



New Electrocatalysts For Fuel Cells

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Materials Sciences Division

Lawrence Berkeley National Laboratory

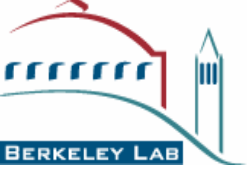
Berkeley, CA 94720

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²Current address: Cabot Superior Micropowders

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

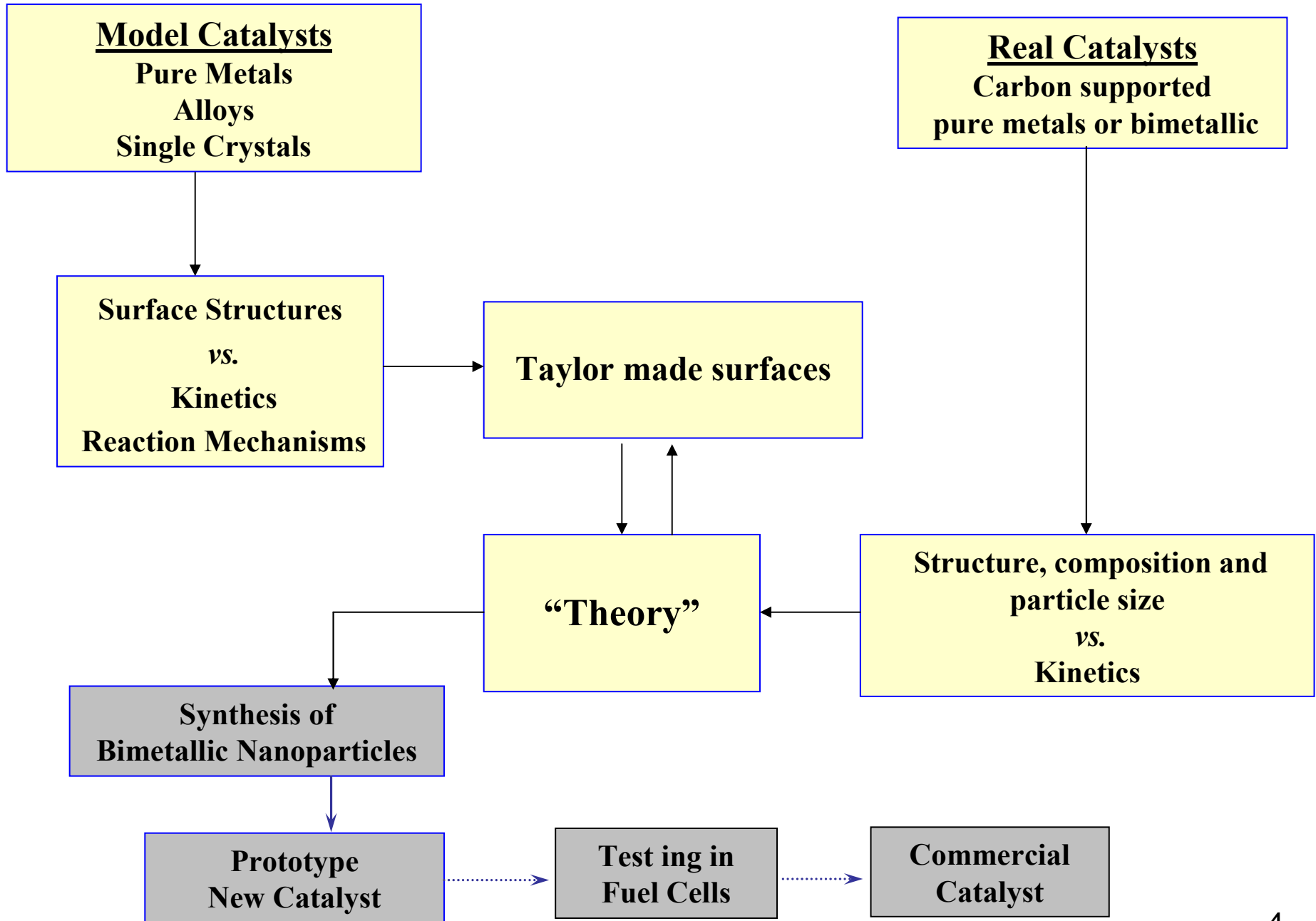
- Interactions/ collaborations
 - General Motors Alternative Power Center (GAPC)
 - 3M

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



LBLN *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**



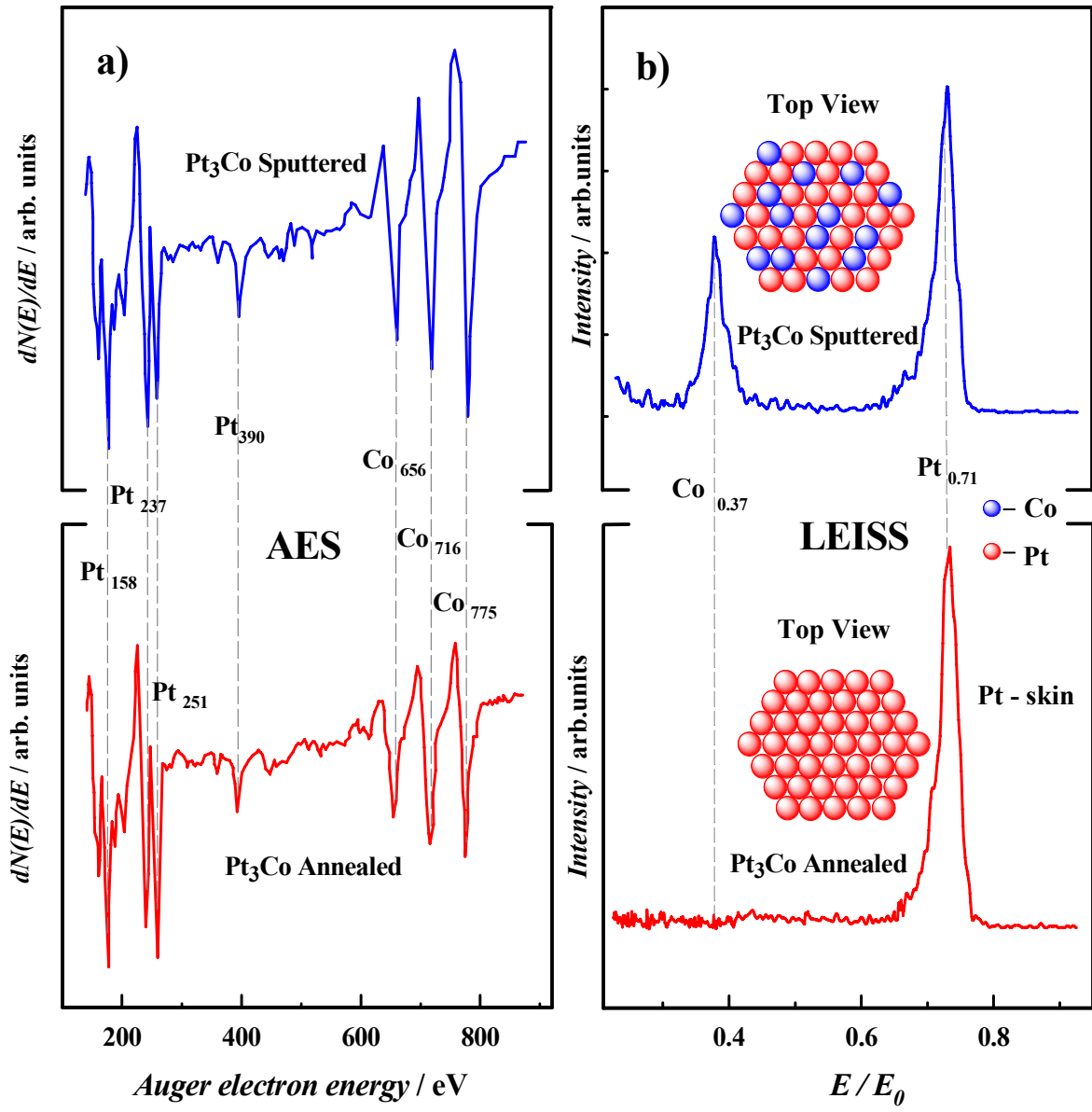
Outline of Presentation

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

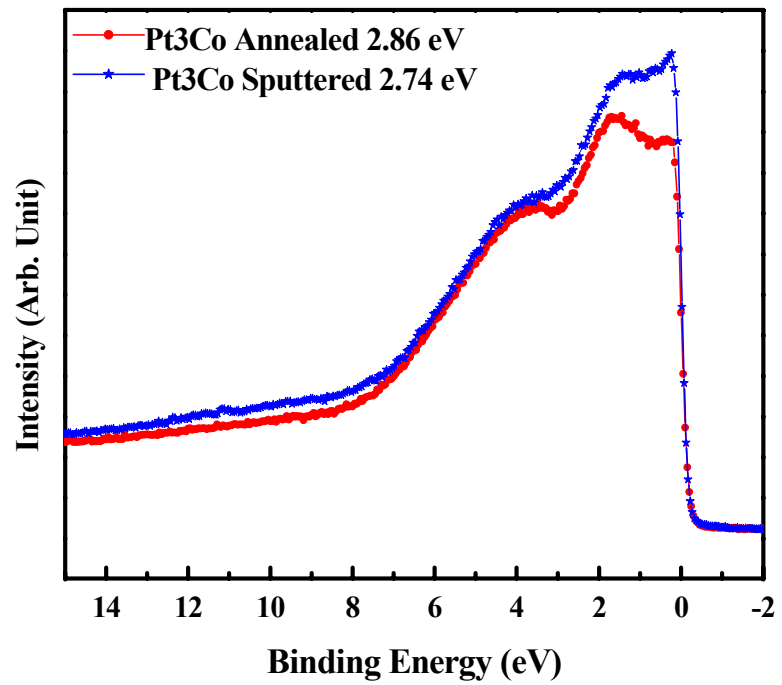
New Results with $\text{Pt}_3\text{Ni}(\text{hkl})$ single crystals point to new opportunities to improve intrinsic activity via control of nanoparticle shape

