New Electrocatalysts For Fuel Cells

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This presentation does not contain any proprietary or confidential information

Project ID
#FC10

Overview

Budget

- Total project funding
  - DOE share 100 %
- Funding for FY05:
  $ 500 K
- Funding for FY06:
  $ 253 K

Barriers

- DOE Technical Barriers for Fuel Cell Components
  - Q. Electrode Performance

Partners

- Interactions/ collaborations

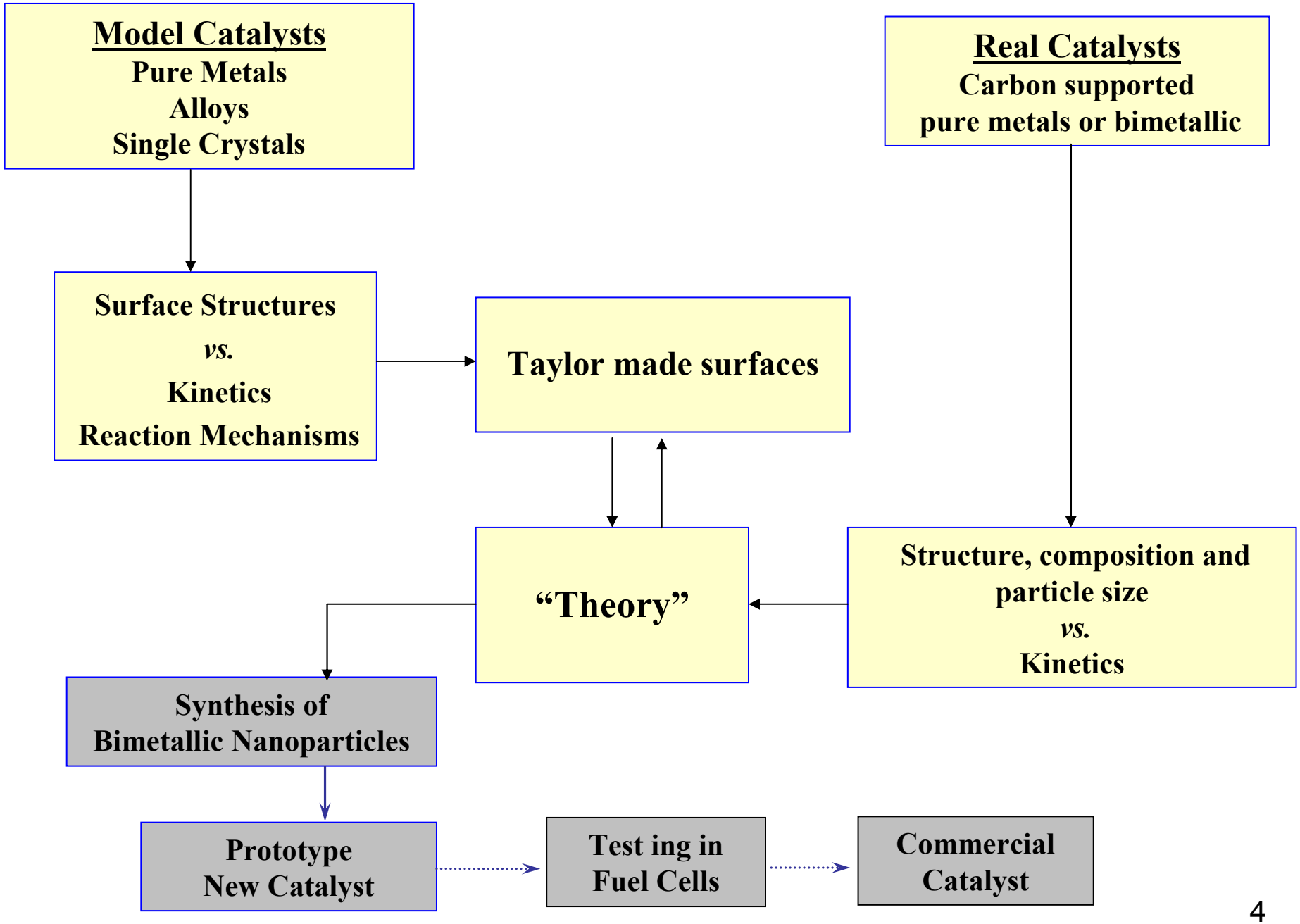
General Motors Alternative Power Center (GAPC)

3M

Objectives

- Reduce cost by reduction of precious metal loading (long term)
- Improve catalyst durability (long term)
- Bring all ongoing work to a conclusion in FY06
- Publish all work in some form, i.e. either archival literature or government reports

LBNL *Materials-by-Design Approach*



Anticipated Gains with Pt Bimetallic Nanoparticles

- **Substitution of Pt atoms "buried" in interior of particle with atoms of non-Pt group element atoms**
- **Possibly higher activity for Pt surface atoms by electronic modification from intermetallic bonding (alloying effect)**
  - **Norskov and Hammer theory correlates the position of d-band center to H_{ad} and O_{ad} adsorption energies**
- **Pt loading reduced (without any loss of performance) by a factor of 4 –5 seems possible**

Outline of Presentation

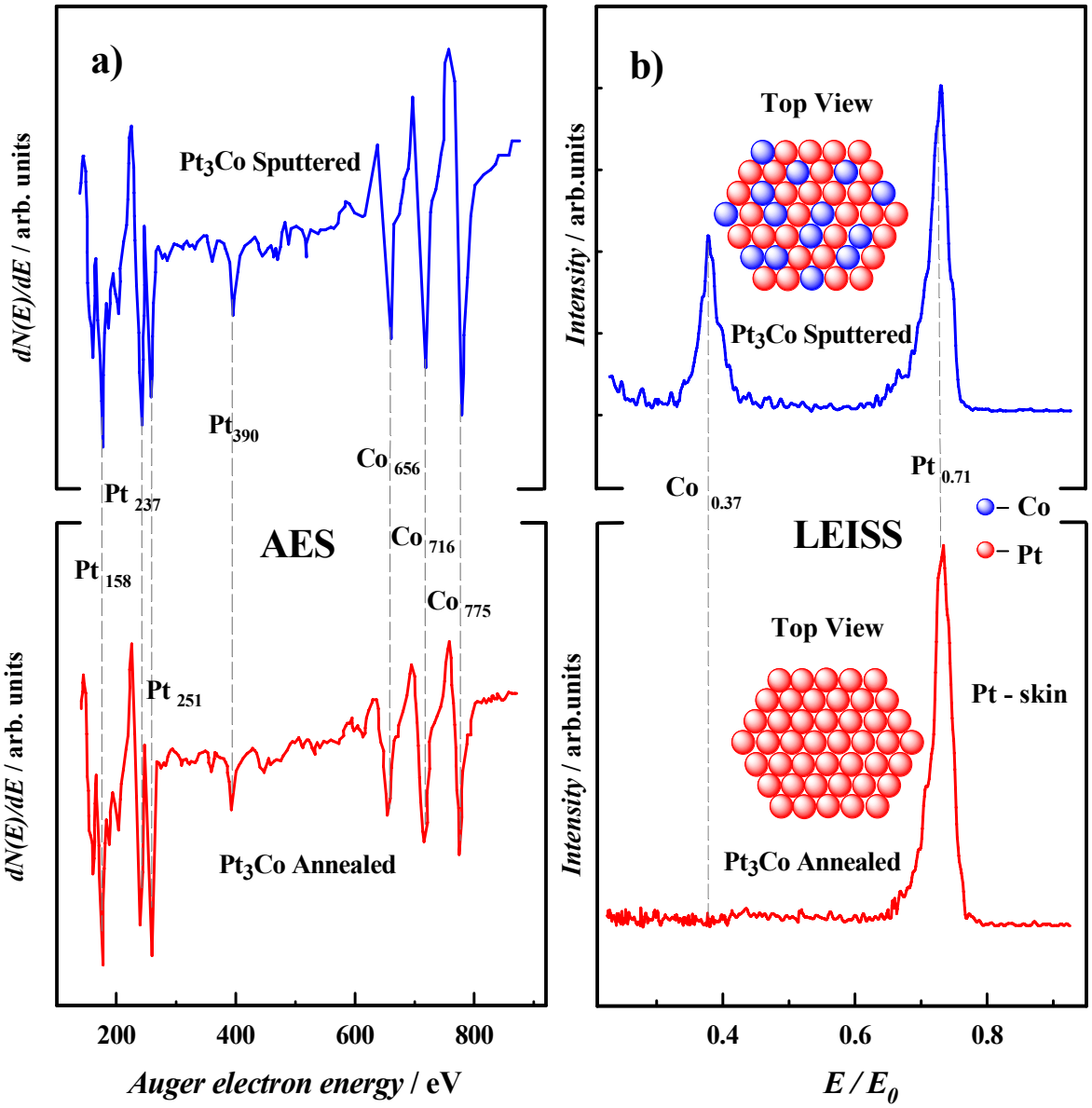
Putting the finishing touches on the following topics:

- Skin vs.skeleton near-surface structures and the relation to kinetics for the oxygen reduction reaction (ORR)

- Understanding the effect of subsurface transition metal atoms on the activity of Pt_3TM surfaces for the ORR – Norskov and Hammer theory of d-band center as measure of electronic effect of subsurface transition metal atoms on heat of adsorption of intermediates

New Results with $Pt_3Ni(hkl)$ single crystals point to new opportunities to improve intrinsic activity via control of nanoparticle shape

