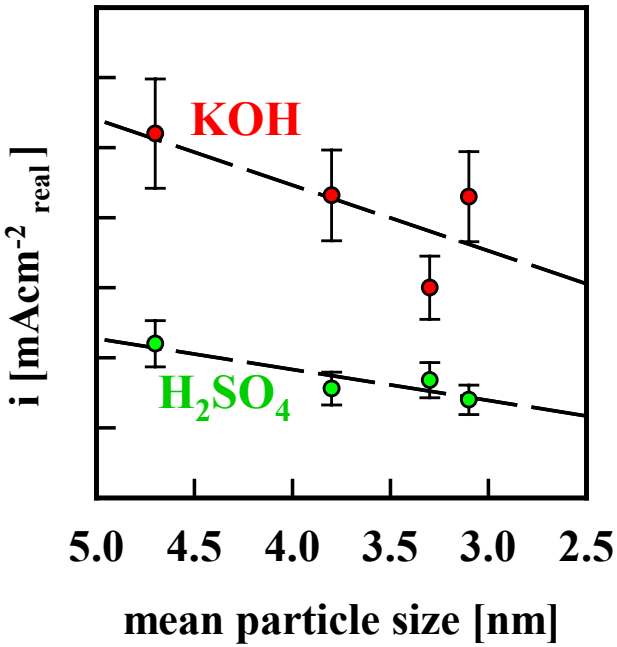


3 nm

40 % Pt/Vulcan



6 nm



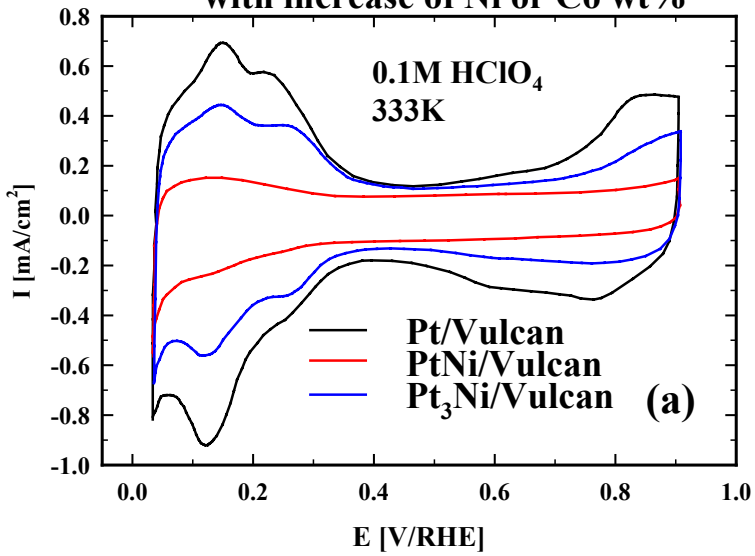
- catalysts: 10, 20, 30, 40% Pt/C
- d=3.1 ± 1 nm, 3.3 ± 0.7 nm, 3.8 ± 1.7 nm, 4.7 ± 2.7 nm

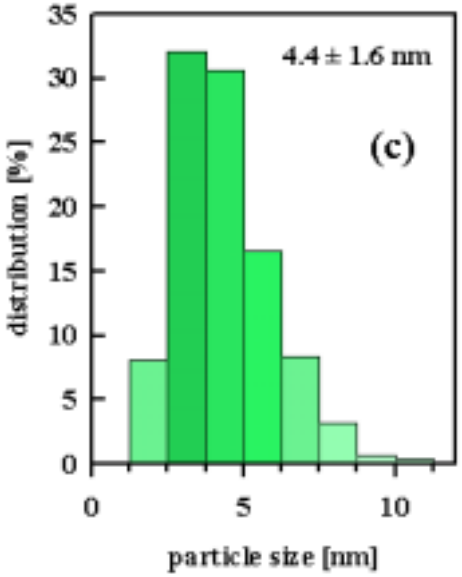
SA increases with SAD(111)

SA increases with SAD(100, e+c)