Summary: Near-surface characterization of Pt₃TM



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

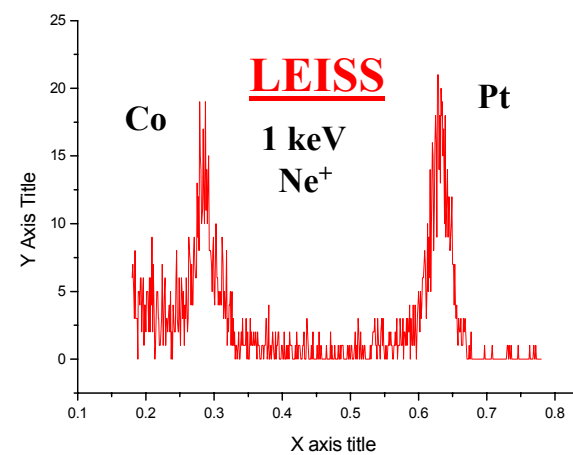
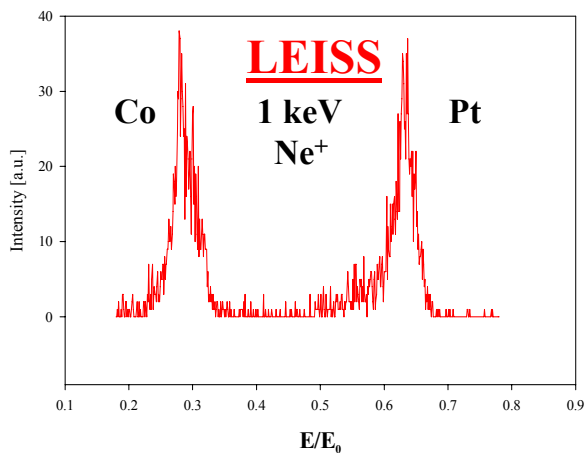
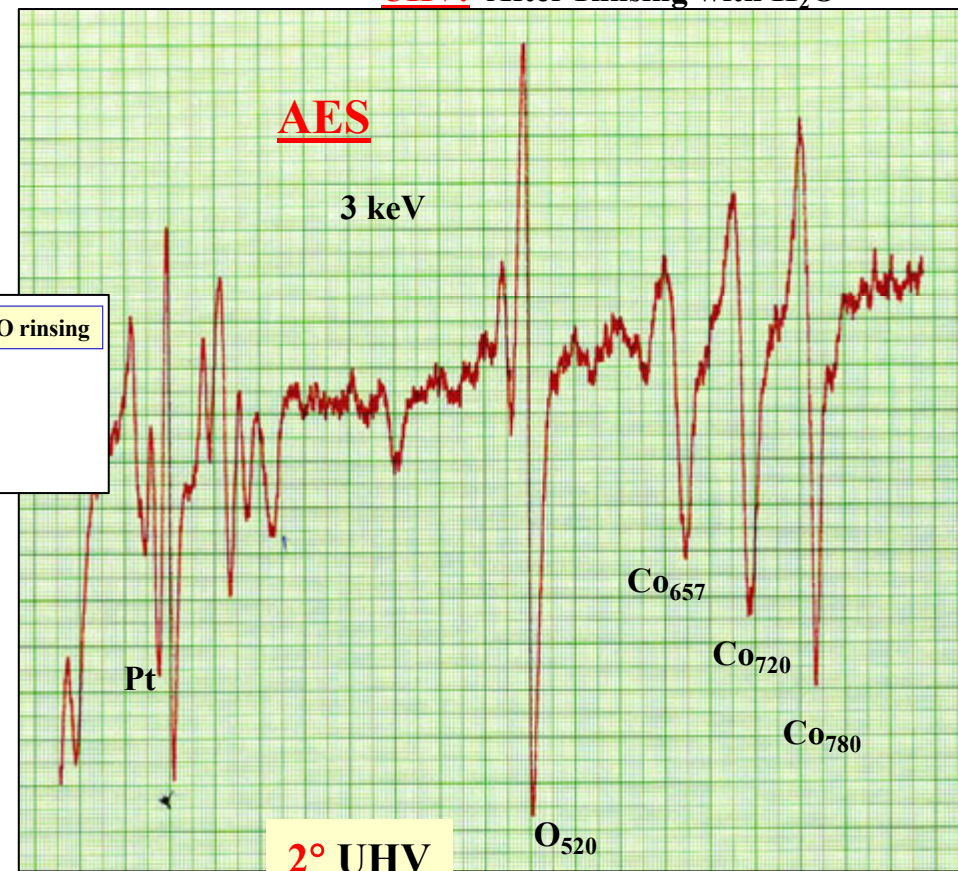
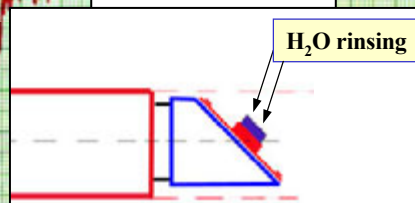
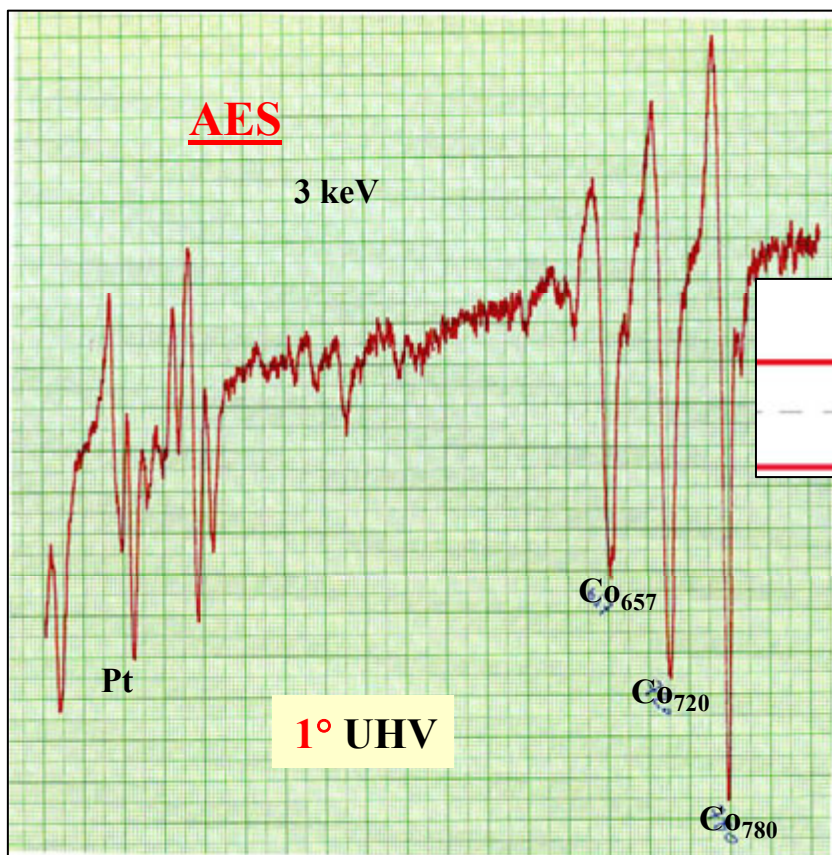
LEISS: surface composition
 sputtered: Pt - 75%, Co - 25%
 annealed: Pt - 100% → Pt 'skin'



UPS: d - band center position
 sputtered: 2.74 eV
 annealed: 2.86 eV

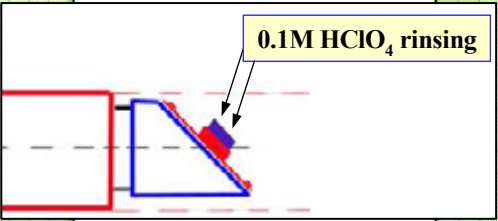
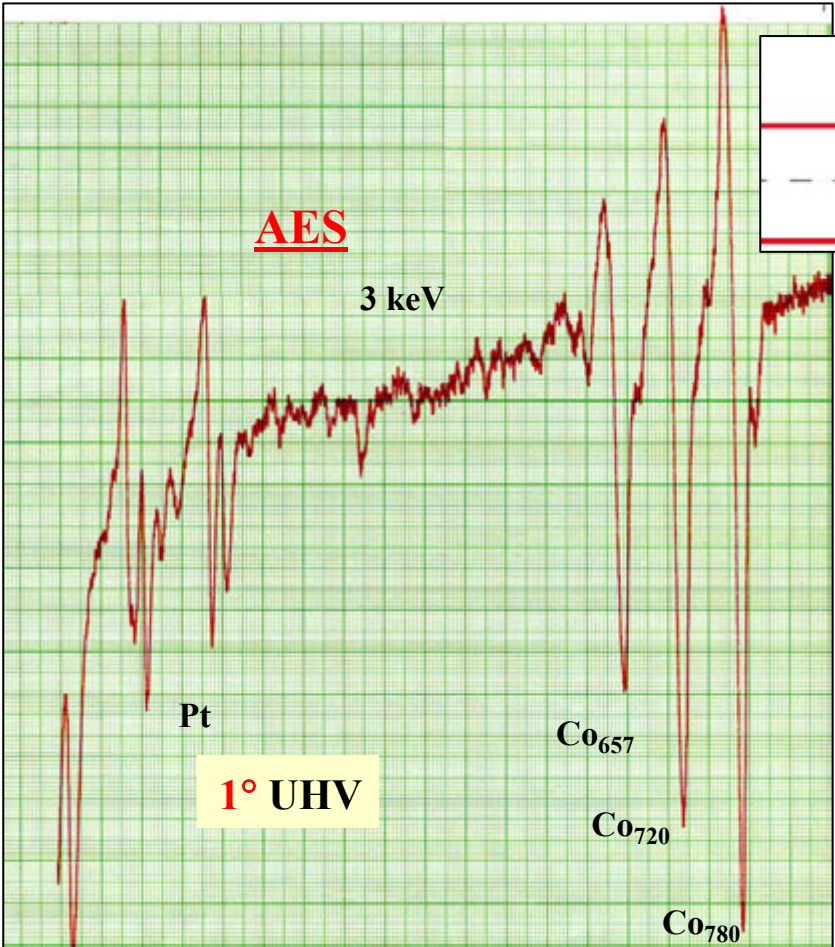
UHV: Before Transfer