Summary: Near-surface characterization of Pt_3TM

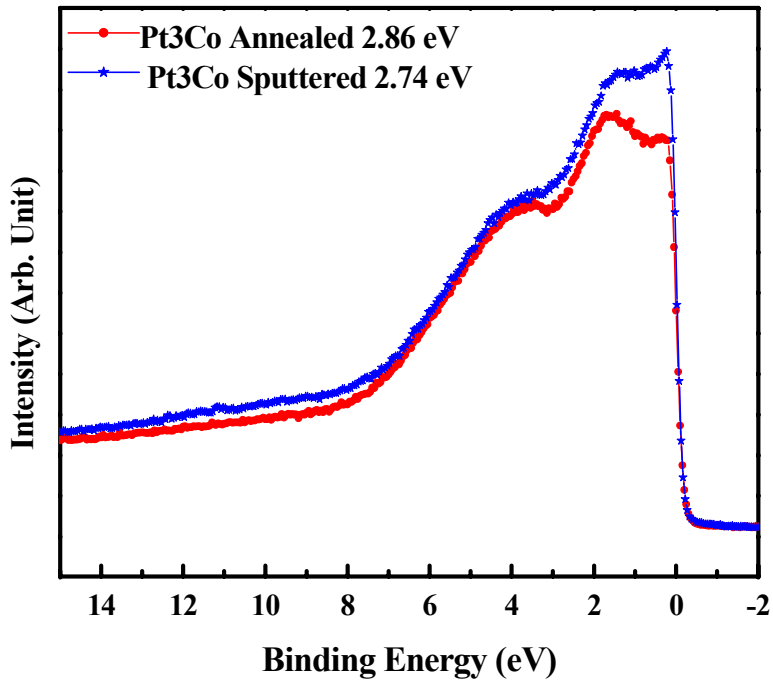


AES: absence of carbon and oxygen, Pt enrichment after annealing

LEISS: surface composition

sputtered: Pt –75%, Co – 25%

annealed: Pt –100% ⇨ Pt 'skin'



