XAS in Electrochemistry: Fuel Cells Applications

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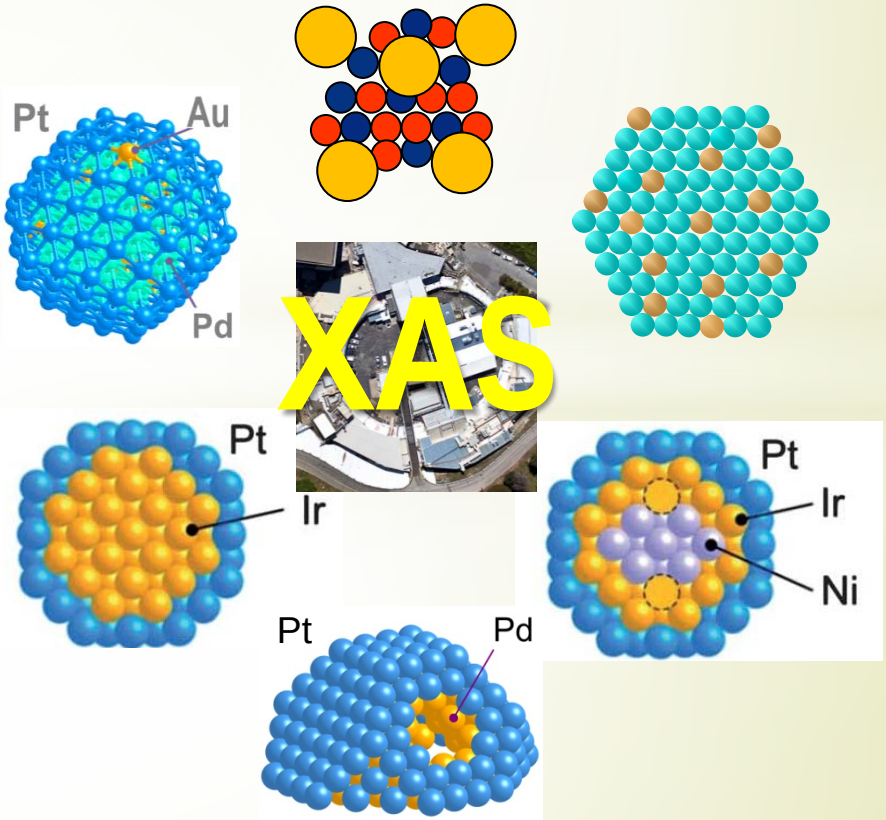
1. **Synthesis methods**
   - Modified polyol method
   - M-Pt core-shell nanoparticles
2. **Ethanol oxidation catalysts**
   - Mechanism
   - Pt/Rh/SnO_2 catalyst optimization
   - Characterization: IR, EXAFS, TEM
   - Rh substitution with alternatives
3. **Oxygen reduction catalysts**
   - EXAFS characterization
   - Pt/Pd core-shell nanocatalysts
   - Ir/Ni-Pt core-shell nanocatalysts
4. **Conclusion**



Introduction to Fuel Cells

Proton Exchange Membrane (PEM) Fuel Cell for transportation applications

The PEM allows only H^+ to pass though a membrane and e^- must flow an external circuit (electric current).