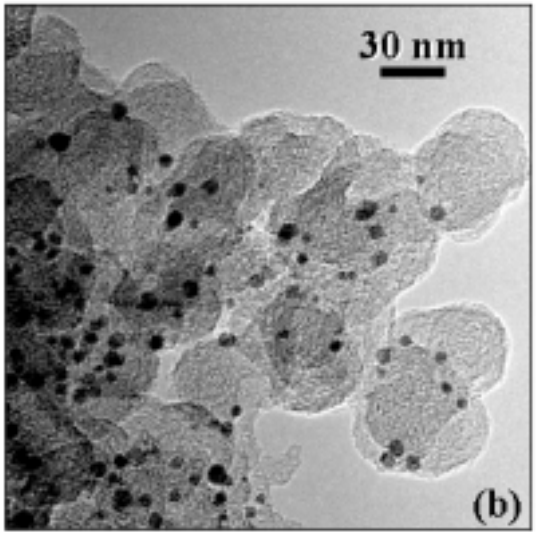
Characterization of PtCo/Ni Vulcan Catalysts

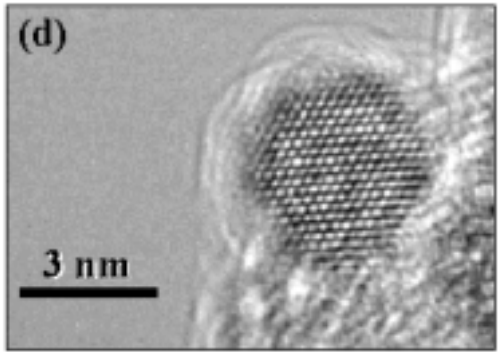
- H_{upd} coverage decreases with increase of Ni or Co wt%





- HR Transmision electron microscopy





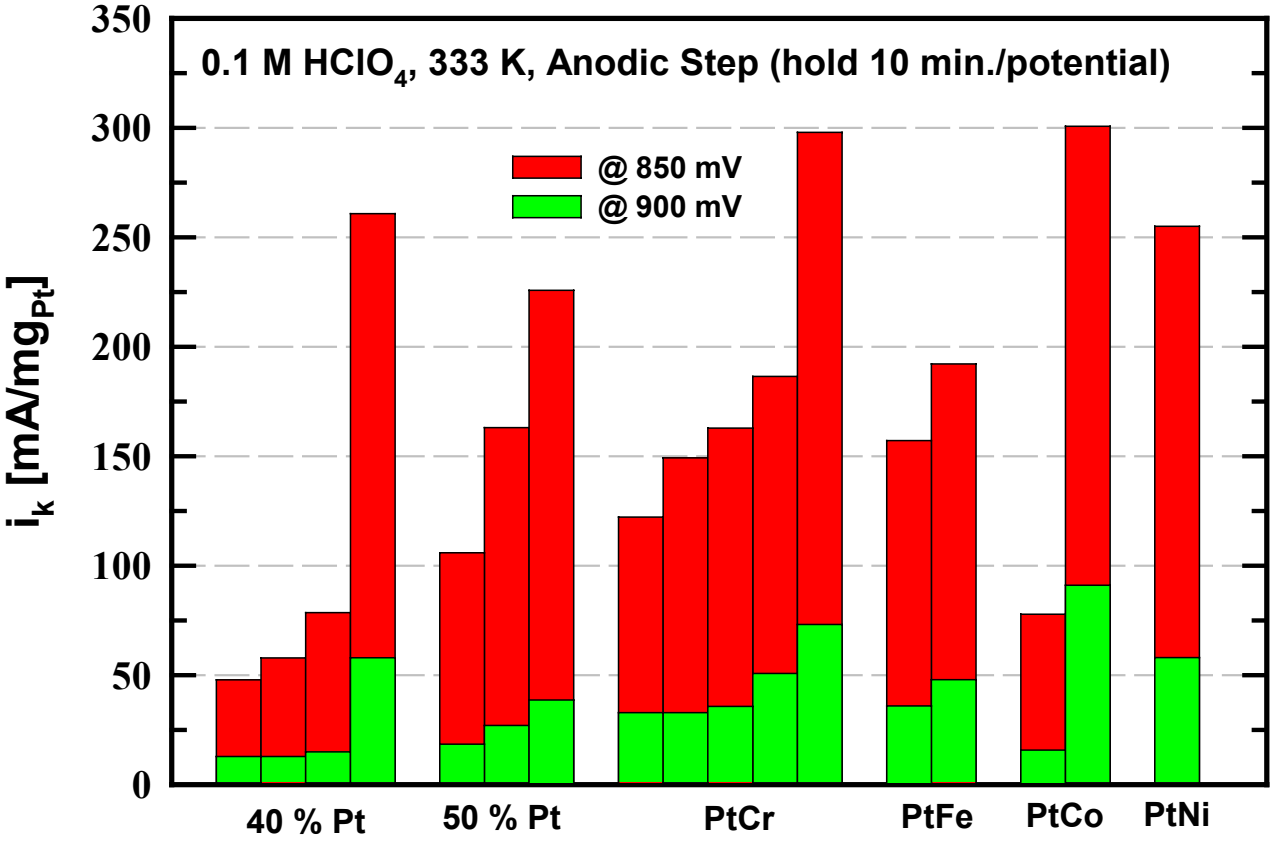
- Cubo-octahedral shape with (111) and (100) facets