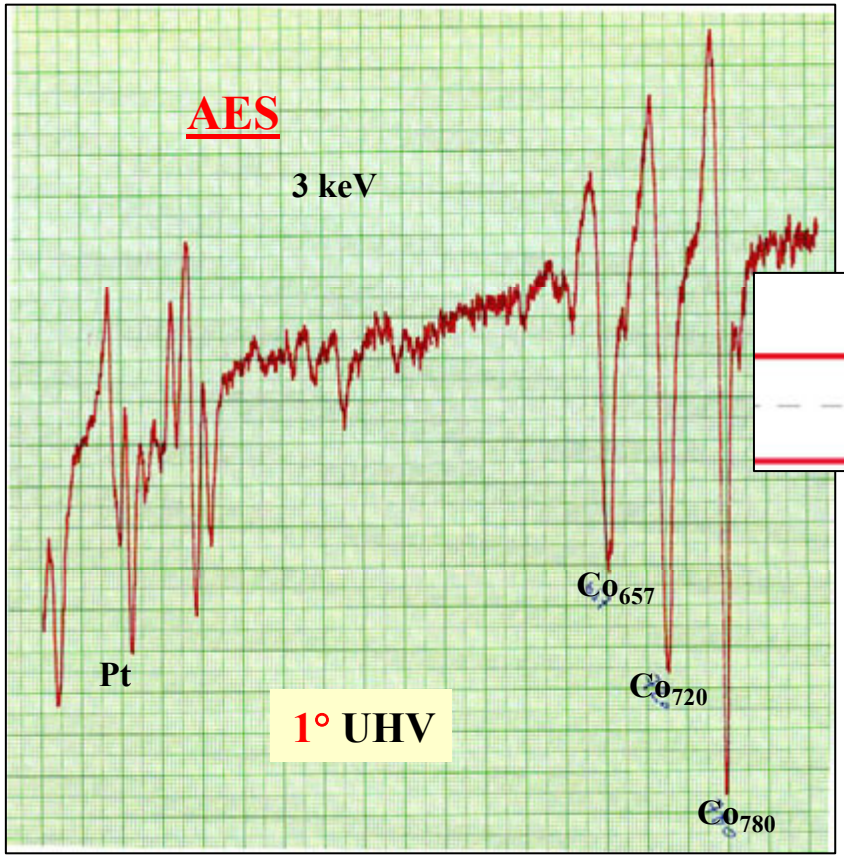
UPS: d – band center position

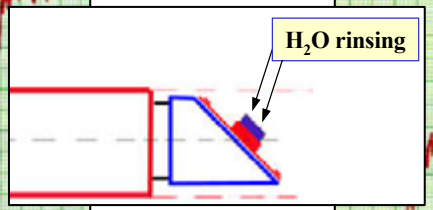
sputtered: 2.74 eV

annealed: 2.86 eV

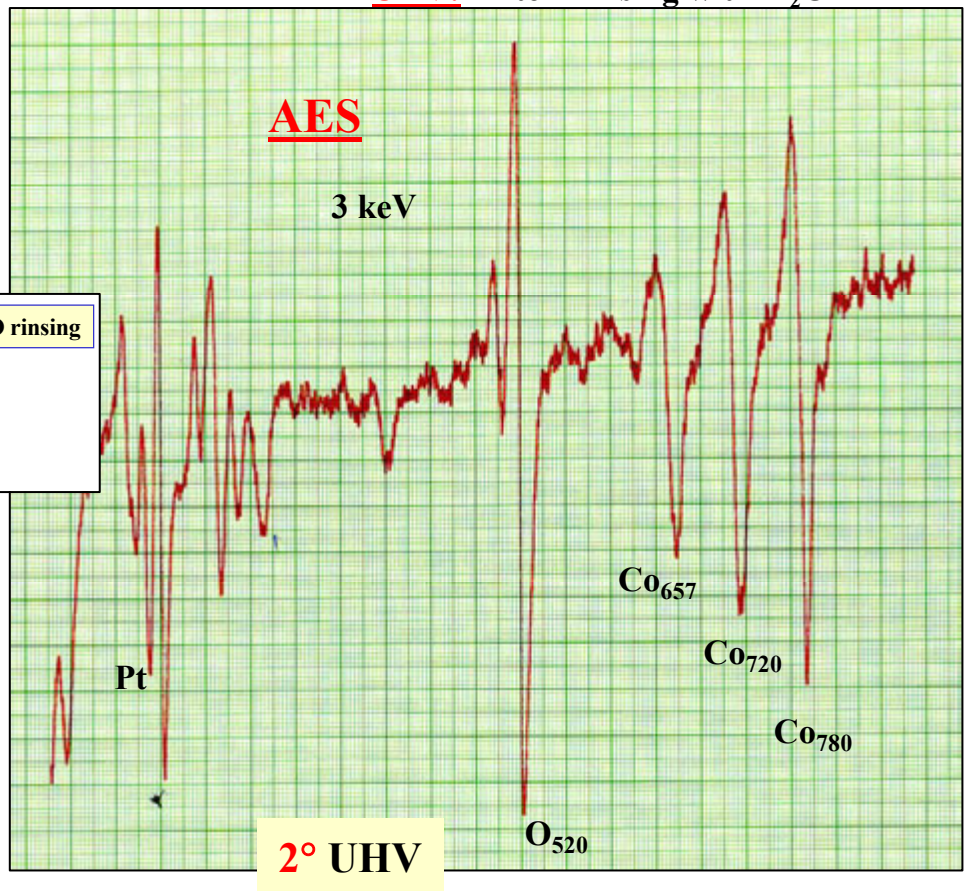
Summary: Stability of Pt_3TM

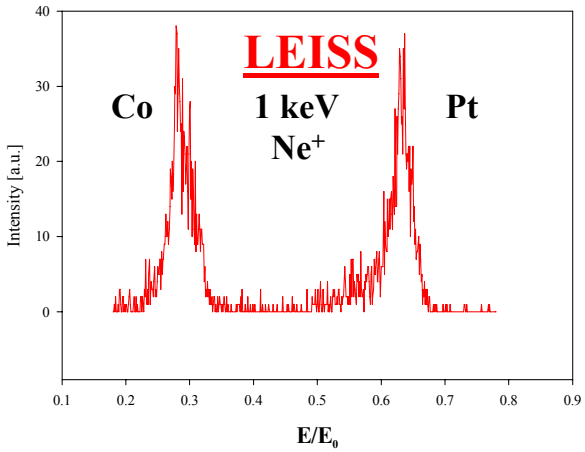
UHV: Before Transfer

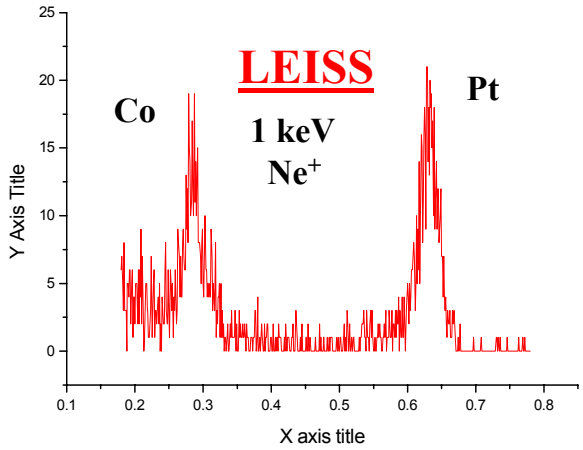




UHV: After Rinsing with H_2O

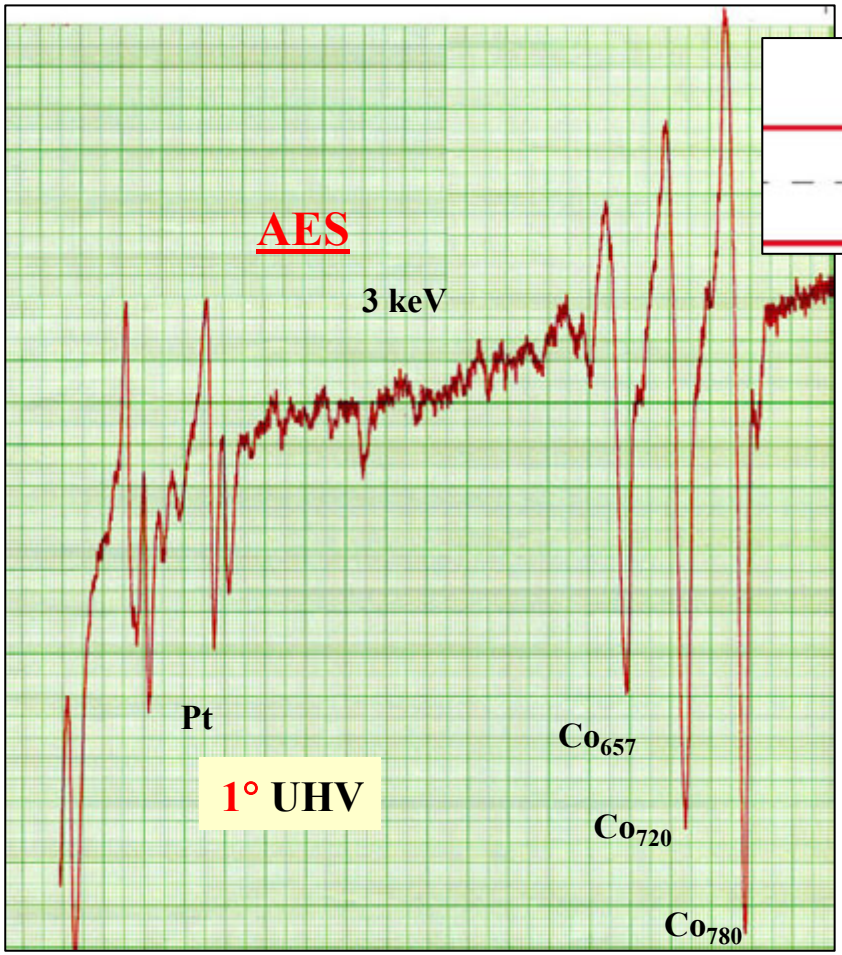


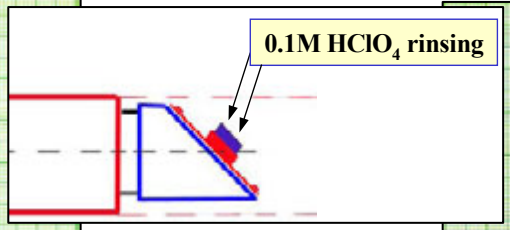




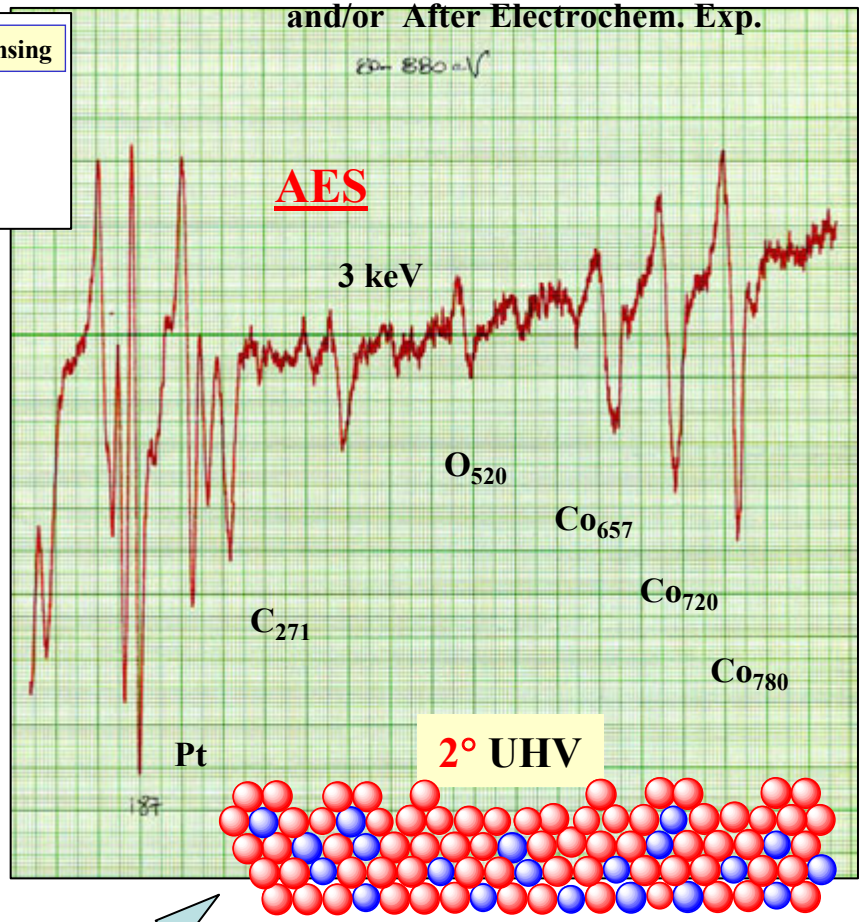
Summary: Stability of Pt_3TM

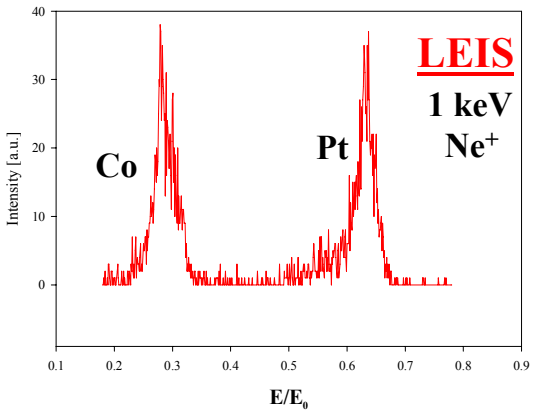
UHV: Before Transfer



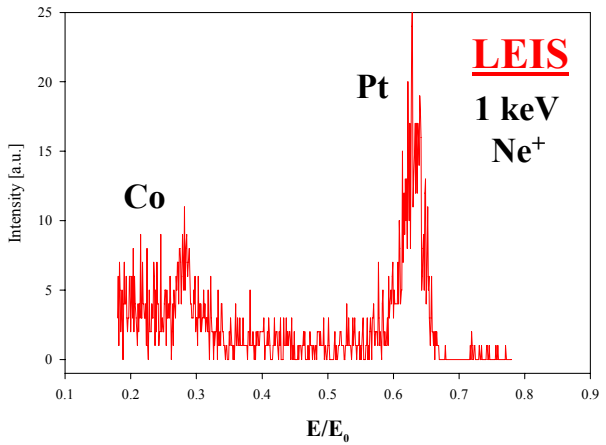


UHV: After rinsing with 0.1M $HClO_4$ and/or After Electrochem. Exp.

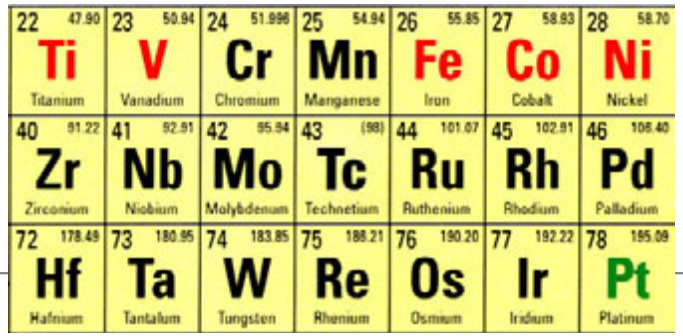


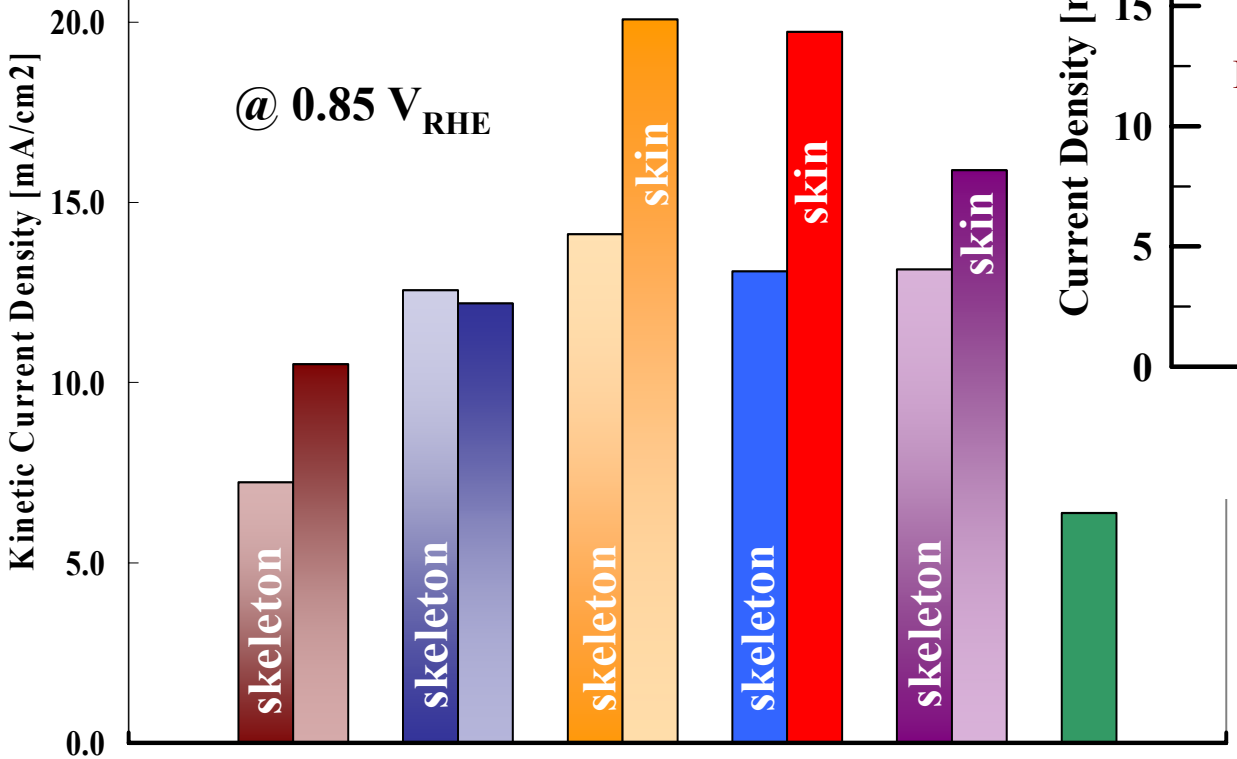


Co leaching out from the surface layers and formation of a **Pt "skeleton"** structure