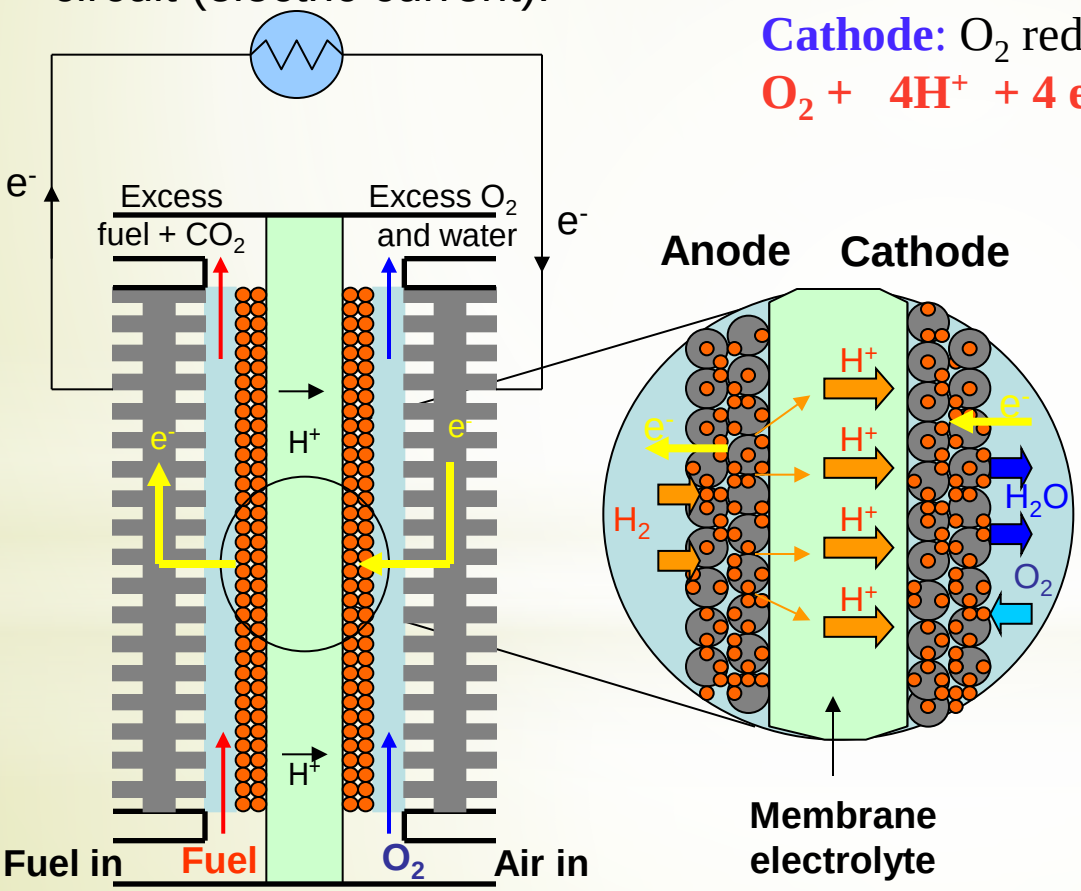
Anode: Fuel Oxidation

$H_2 \rightarrow 2H^+ + 2e^-$ (fast) $E° = 0.000V$

$C_2H_5OH \rightarrow CO_2 + H_2O + 12\ e^-$ (slow) $E° = 0.085V$

Cathode: O_2 reduction reaction (ORR)

$O_2 + 4H^+ + 4\ e^- \rightarrow 2H_2O$ (slow) $E° = 1.229V$



The single cell is called MEA (Membrane Electrode Assembly)

- ✔ **High efficiency conversion**
- ✔ **Ideal for automotive applications**

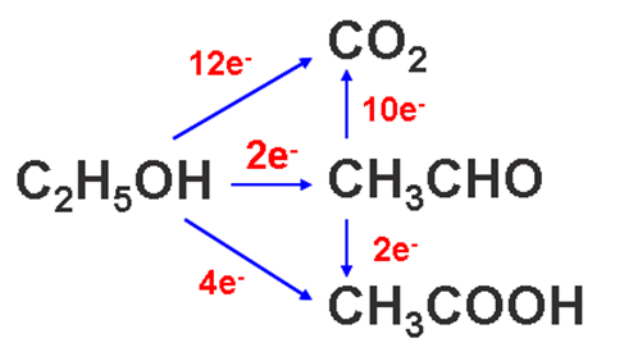
- ✕ Slow kinetics
- ✕ High cost (noble metals)
- ✕ Insufficient durability

Both anode and cathode side catalysts need improvements.

Anode side: Direct Ethanol Fuel Cell

Ethanol - an almost ideal fuel candidate for fuel cells:

- 'green' fuel; replenishable; liquid; high current density
- oxidation kinetics is slow or incomplete
- C-C bond splitting difficult