UHV: After Rinsing with H₂O

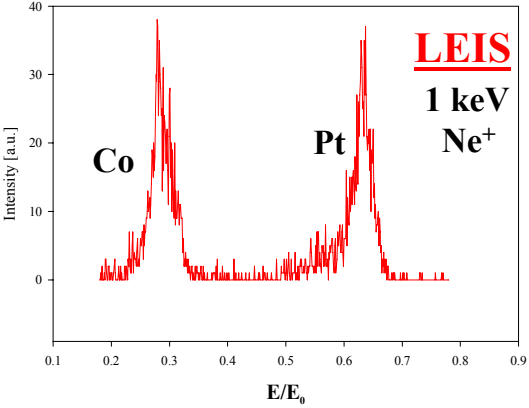
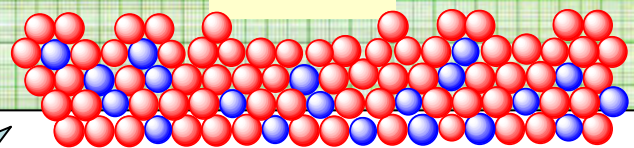
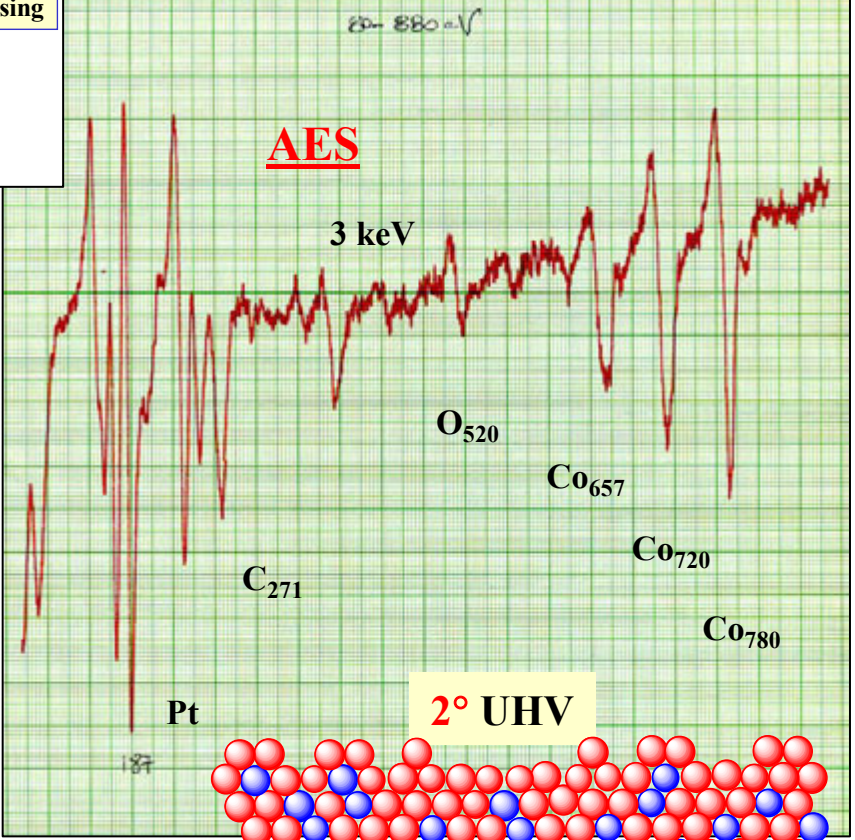


Summary: Stability of Pt₃TM

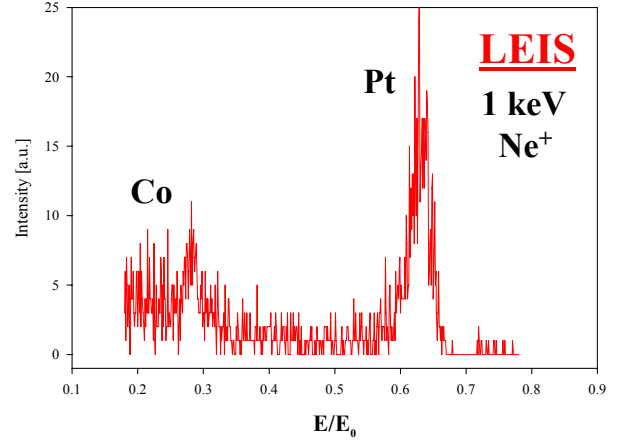
UHV: Before Transfer



UHV: After rinsing with 0.1M HClO₄ and/or After Electrochem. Exp.

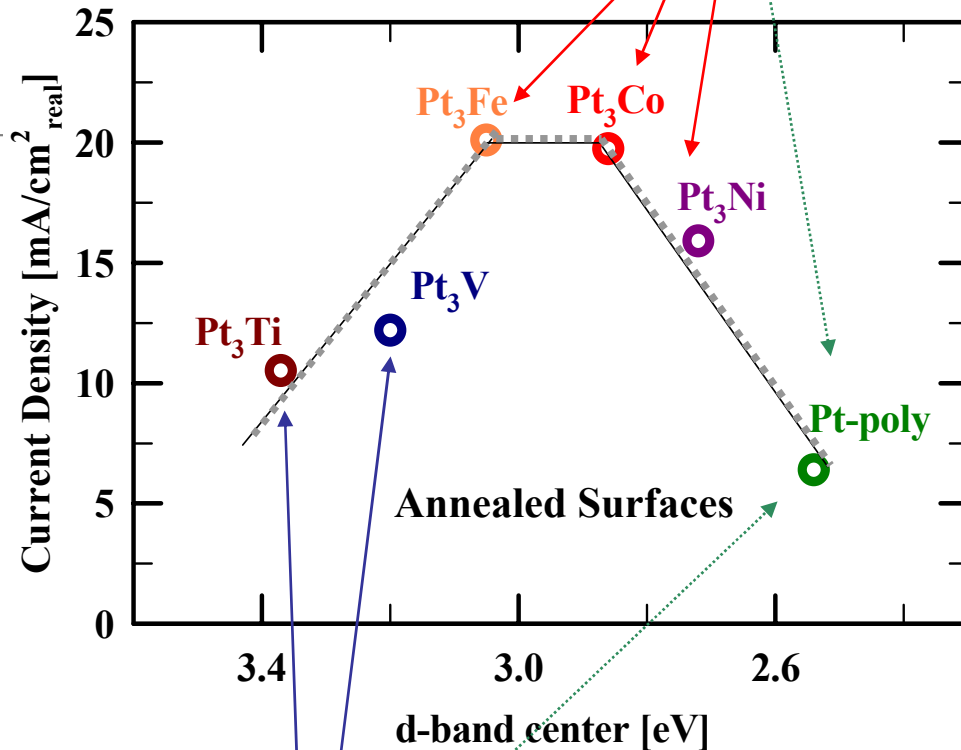
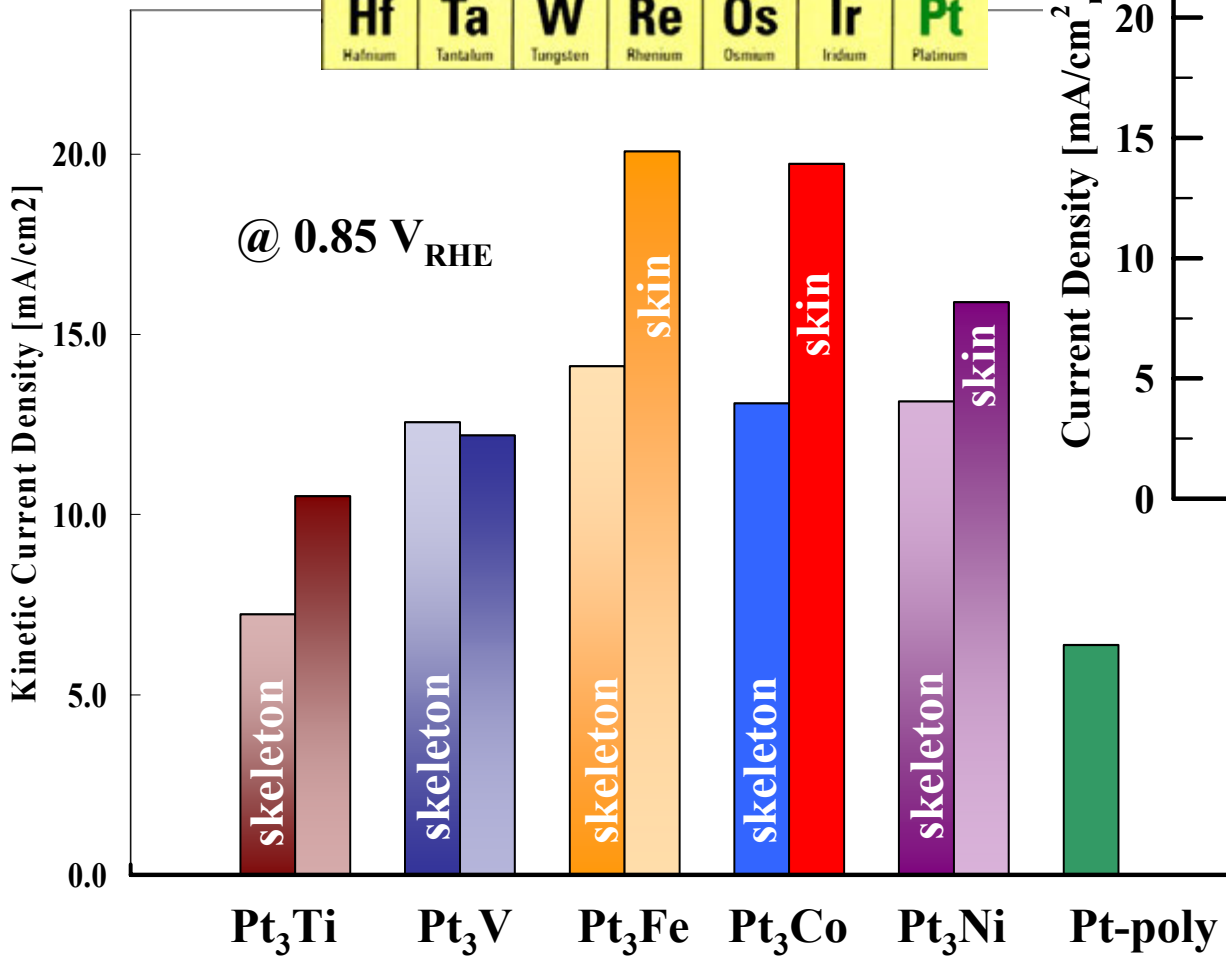