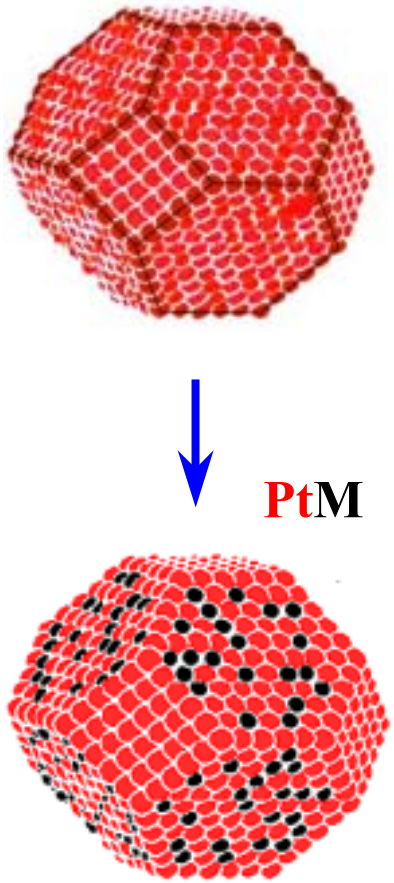
- Complete alloying

ORR Kinetics on Pt-bimetallic Surfaces

Fuel Cells Relevant Conditions

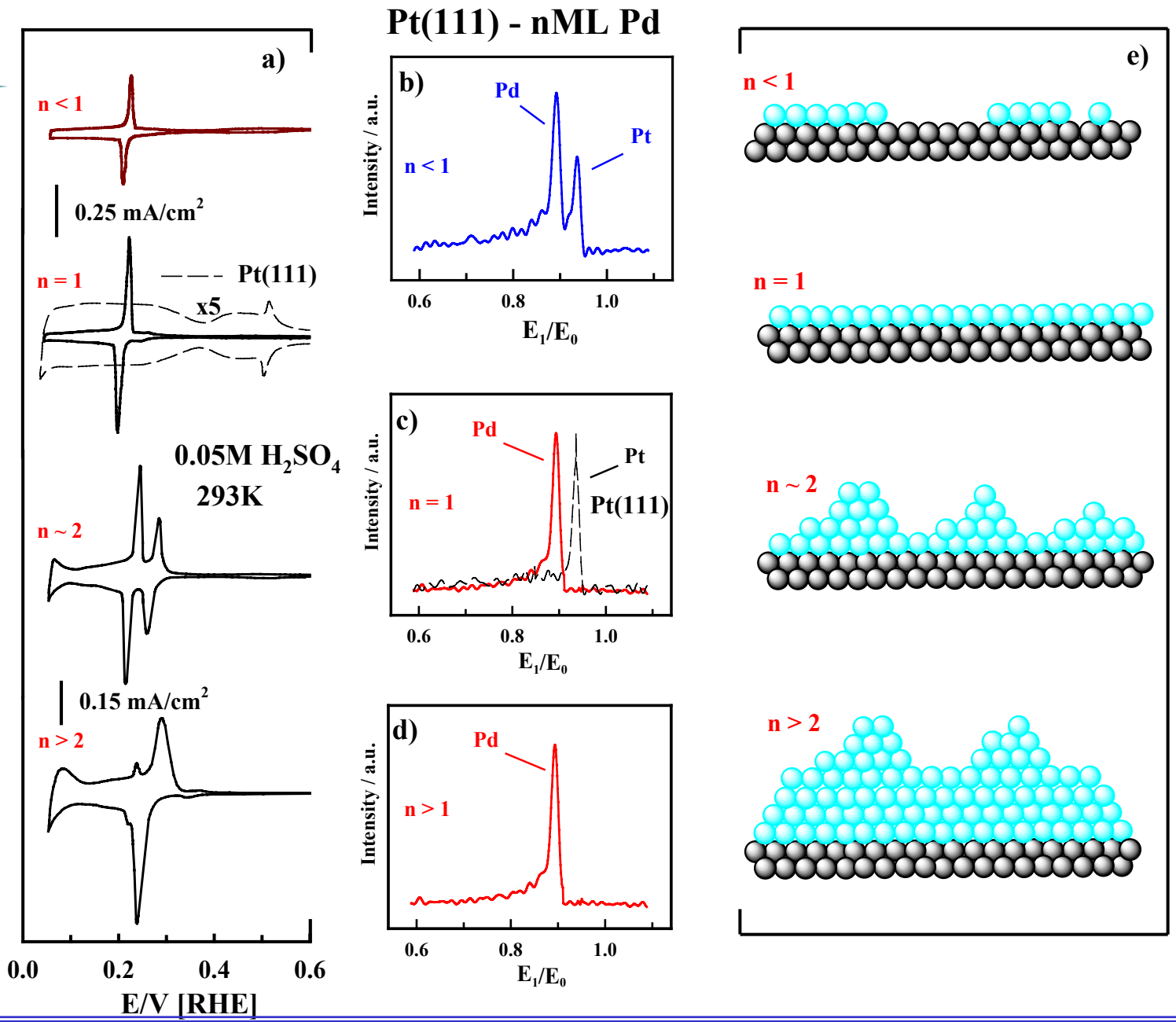
- Some Pt-M alloys have better performance than Pt
- Pt-Co has the highest activity