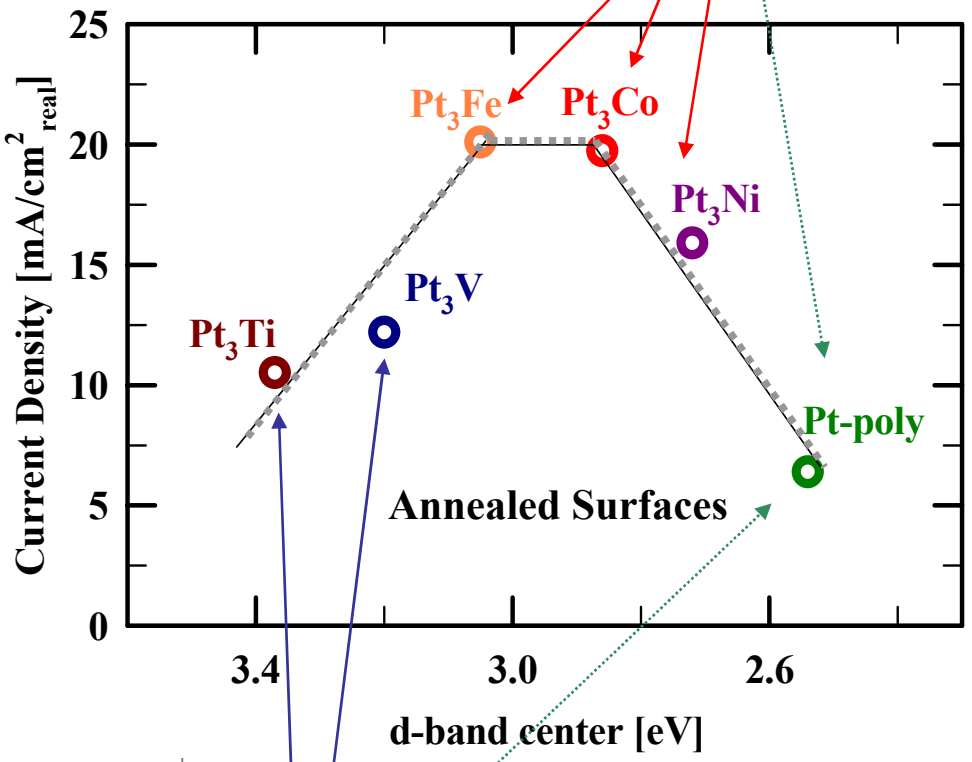


Summary: ORR activity vs. d-band center Pt_3TM





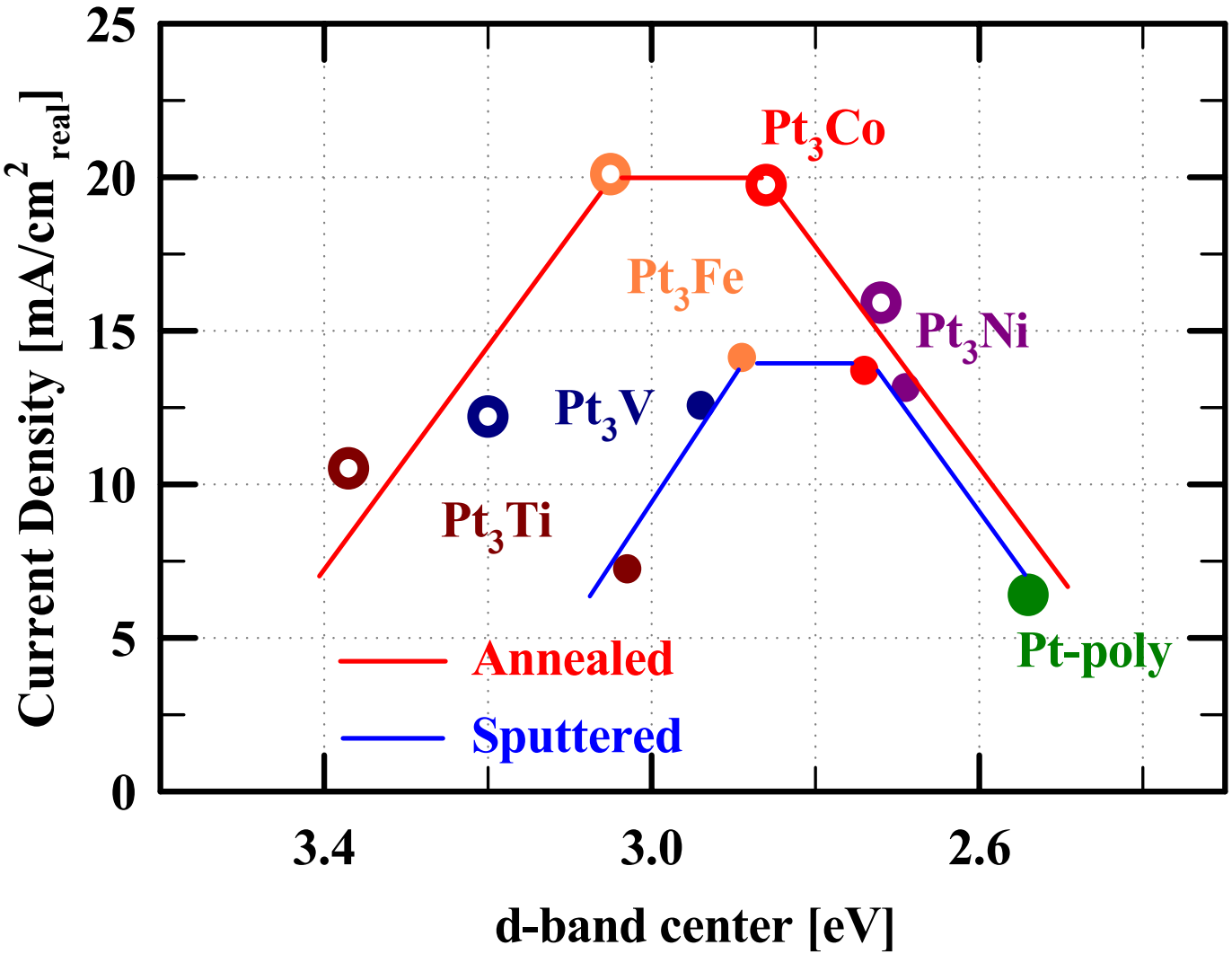
	Pt_3Ti	Pt_3V	Pt_3Fe	Pt_3Co	Pt_3Ni	Pt-poly
Sputtered	3.03 eV	2.94 eV	2.89 eV	2.74 eV	2.69 eV	2.53 eV
Annealed	3.37 eV	3.20 eV	3.05 eV	2.86 eV	2.72 eV	2.54 eV



$(1-\Theta_{ad})$ term

$(1-\Theta_{ad})$ term and ΔG_{ad} term

ORR activity vs. d-band center: Pt_3TM annealed(skin) vs sputtered(skeleton) surfaces



Summary: Skin vs. Skeleton near-surface structure

1. ⇨ **Complete segregation of Pt over Pt_3M surfaces after annealing in UHV**

Only Pt atoms over Pt_3(Co, Ni, Fe)

Possible to create two different surfaces in UHV: Pt-skin and Pt_3M

75% Pt and 25% M

2. ⇨ **Alloying components are dissolved instantaneously from the surface in contact with acid electrolyte. Pt-skeleton surface is formed**

3. ⇨ **Pt-skin, Pt-skeleton and Pt-poly have the same surface composition but different electronic properties || Pt-skin has protective role**

4. ⇨ **Different position of d-band center provides different adsorption properties**

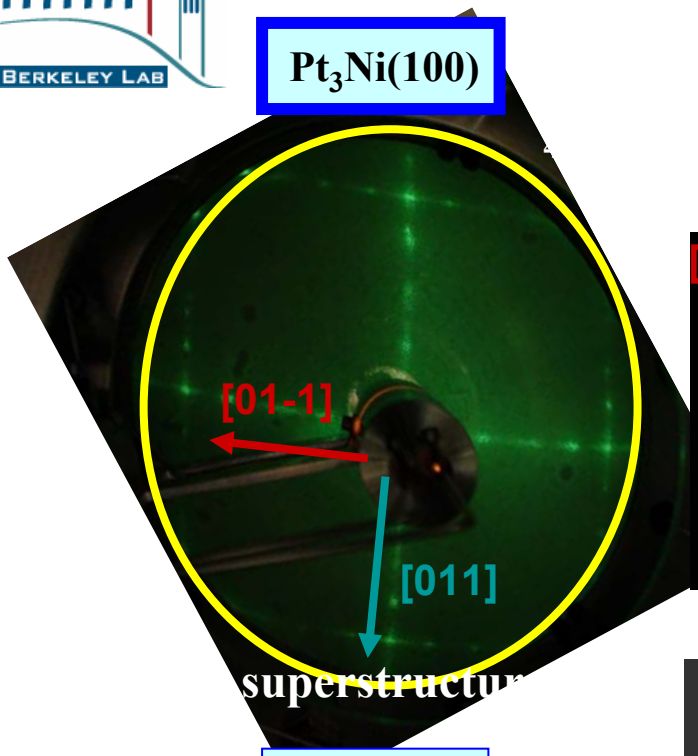
5. ⇨ **The same/similar Tafel slope, activation energy, peroxide production → ORR pathway**

6. ⇨ **Blocking species are less adsorbed on Pt-skin, kinetics determined by (1-Θ) term**

7. ⇨ **With decrease of atomic number, d-band center shift increases, kinetics determined by both (1-Θ) term and ΔG_{ad} term**

$Pt_3Ni(hkl)$: Surface Characterization | LEED

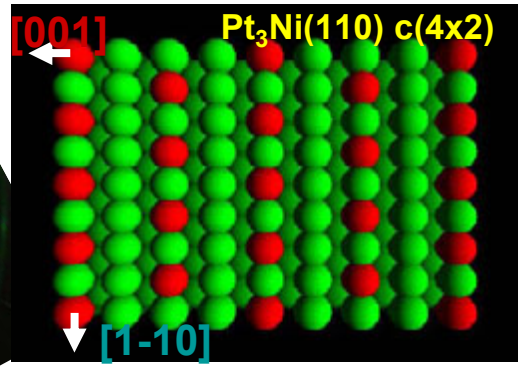
$Pt_3Ni(100)$



$Pt_3Ni(111)$

-Does not have a superstructure

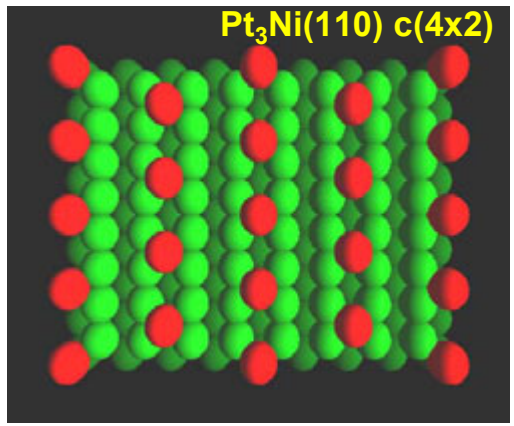
-p(1x1)