Co leaching out from the surface layers and formation of a Pt "skeleton" structure



Summary: ORR activity vs. d-band center Pt₃TM

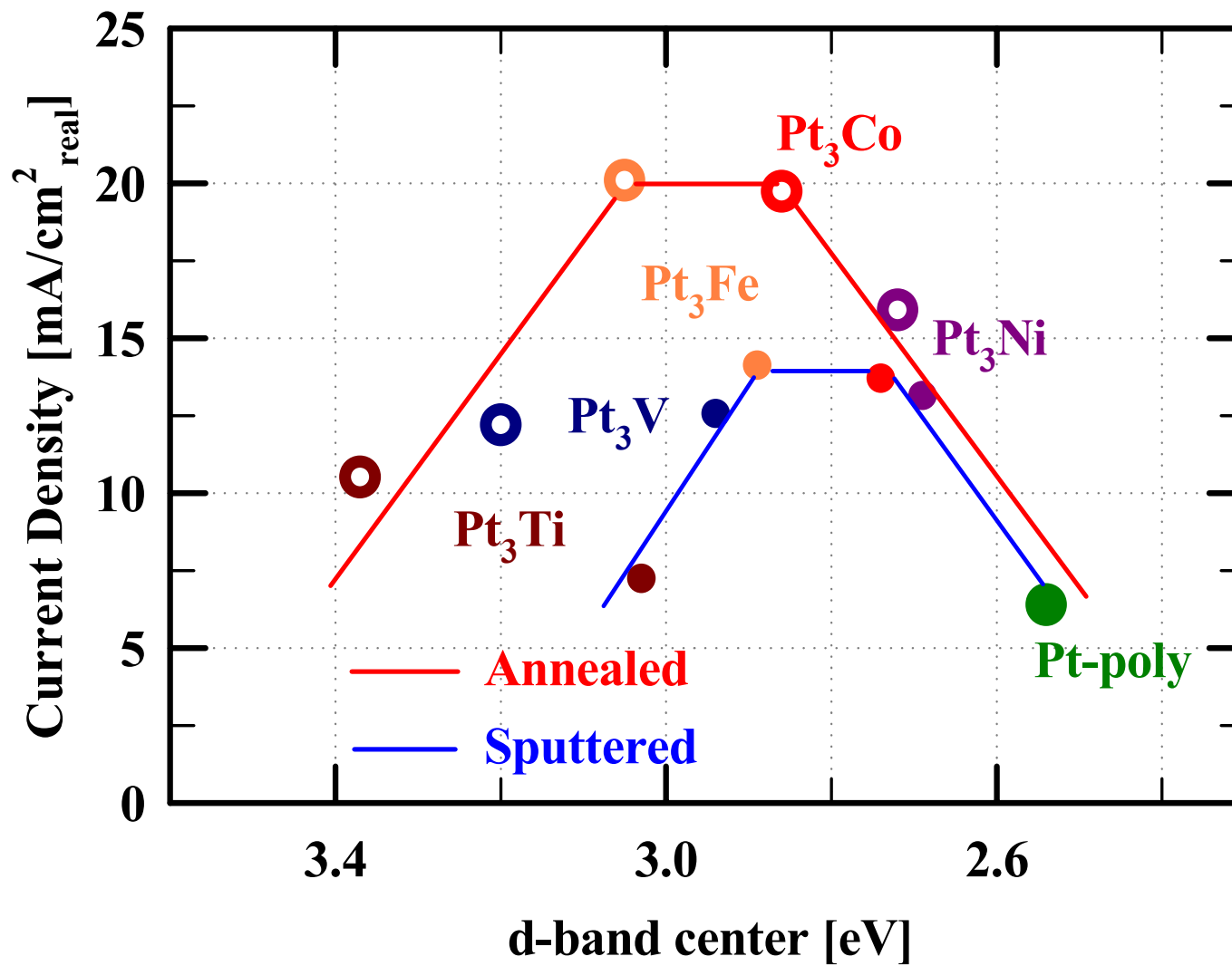
22 47.90 Ti Titanium	23 50.94 V Vanadium	24 51.996 Cr Chromium	25 54.94 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.70 Ni Nickel
40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 (98) Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.40 Pd Palladium
72 178.48 Hf Hafnium	73 180.95 Ta Tantalum	74 183.85 W Tungsten	75 188.21 Re Rhenium	76 190.20 Os Osmium	77 192.22 Ir Iridium	78 195.08 Pt Platinum



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

	Pt ₃ Ti	Pt ₃ V	Pt ₃ Fe	Pt ₃ Co	Pt ₃ Ni	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

*ORR activity vs. d-band center: Pt₃TM
annealed(skin) vs sputtered(skeleton) surfaces*





Summary: Skin vs. Skeleton near-surface structure

1. ⇒ Complete segregation of Pt over Pt₃M surfaces after annealing in UHV

Only Pt atoms over Pt₃(Co, Ni, Fe)

Possible to create two different surfaces in UHV: **Pt-skin** and **Pt₃M**

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

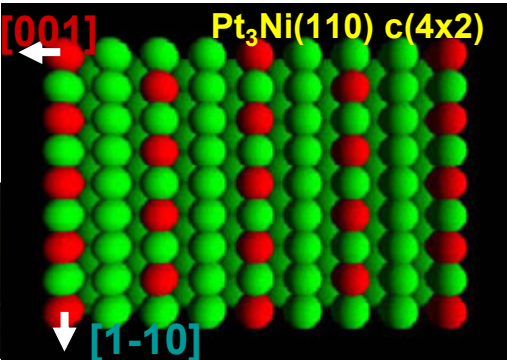
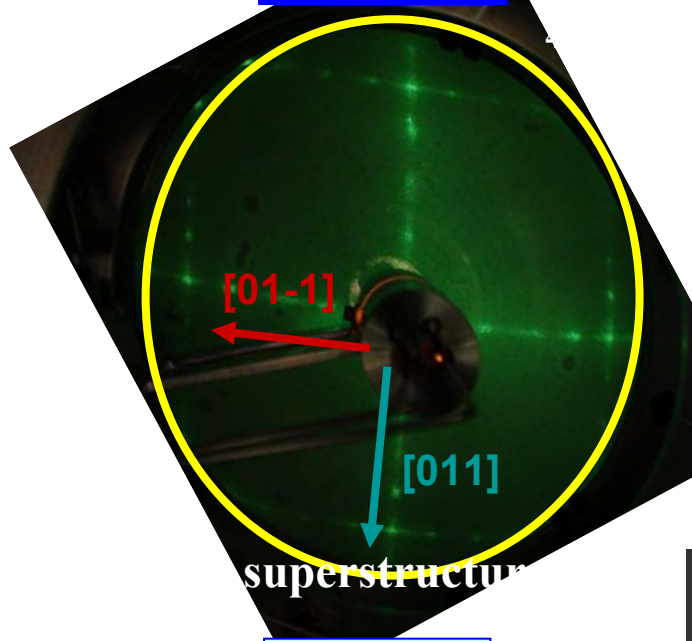
5. ⇒ The same/similar Tafel slope, activation energy, peroxide production → ORR pathway