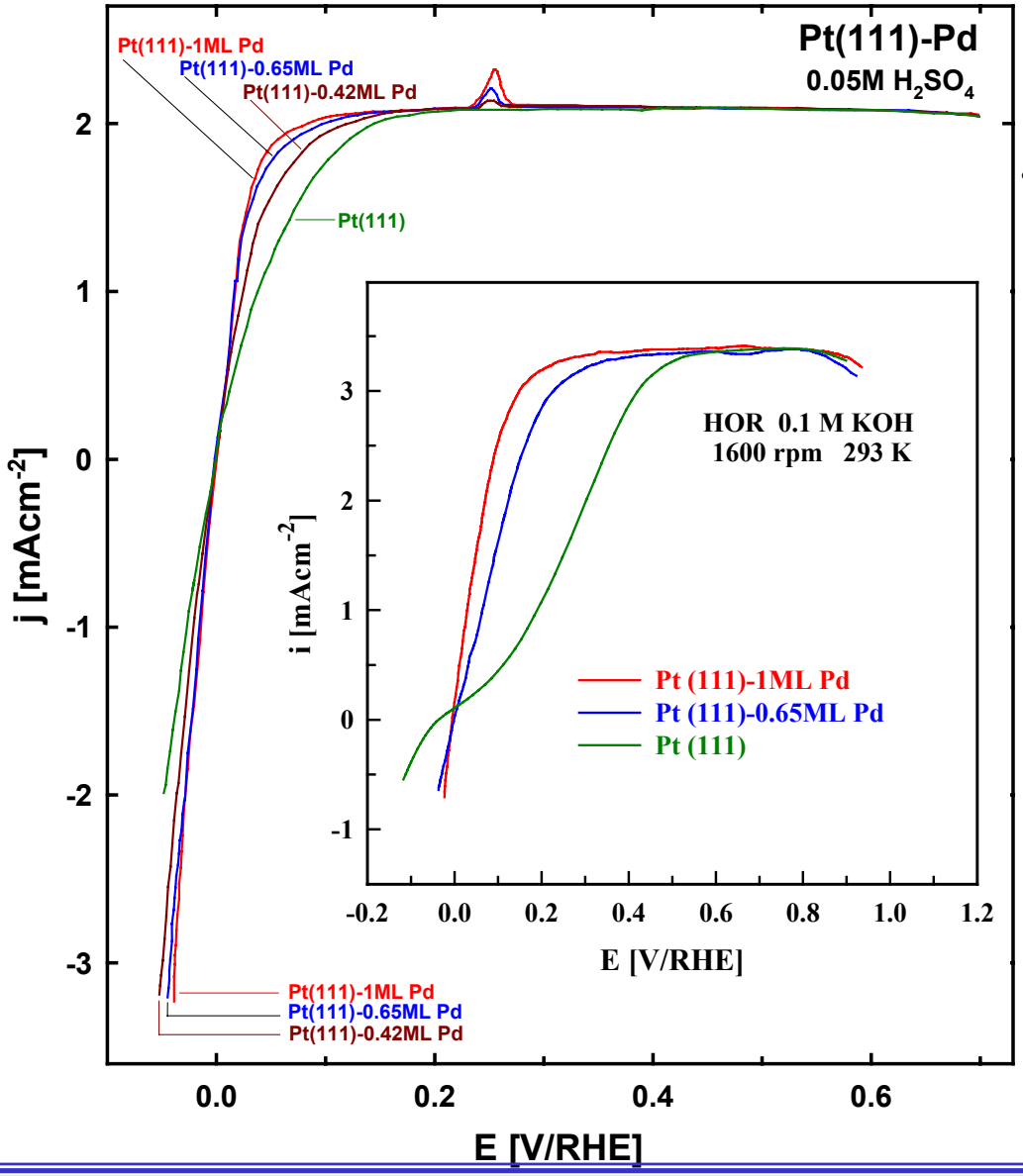


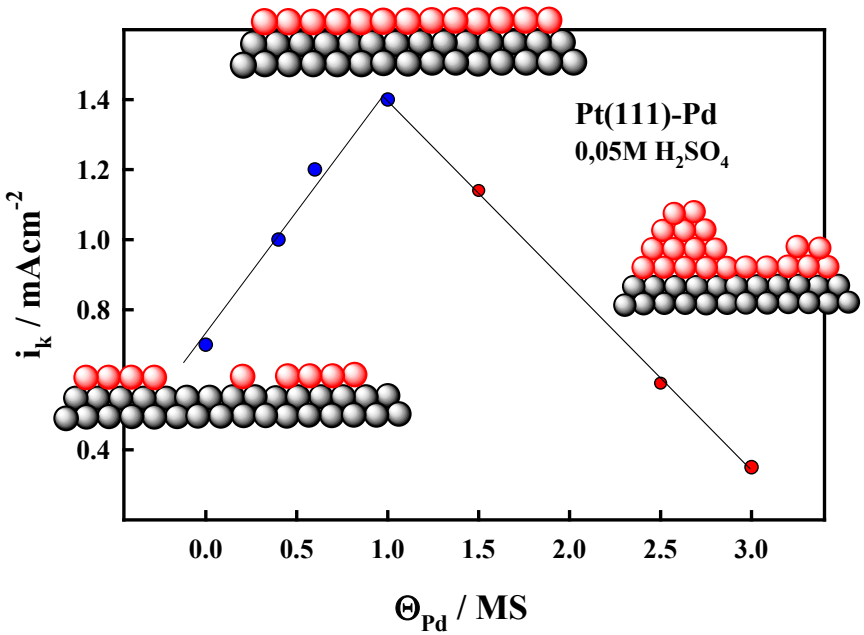
- Benefits:
  - Higher activity (!?)
  - Substitution of Pt