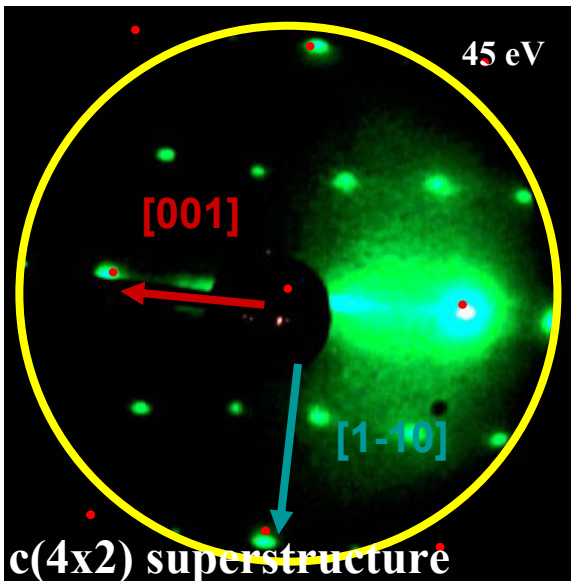
$Pt_3Ni(110)$

-c(4x2) superstructure with different arrangement of surface atoms

-Different possible compositions

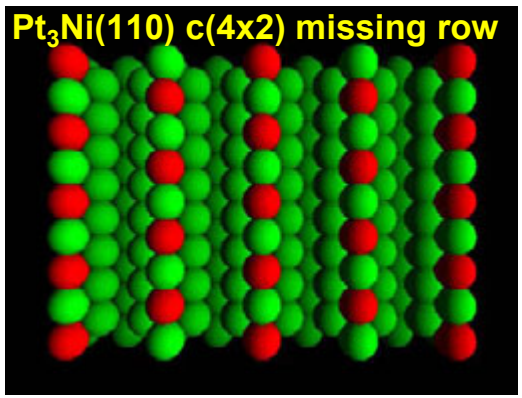


$Pt_3Ni(110)$

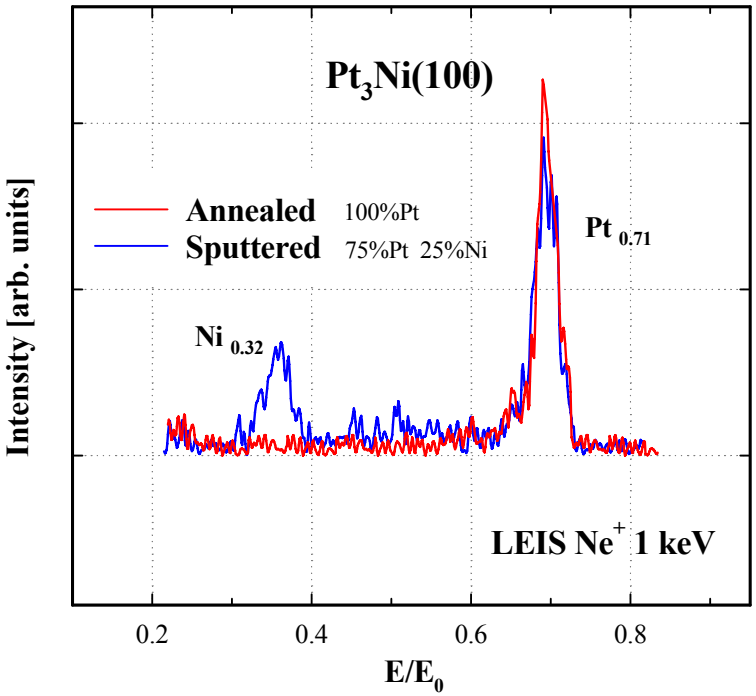


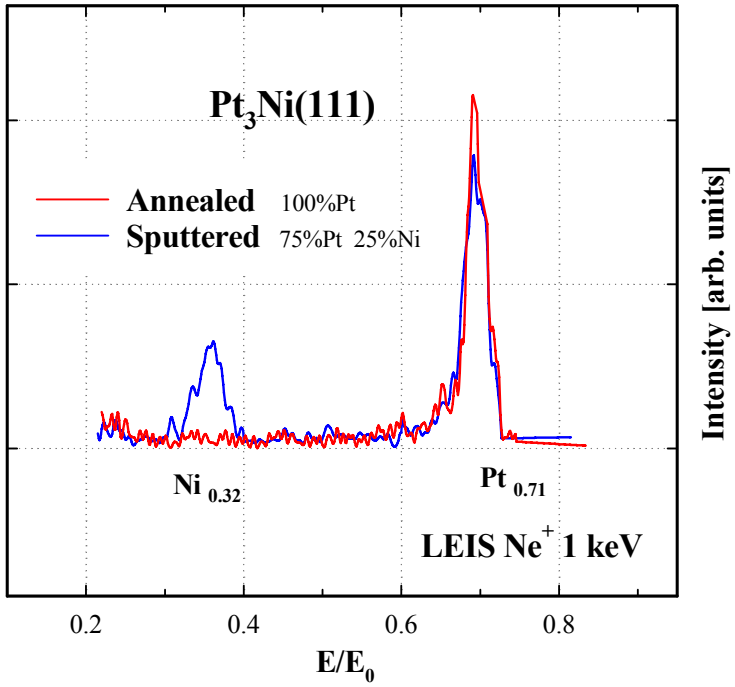
Pt

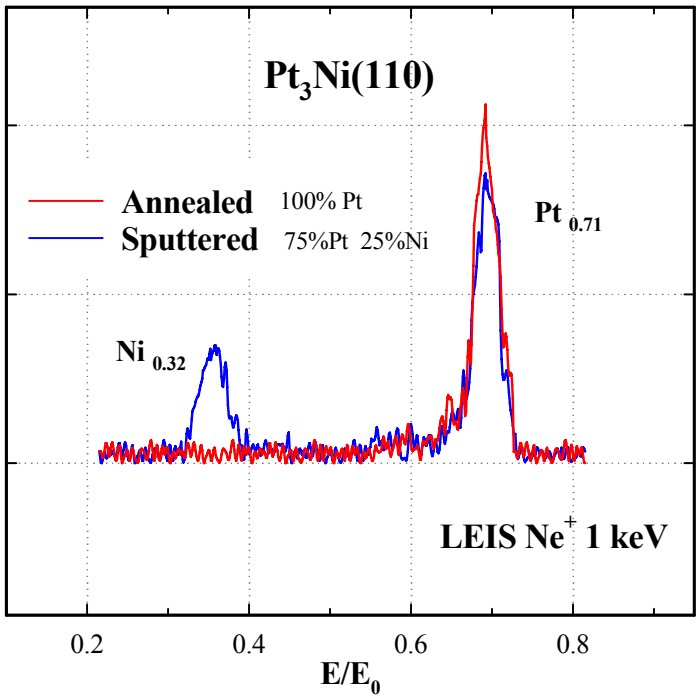
Ni



$Pt_3Ni(hkl)$: Surface Characterization

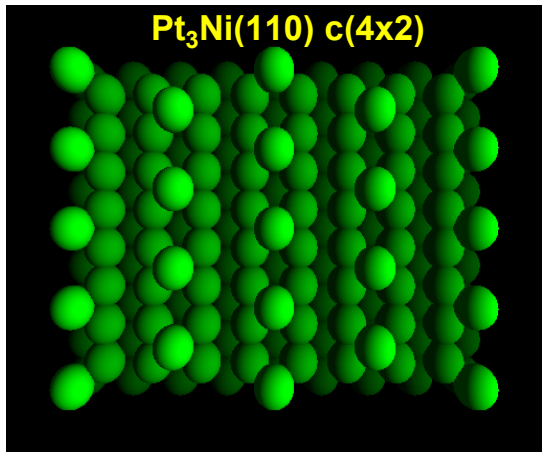