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

$Pt_3Ni(100)$



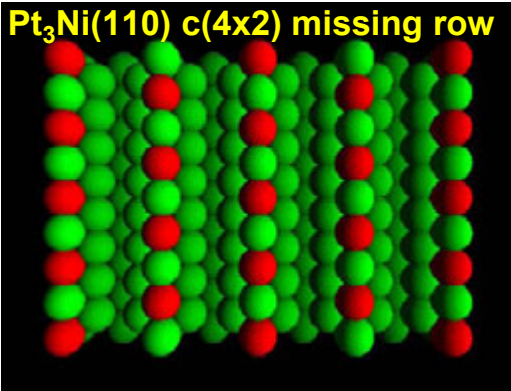
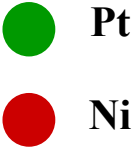
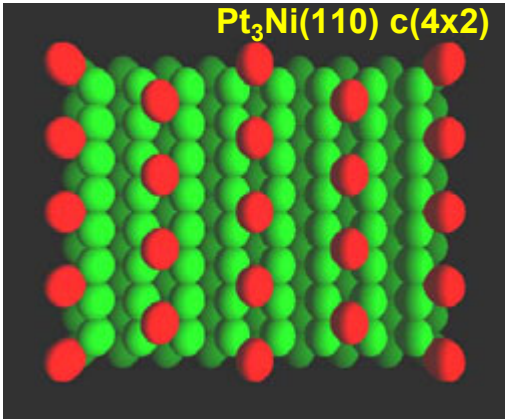
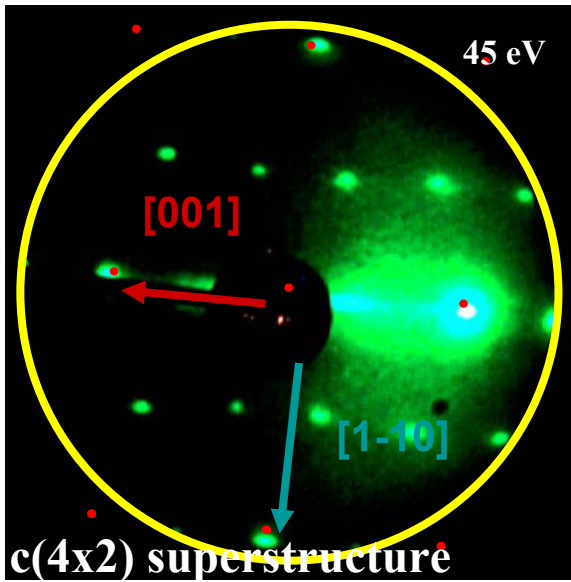
$Pt_3Ni(111)$

- Does not have a superstructure
- p(1x1)

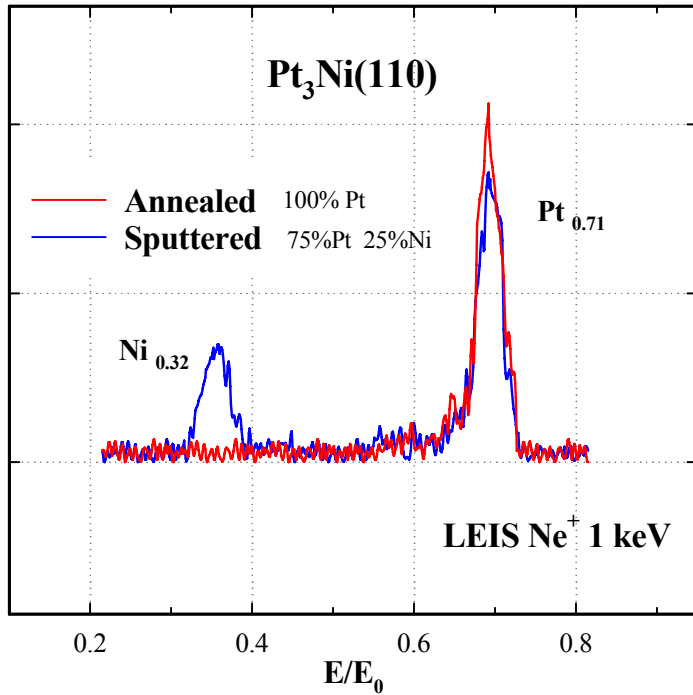
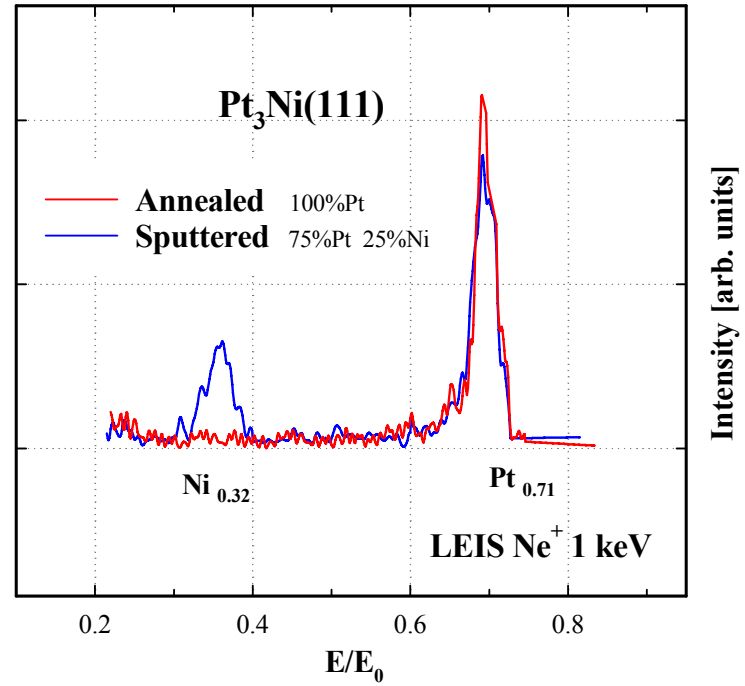
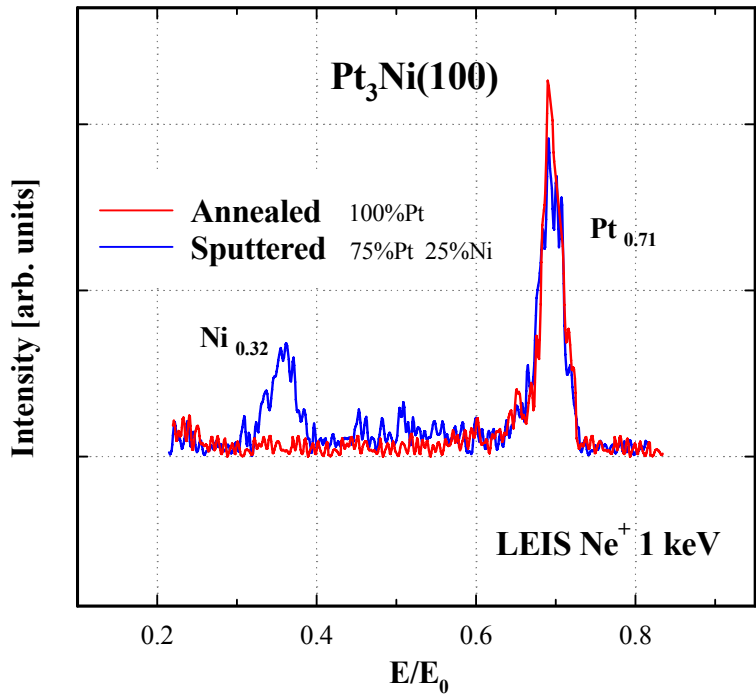
$Pt_3Ni(110)$