Pd thin metal films on Pt(111)



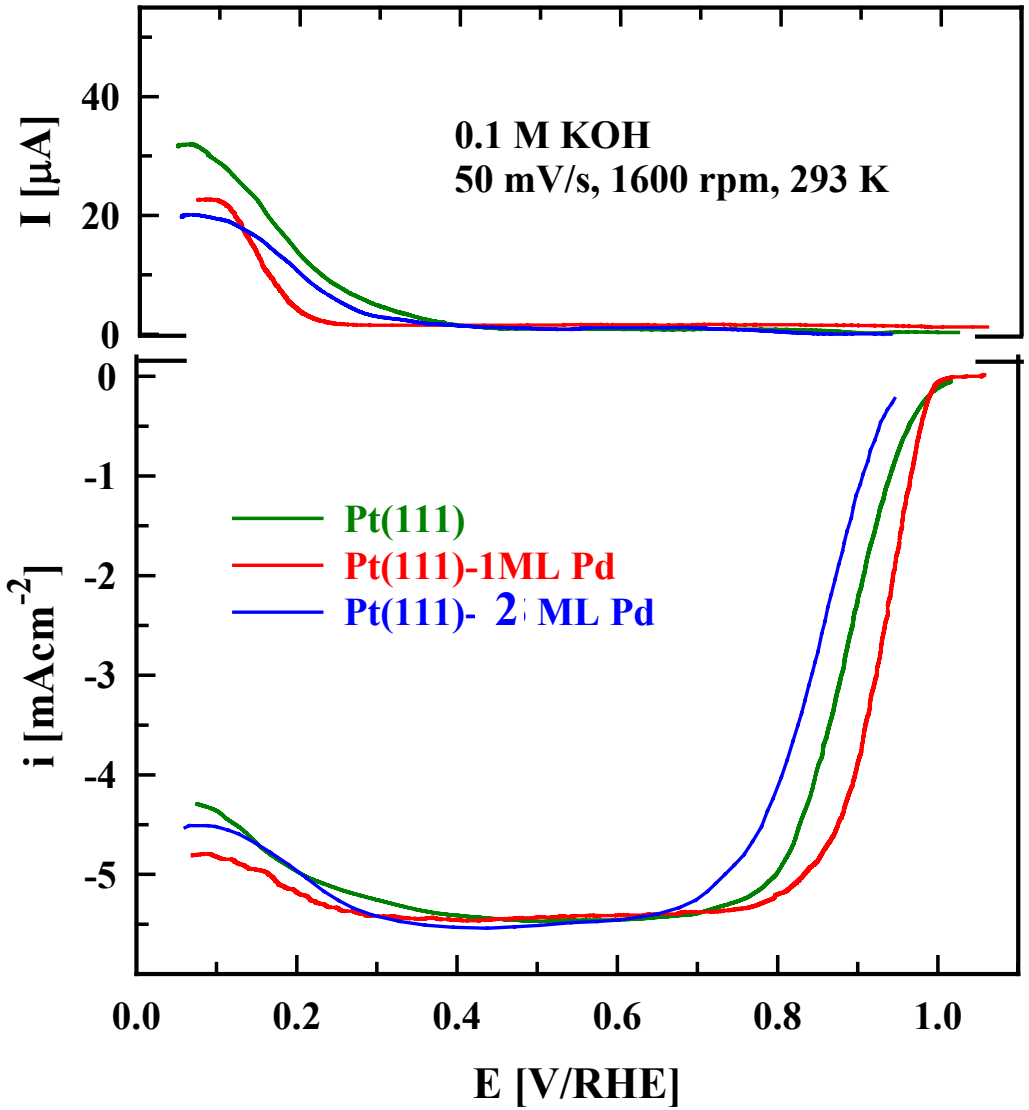
HER/HOR on Pt(111)-Pd in H_2SO_4/KOH

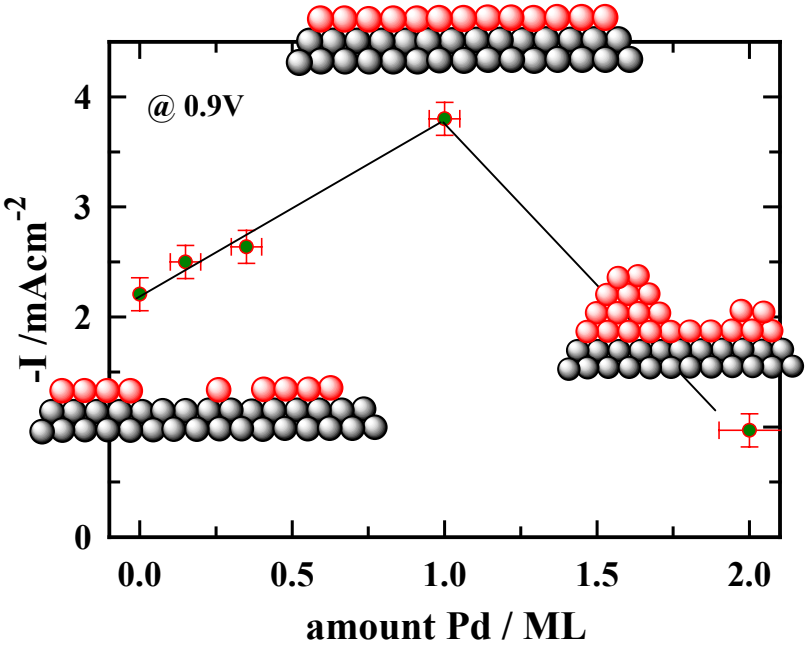




- Maximum catalytic activity for 1 ML of Pd film
  - Adsorption vs Absorption of H
- Activation energy:
  - Reduced by 50% on 1ML Pd