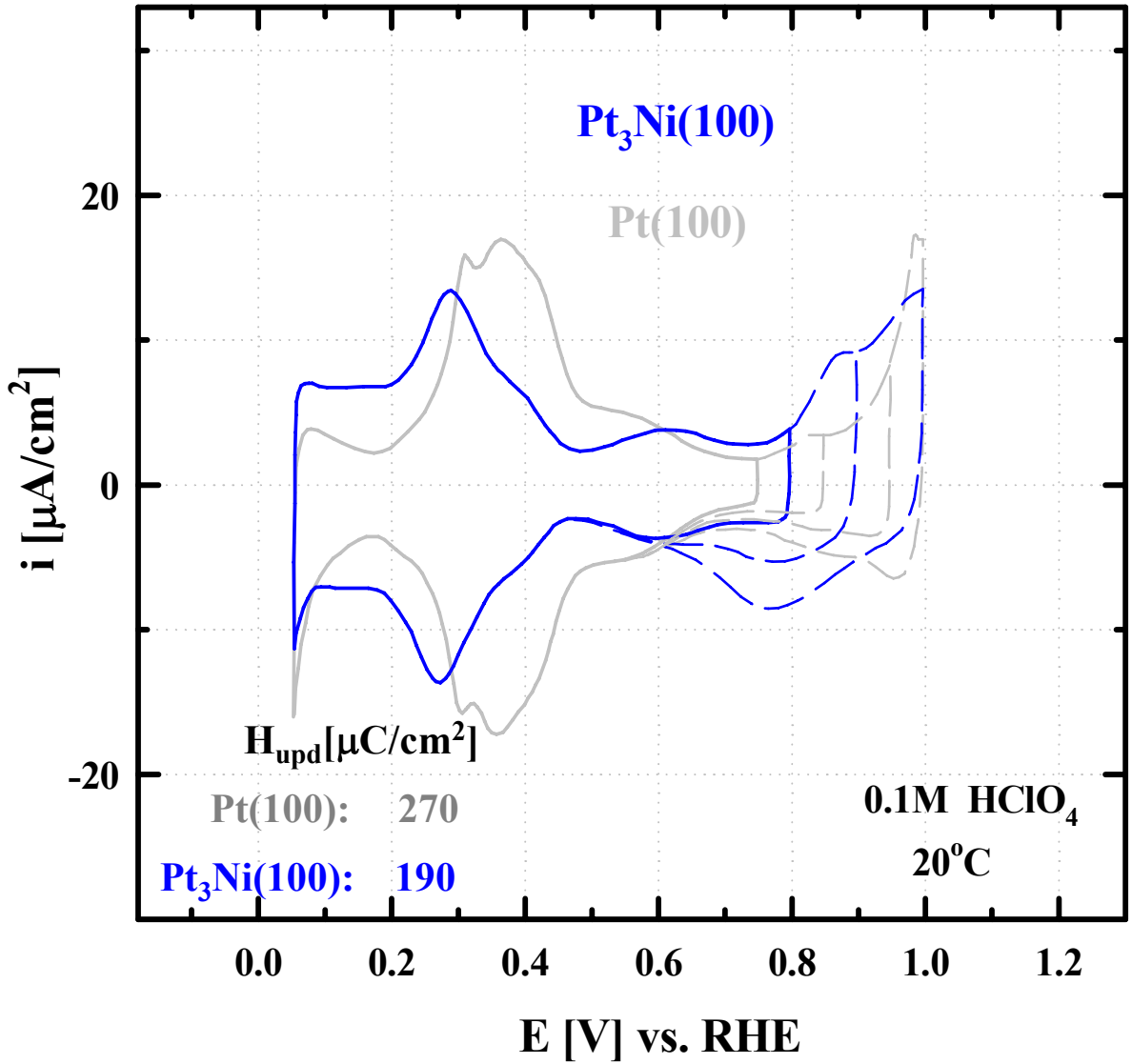


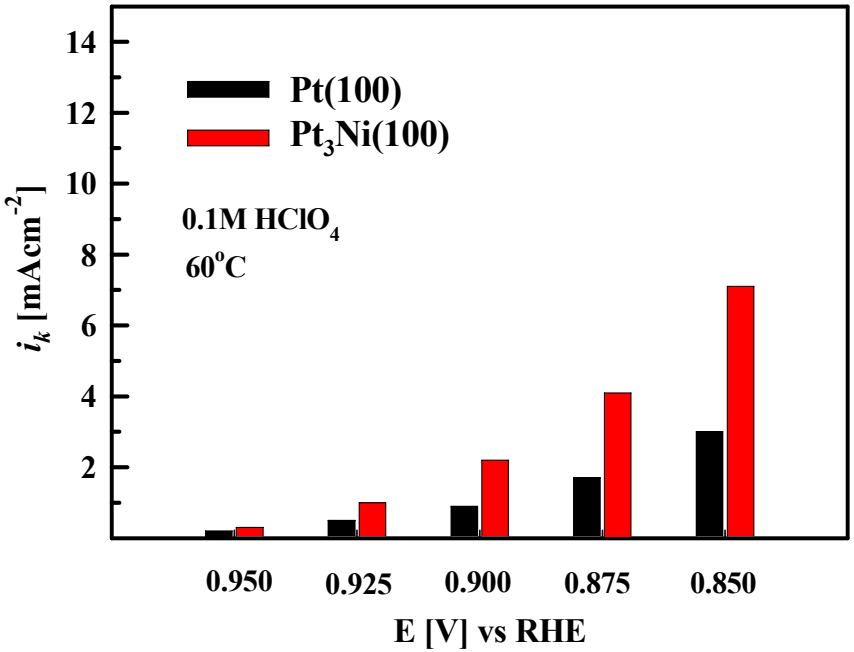
❑ **LEISS:**

-Complete Pt enrichment on the annealed $Pt_3Ni(hkl)$ surfaces



$Pt_3Ni(100)$: EC Characterization

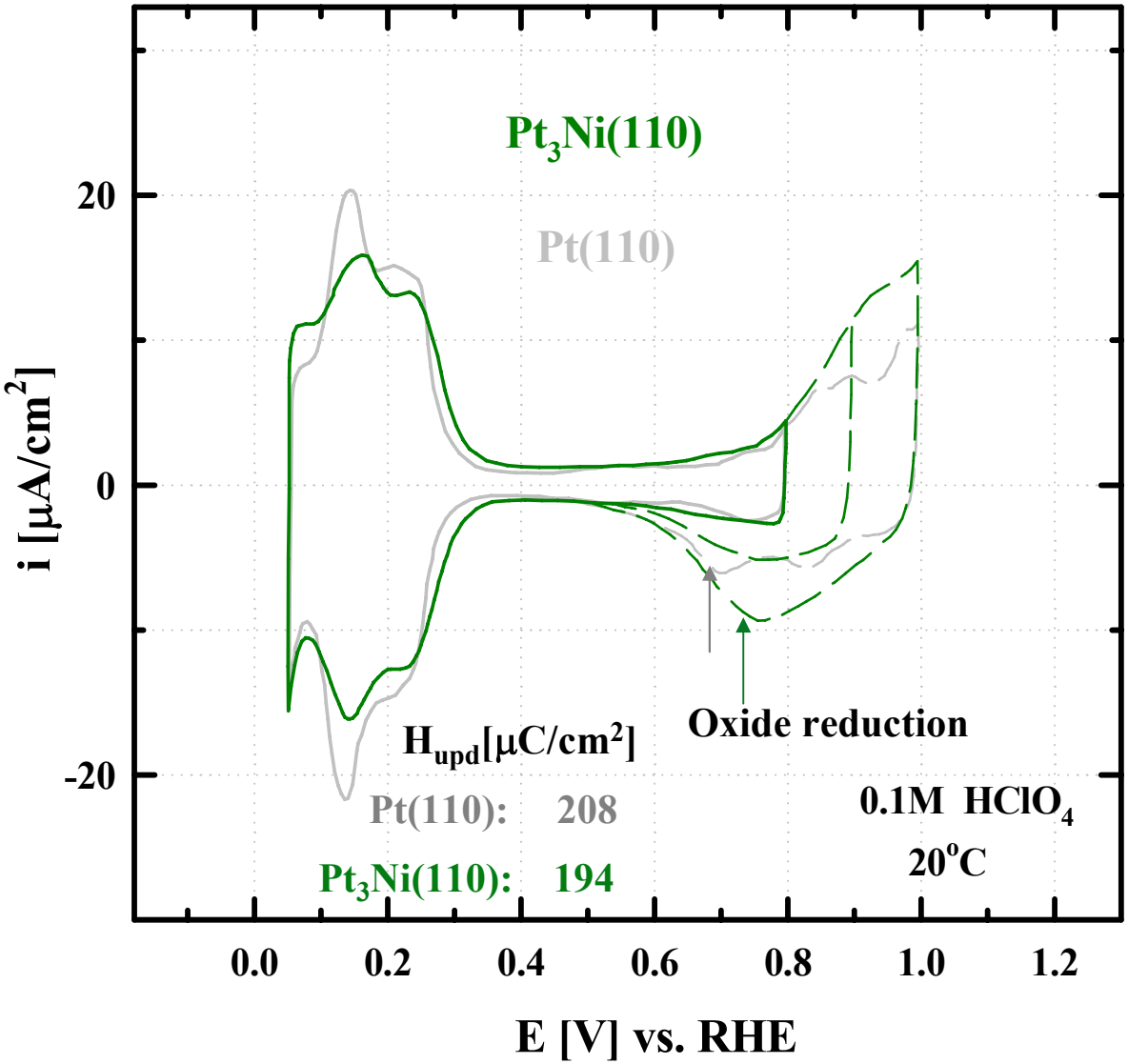


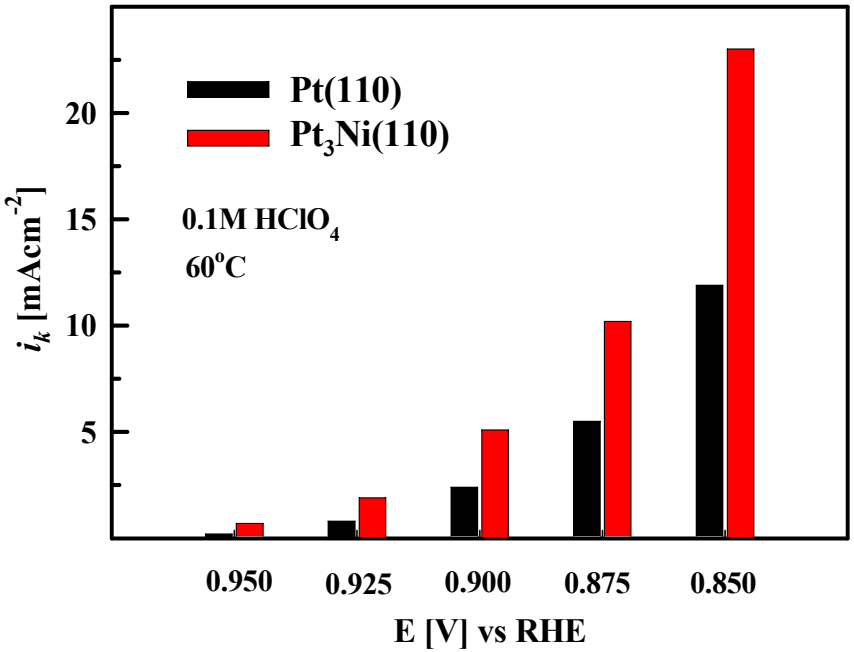


	Pt(100)	$Pt_3Ni(100)$
I_k @ 0.850V :	3 ± 0.3	7.1 ± 0.7
I_k @ 0.875V :	≈ 1.7	≈ 4.1
I_k @ 0.900V :	≈ 0.9	≈ 2.2
I_k @ 0.925V :	≈ 0.5	≈1.0
I_k @ 0.950V :	≈ 0.2	≈ 0.3