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

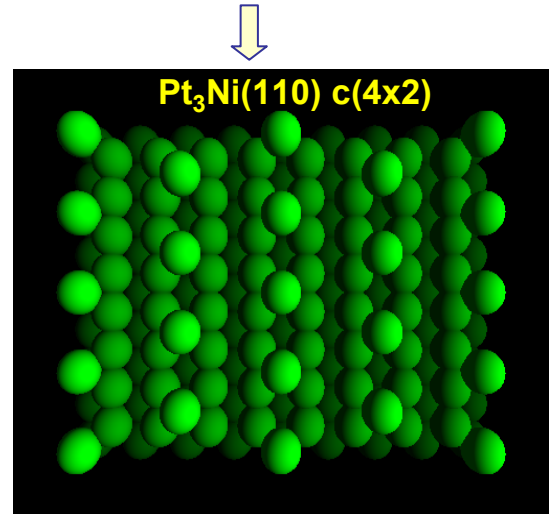
$Pt_3Ni(110)$



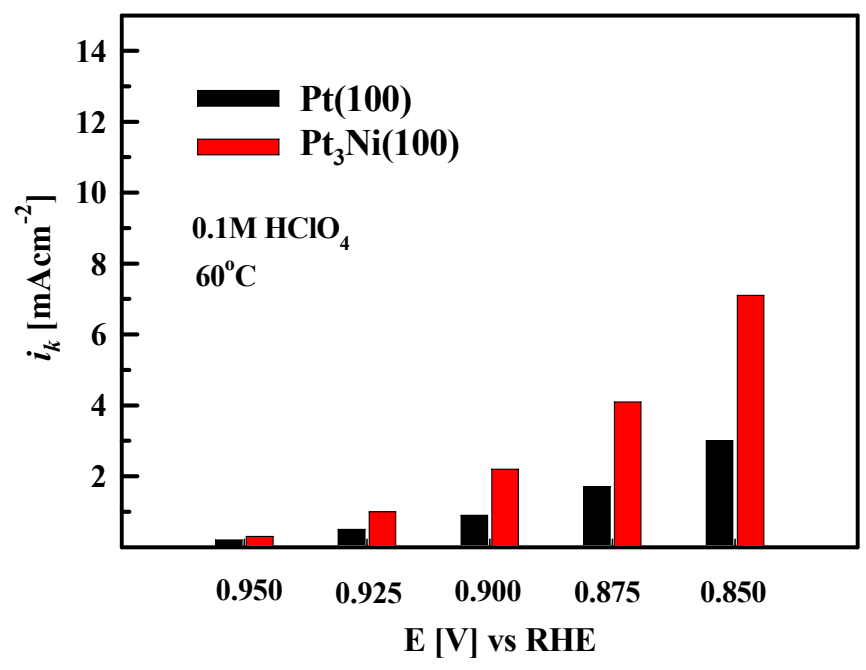
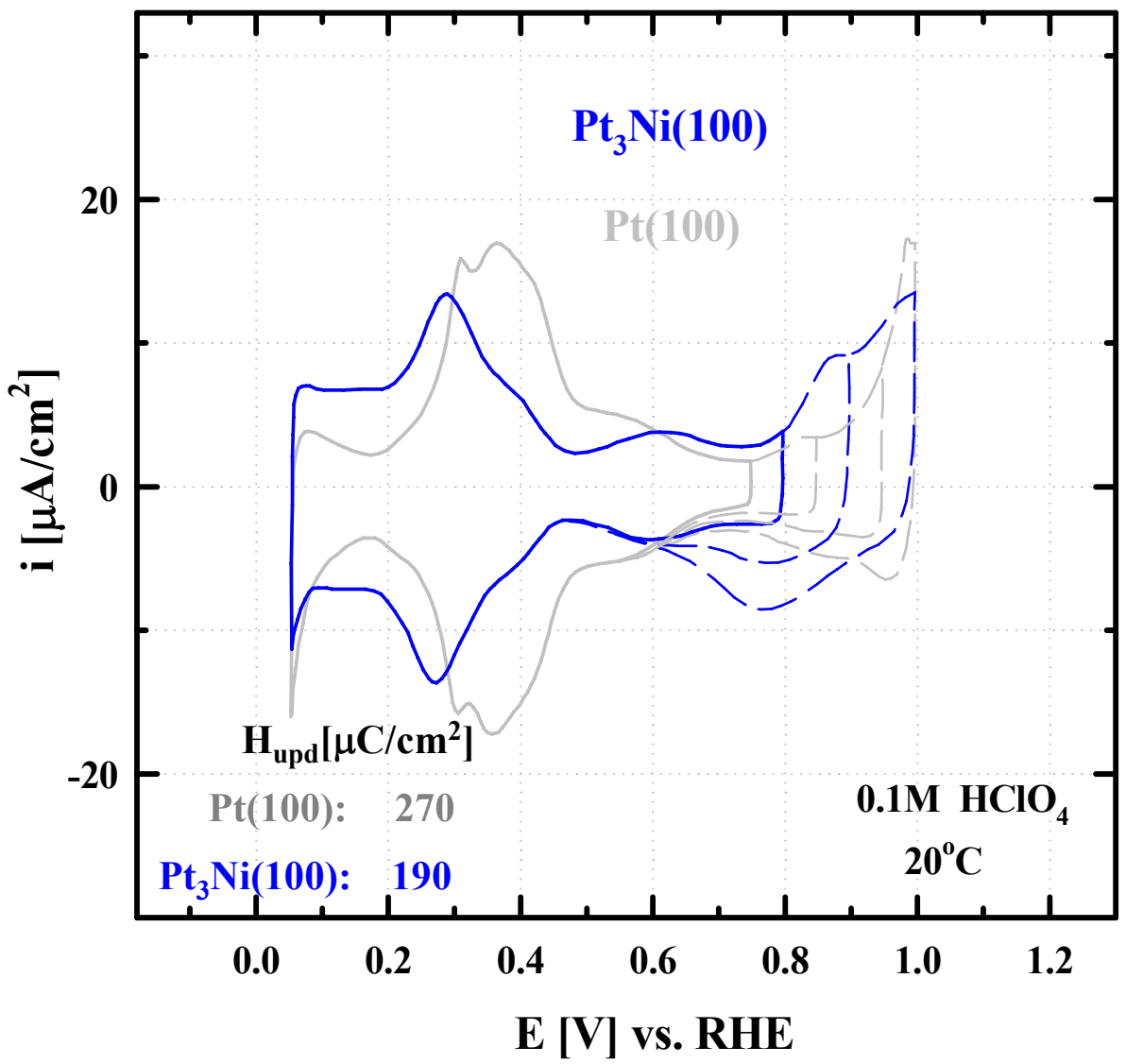
Pt₃Ni(hkl): Surface Characterization



LEISS:
 -Complete Pt enrichment on the annealed Pt₃Ni(hkl) surfaces



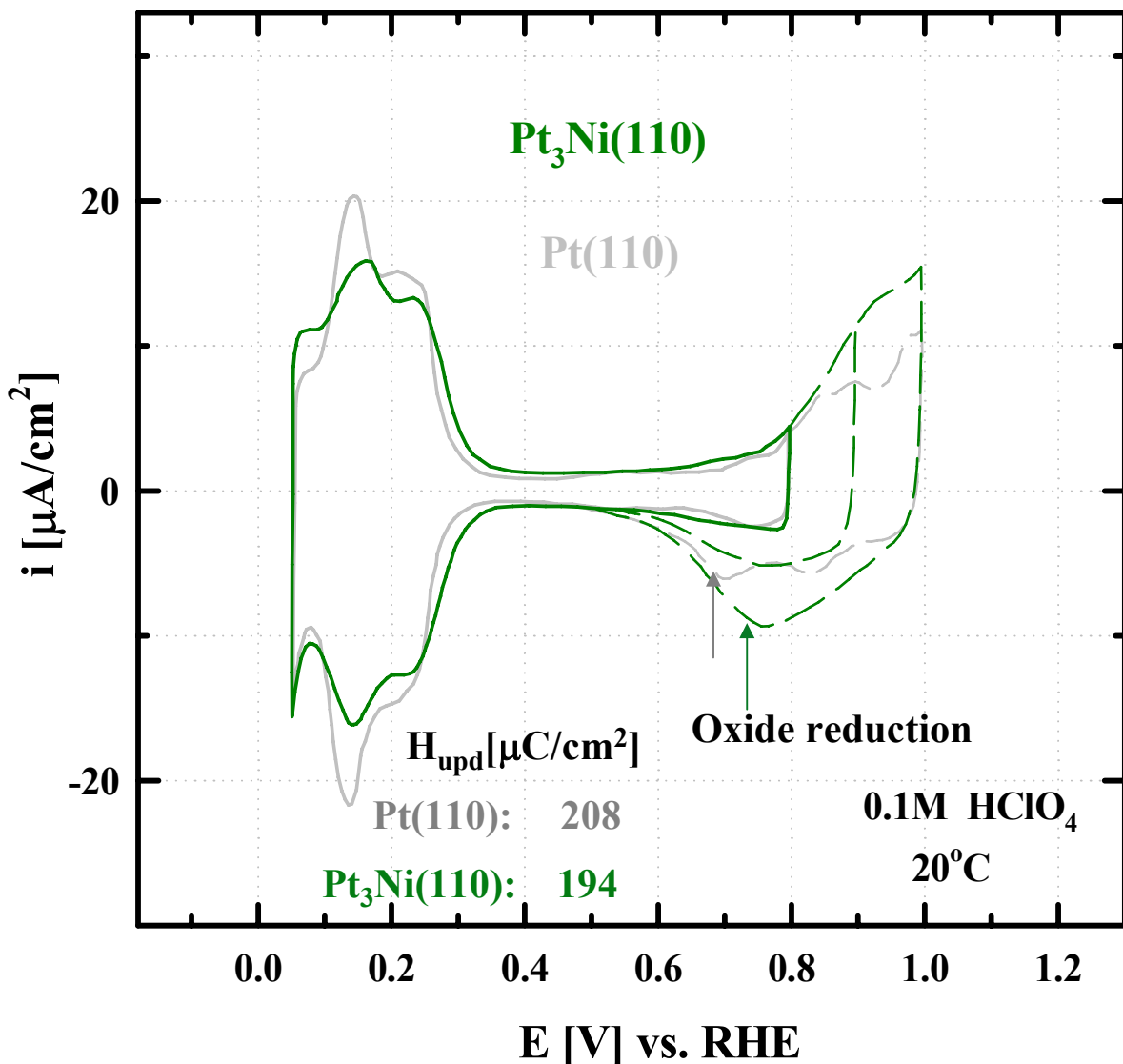
Pt₃Ni(100): EC Characterization



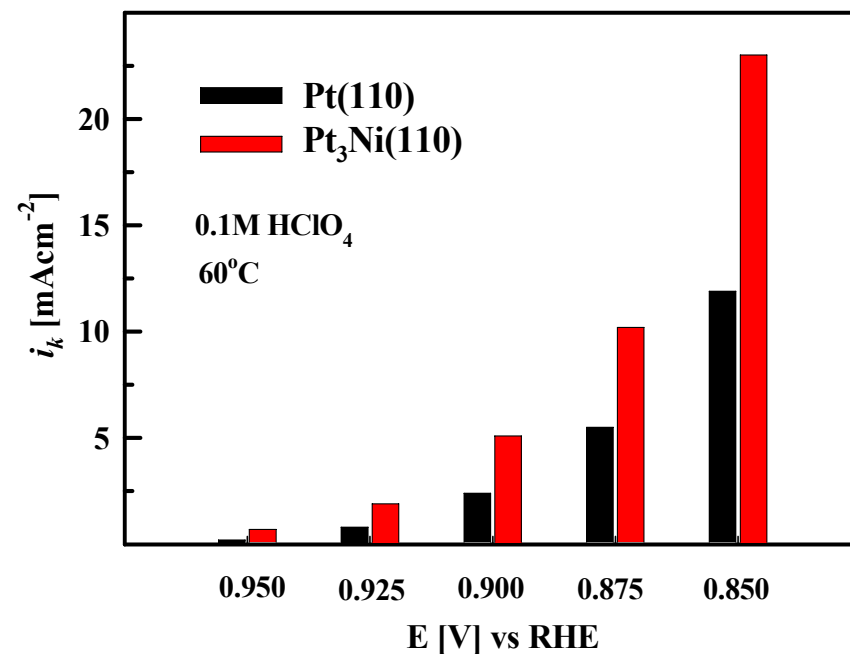
Pt(100)	 	Pt₃Ni(100)
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	↓	
Ik @ 0.850V :	3 ± 0.3	7.1 ± 0.7
Ik @ 0.875V :	≈ 1.7	≈ 4.1
Ik @ 0.900V :	≈ 0.9	≈ 2.2
Ik @ 0.925V :	≈ 0.5	≈ 1.0
Ik @ 0.950V :	≈ 0.2	≈ 0.3