ORR on Pt(111)-x Pd in KOH

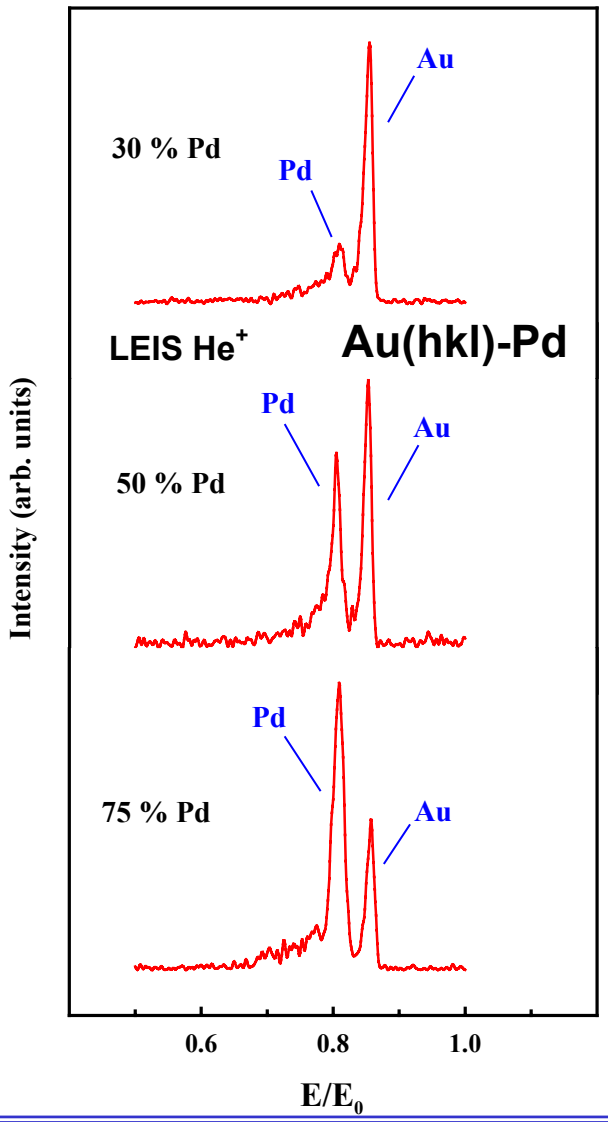




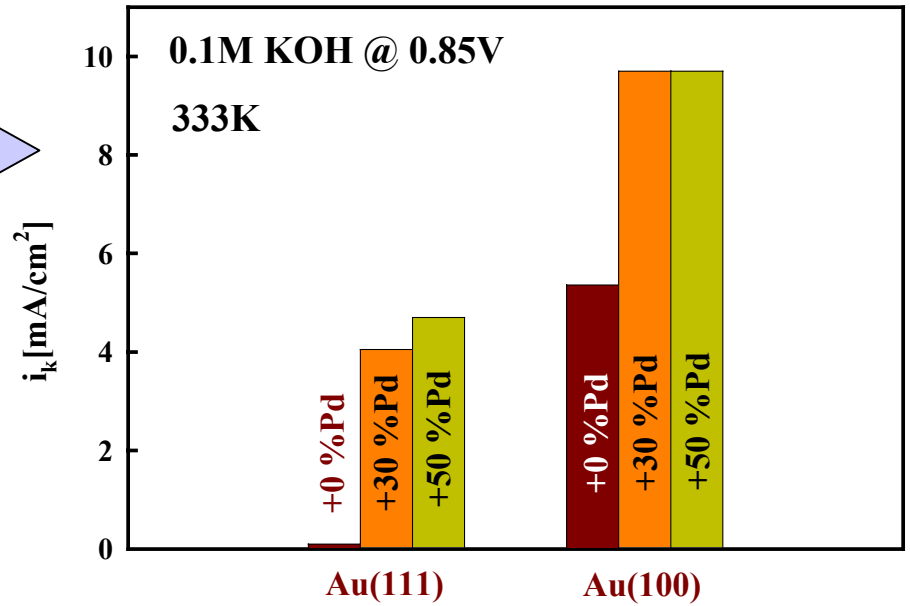
- "Vulcano Plot"
- Electronic Effect