Activity Improvement Factor: 2.3

$Pt_3Ni(110)$: EC Characterization

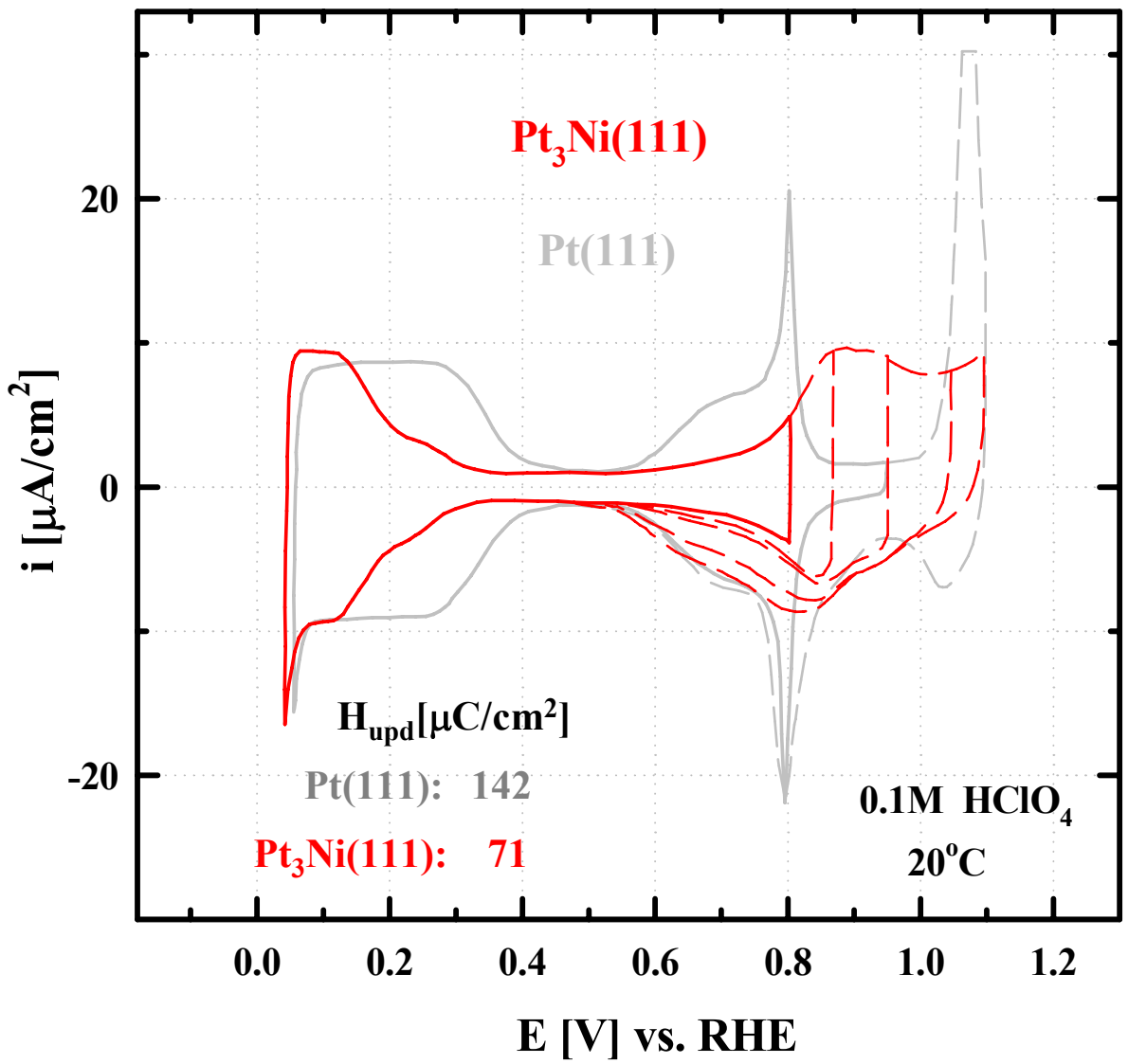


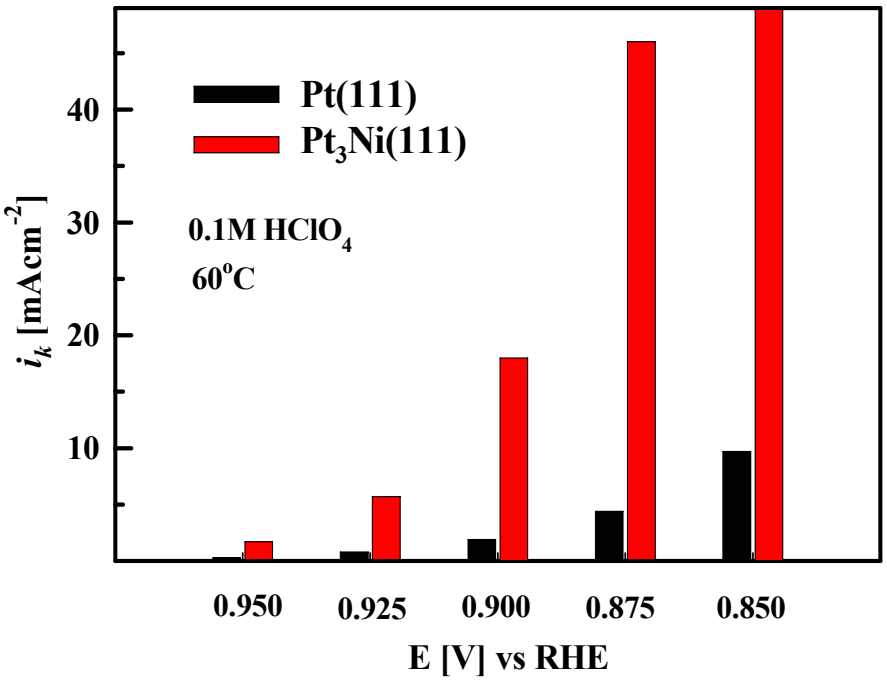


	Pt(110)	$Pt_3Ni(110)$
I_k @ 0.850V :	11.5 ± 1	23 ± 2
I_k @ 0.875V :	≈ 5.0	≈ 10.7
I_k @ 0.900V :	≈ 2.2	≈ 5.1
I_k @ 0.925V :	≈ 0.7	≈ 1.9
I_k @ 0.950V :	≈ 0.2	≈ 0.7

Activity Improvement Factor: 2.1

$Pt_3Ni(111)$: EC Characterization

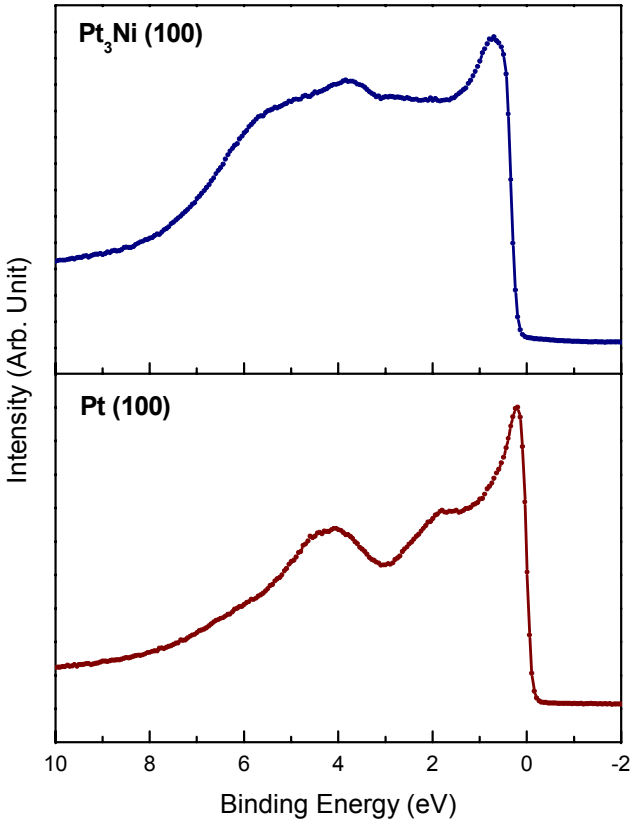


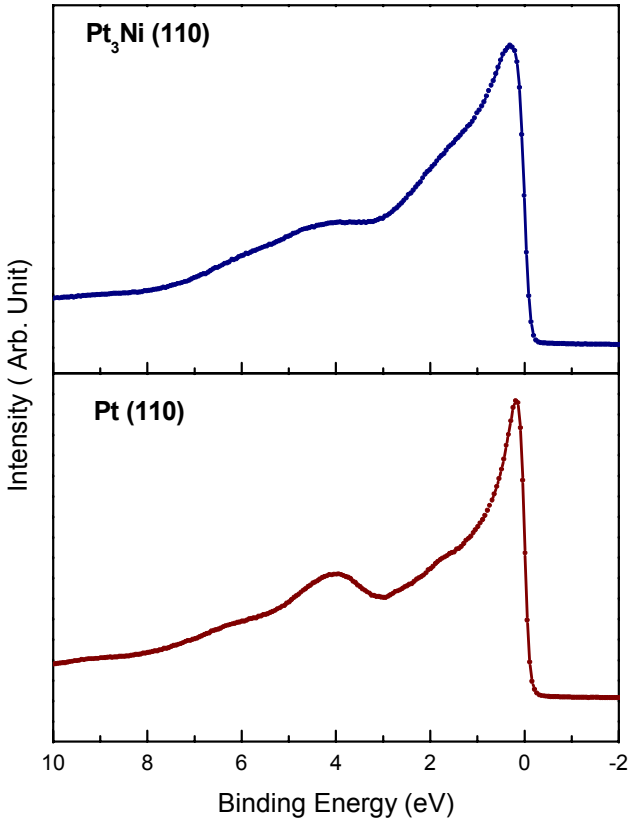


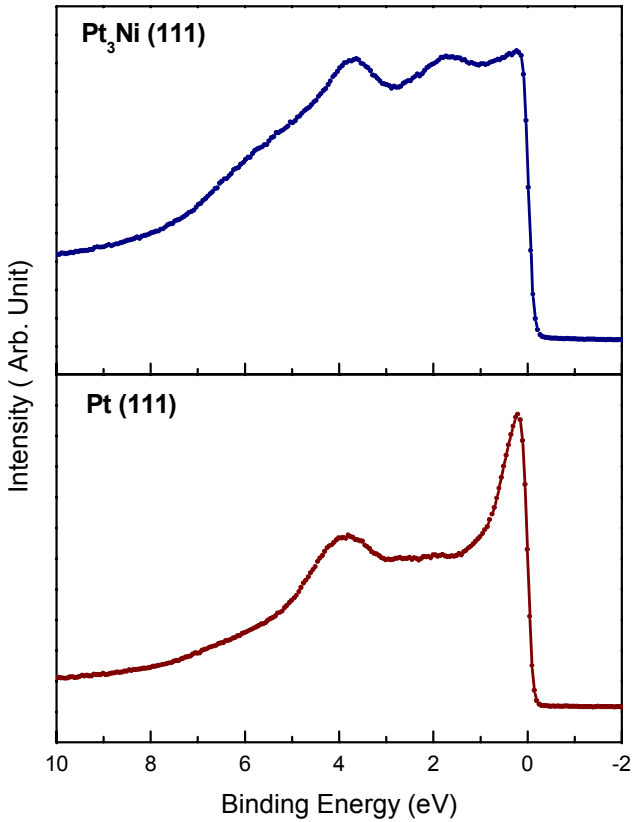
	Pt(111)	Pt$_3$Ni(111)
I_k @ 0.850V :	9 ± 1	(108 ± 10)
I_k @ 0.875V :	≈ 4.4	≈ 46
I_k @ 0.900V :	≈ 1.9	≈ 18
I_k @ 0.925V :	≈ 0.8	≈ 5.7
I_k @ 0.950V :	≈ 0.3	≈ 1.7