Activity Improvement Factor: 2.3

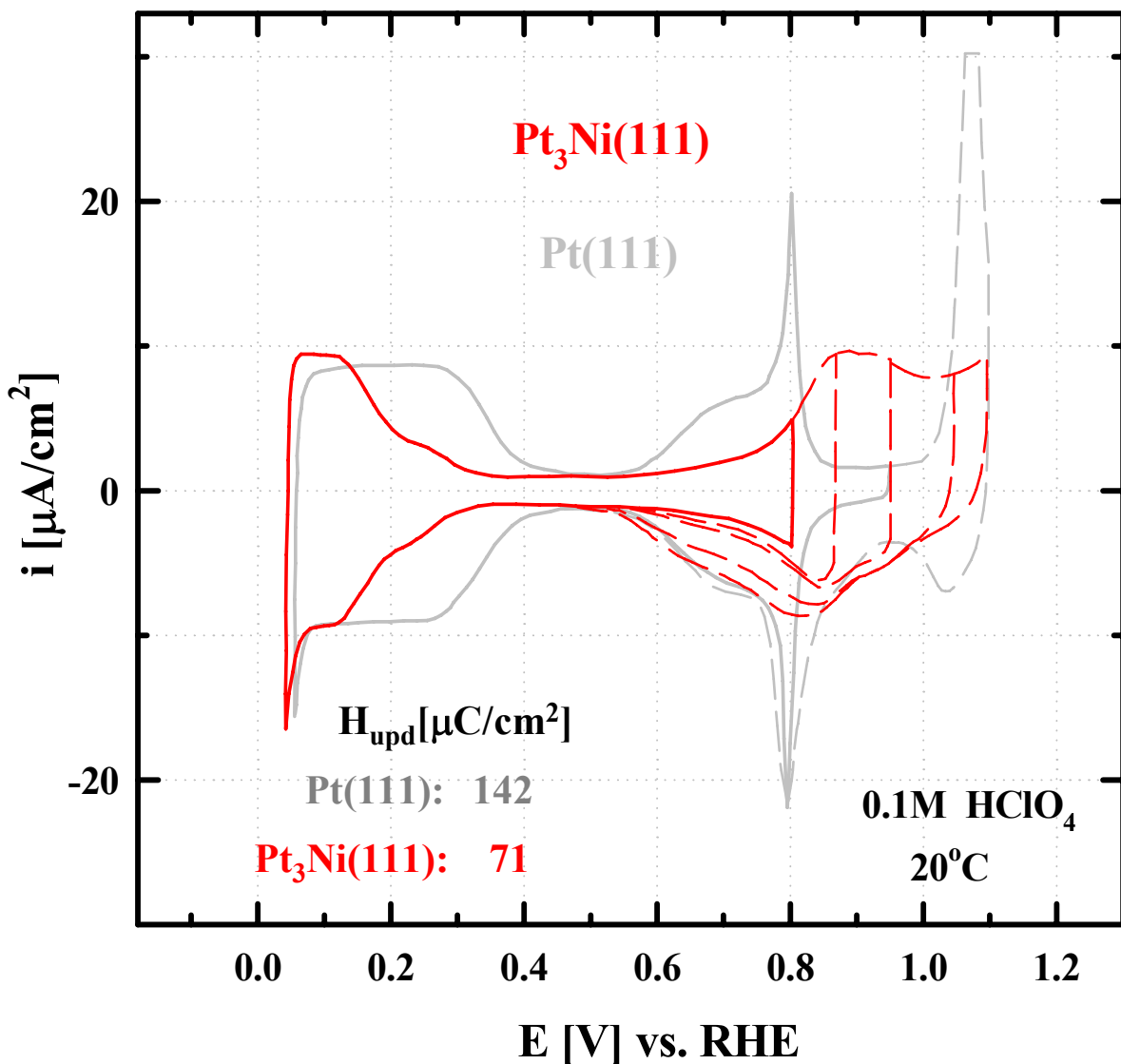


Activity Improvement Factor: 2.1

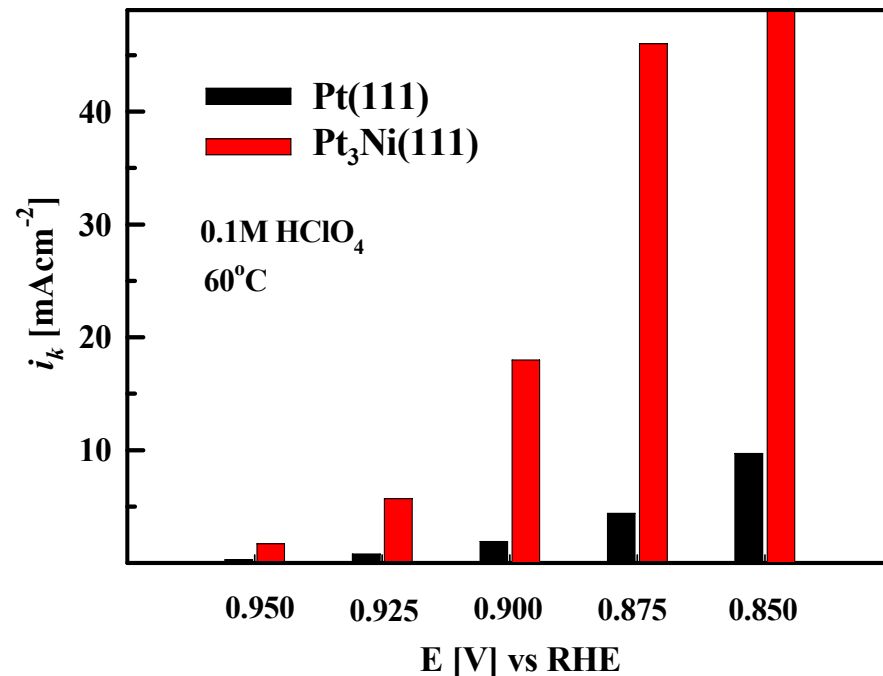


	Pt(110)	Pt ₃ Ni(110)
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I_k @ 0.850V :	11.5 ± 1	23 ± 2
I_k @ 0.875V :	≈ 5.0	≈ 10.7
I_k @ 0.900V :	≈ 2.2	≈ 5.1
I_k @ 0.925V :	≈ 0.7	≈ 1.9
I_k @ 0.950V :	≈ 0.2	≈ 0.7



Activity Improvement Factor: > 10



	Pt(111)	Pt ₃ Ni(111)
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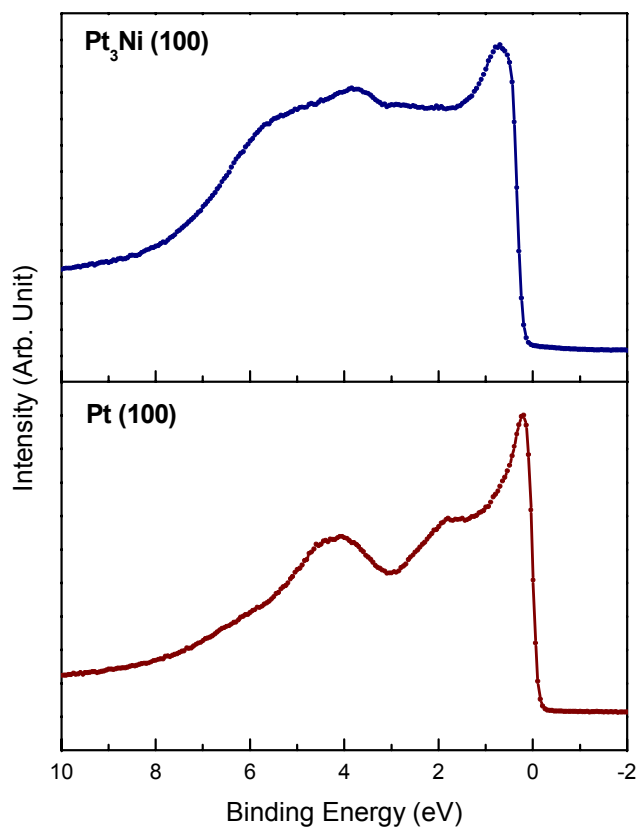
I_k @ 0.850V :	9 ± 1	(108 ± 10)
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I_k @ 0.875V :	≈ 4.4	≈ 46
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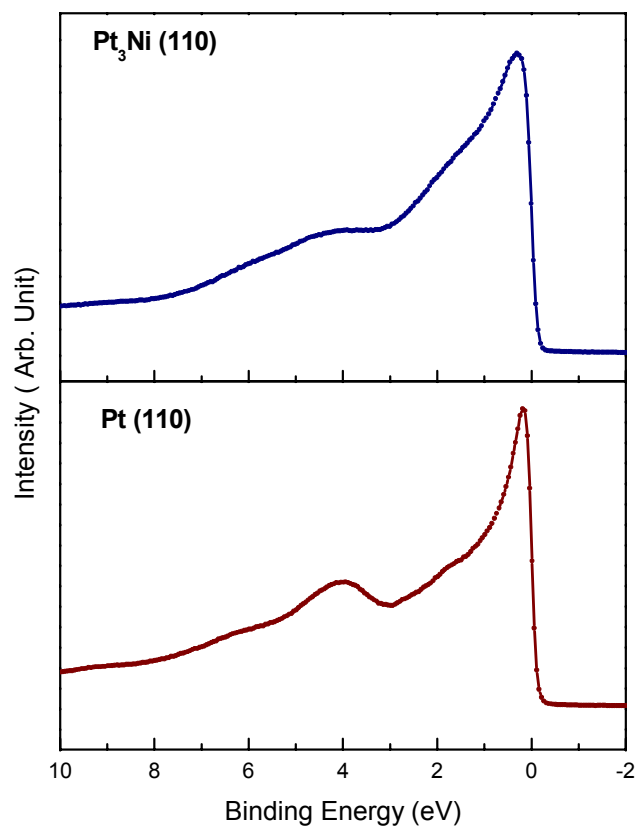
I_k @ 0.900V :	≈ 1.9	≈ 18
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I_k @ 0.925V :	≈ 0.8	≈ 5.7
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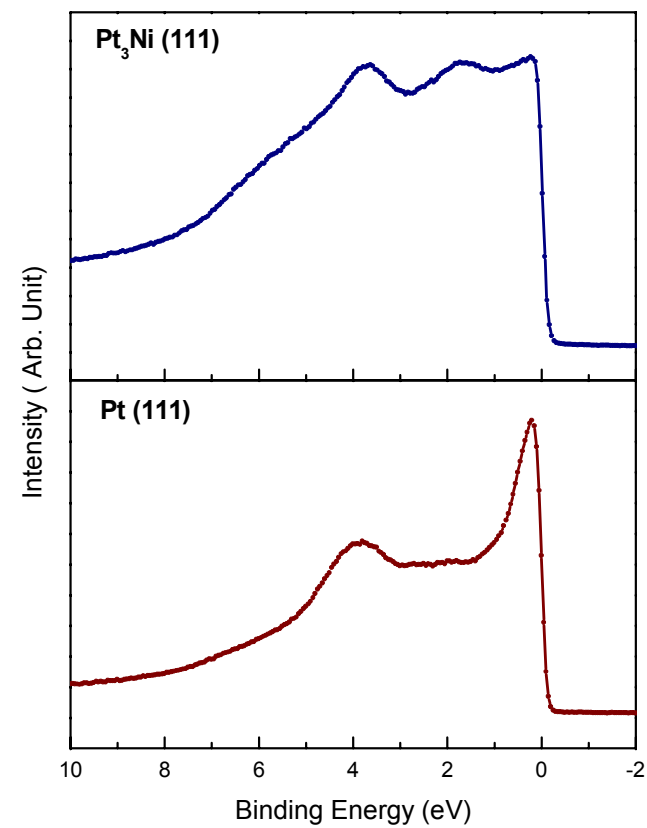
I_k @ 0.950V :	≈ 0.3	≈ 1.7
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	Pt (100)	Pt3Ni(100)
<i>d</i>-band center	2.90 eV	3.14 eV
Δ <i>d</i>-band		0.24 eV