Electrocatalysts for ethanol oxidation

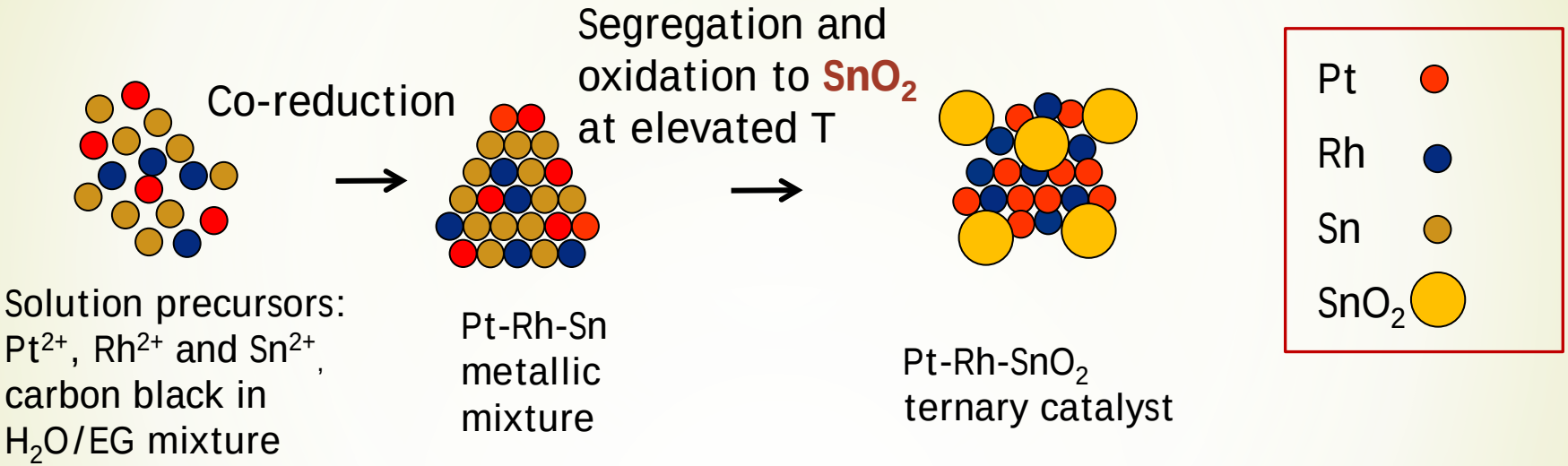
- Pt-based catalysts: Pt-Sn, Pt-Ru, oxide-supported…
- **Rh/Pt/SnO_2 ternary electrocatalyst can break the C-C bond at low overpotentials**

Efforts in obtaining a novel electrocatalyst with less expensive materials

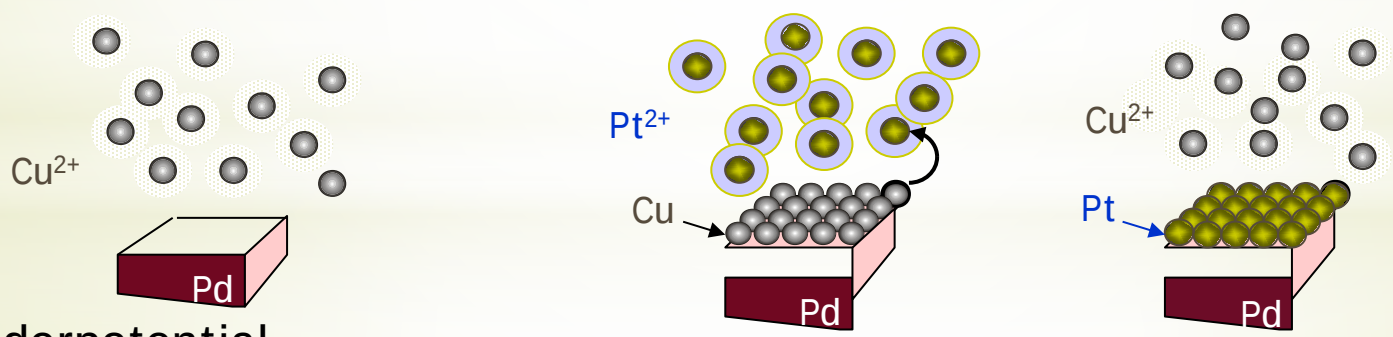
- Ir and Ir-M (Pt, Au, Sn) electrocatalysts for EtOH oxidation
- **Evidence for splitting C-C bond in partial oxidation and CO_2 generation**