Activity Improvement Factor: > 10

$Pt_3Ni(hkl)$: UPS Characterization





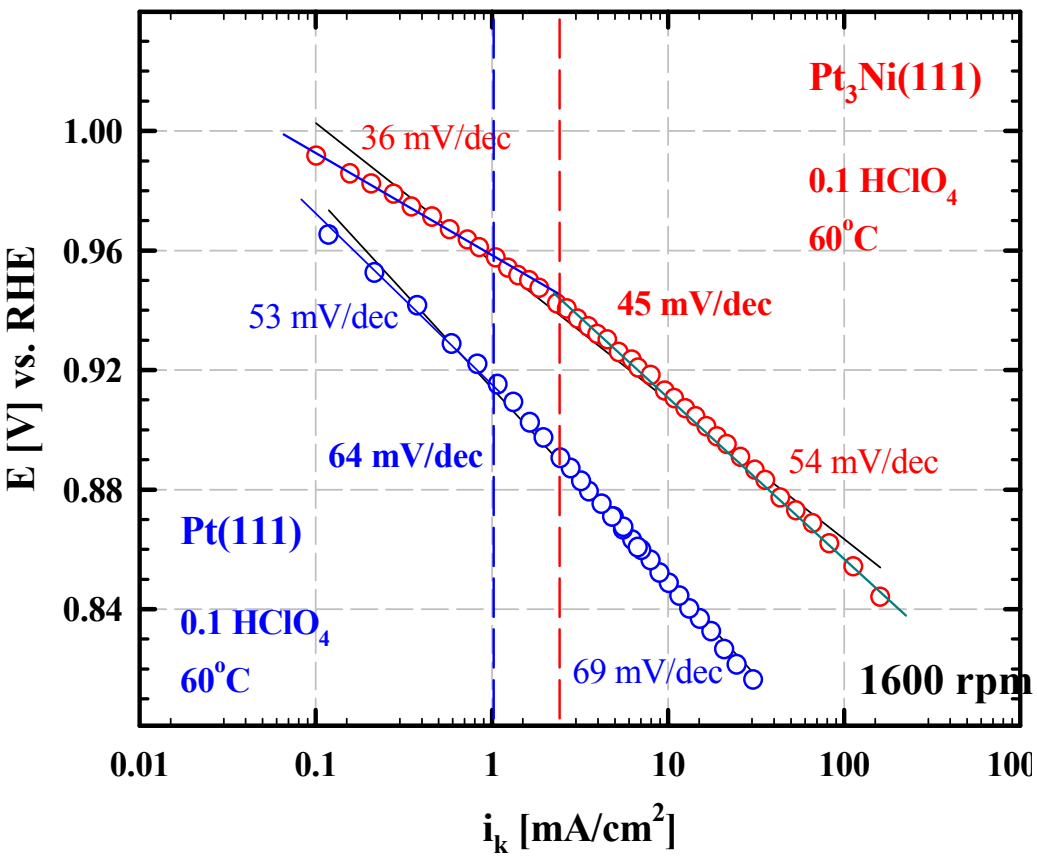


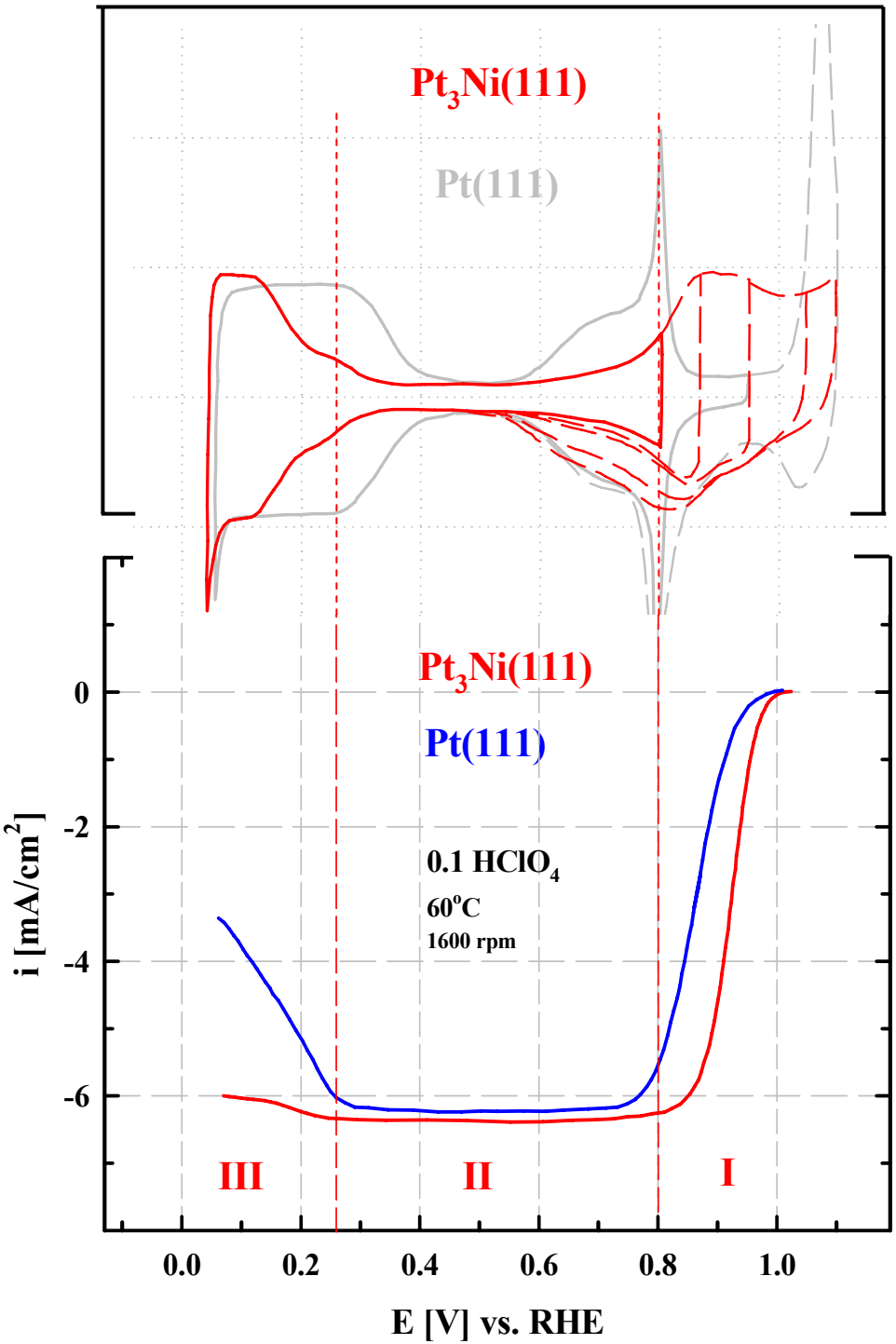
	Pt (100)	Pt3Ni(100)
d-band center	**2.90 eV**	**3.14 eV**
Δ d-band		**0.24 eV**

	Pt (110)	Pt3Ni(110)
d-band center	**2.70 eV**	**2.53 eV**
Δd-band		**-0.17 eV**

	Pt (111)	Pt3Ni(111)
d-band center	**2.76 eV**	**3.09 eV**
Δ d-band		**0.33 eV**

$Pt_3Ni(111)$: ORR Activity





Publications and Presentations

Journal Publications

Mayrhofer, K., B. Blizanac, M. Arenz, V. Stamenkovic, P. Ross, N. Markovic, "The impact of geometric and surface electronic properties of Pt-nanocatalysts on the particle size effect in electrocatalysis", *J. Phys. Chem. B* **109**, 14433 JUL 13 2005.

Mayrhofer, K., B. Blizanac, M. Arenz, V. Stamenkovic, P. Ross, N. Markovic, "CO surface electrochemistry on Pt-nanoparticles: A selective review", *Electrochimica Acta* **50**, 5144 JUL 1 2005.

Arenz M, Stamenkovic V, Blizanac BB, Markovic NM, Ross PN, "Carbon-supported Pt-Sn electrocatalysts for the anodic oxidation of H_2, CO, and H_2/CO mixtures. Part II: The structure-activity relationship" *J. Catal.* **232** (2): 402-410 JUN 10 2005

Mun BS, Lee C, Stamenkovic V, Markovic NM, Ross PN, "A photoemission study of Pd ultrathin films on Pt(111)" *J. Chem. Phys.* **122**(18): 184712 MAY 8 2005

Radmilovic V, Richardson TJ, Chen SJ, Markovic NM, Ross PN, “Carbon-supported Pt-Sn electrocatalysts for the anodic oxidation of H_2, CO, and H_2/CO mixtures. Part I. Microstructural characterization” *J. Catal.* **232** (1): 199-209 MAY 15 2005

Arenz M, Mayrhofer KJ, Stamenkovic V, Markovic NM, Ross PN, “The effect of the particle size on the kinetics of CO electrooxidation on high surface area Pt catalysts” *J. Amer. Chem. Soc.***127** (18): 6819-6829 MAY 11 2005

Mun BS, Lee C, Stamenkovic V, Markovic NM, Ross PN, “Electronic structure of Pd thin films on Re(0001) studied by high-resolution core-level and valence-band photoemission” *Phys. Rev B* **71** (11): 115420 MAR 2005

Future Plans

FY2007
P.I. Retires from Berkeley Lab and program in its present form concludes

Good night and good luck !