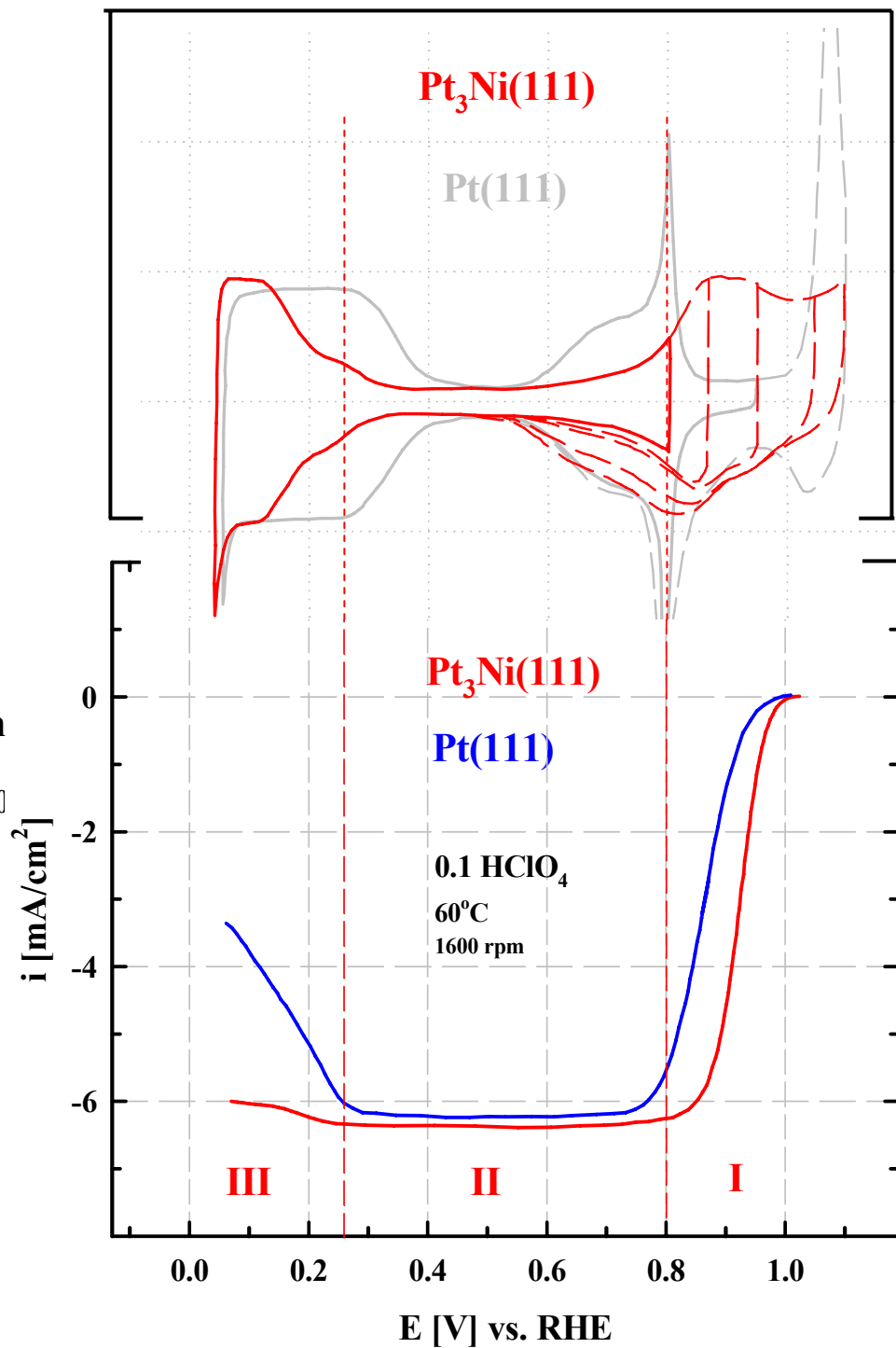
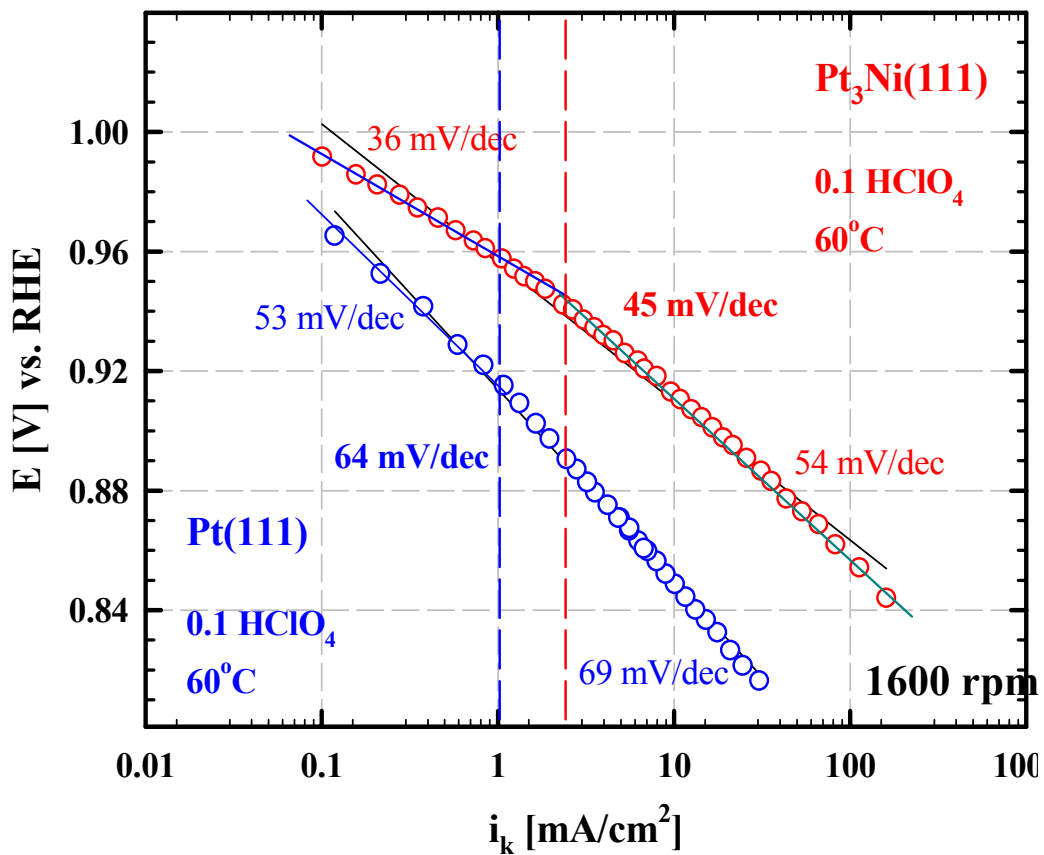


	Pt (110)	Pt3Ni(110)
<i>d</i>-band center	2.70 eV	2.53 eV
Δ <i>d</i>-band		-0.17 eV



	Pt (111)	Pt3Ni(111)
<i>d</i>-band center	2.76 eV	3.09 eV
Δ <i>d</i>-band		0.33 eV

Pt₃Ni(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 H₂, CO, and H₂/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 H₂, CO, and H₂/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 !