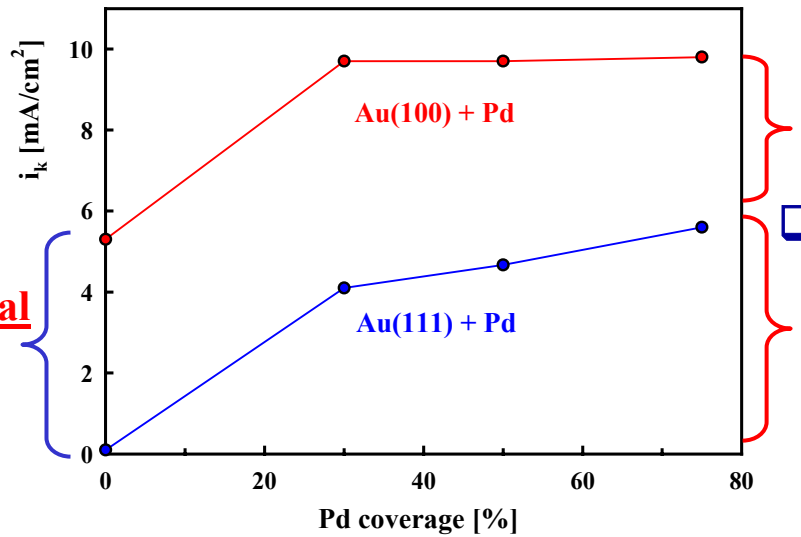
ORR on UHV Prepared Au(hkl)-Pd Alloy Surfaces

- Vapor deposition of Pd



ORR





- Structural Effect
- Electronic Effect