Nanoparticle Synthesis

1. Polyol /Thermal Treatment Pt-Rh-SnO_2 Synthesis



2. Pt / Pd Core-Shell Electrochemical / Electroless Synthesis



Underpotential deposition (UPD) of Cu monolayer on Pd

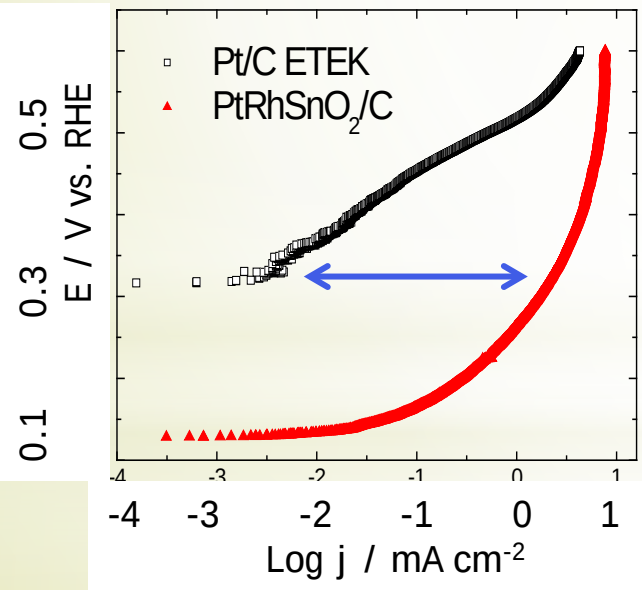
$Cu_{UPD}/Pd + Pt^{2+} \longrightarrow Pt_{ML}/Pd + Cu^{2+}$

Single displacement reaction (electroless)

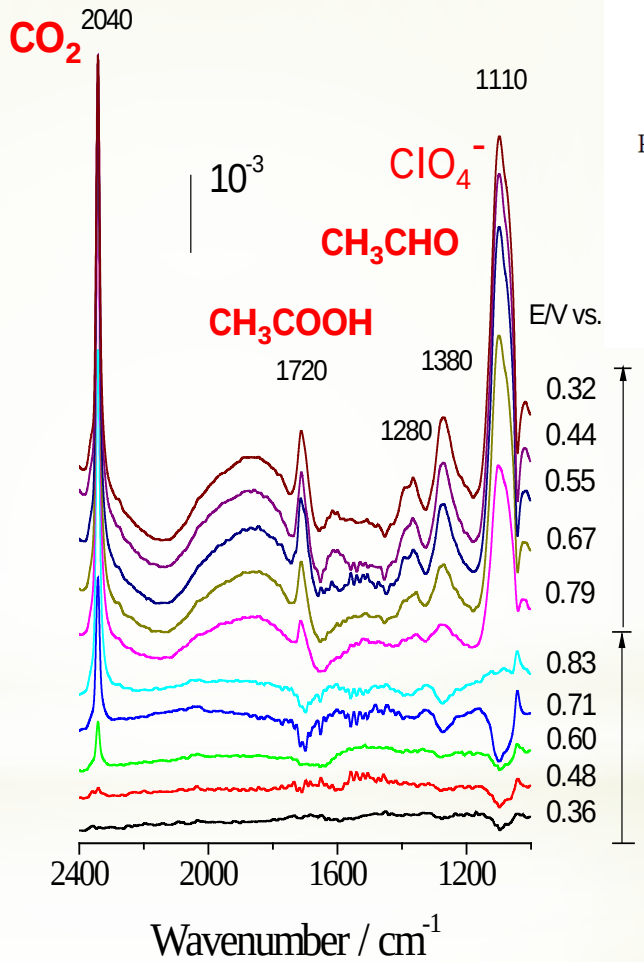
Previous Results on Pt-Rh-SnO_2 Nanoparticles

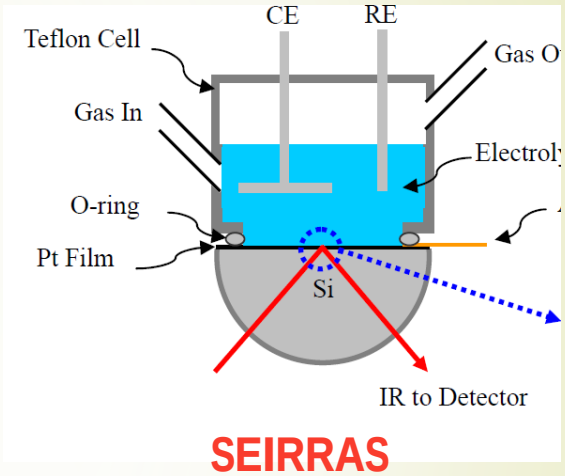
Particle size range: 1-3 nm; Homogeneous distribution of Pt and Rh throughout the particles.

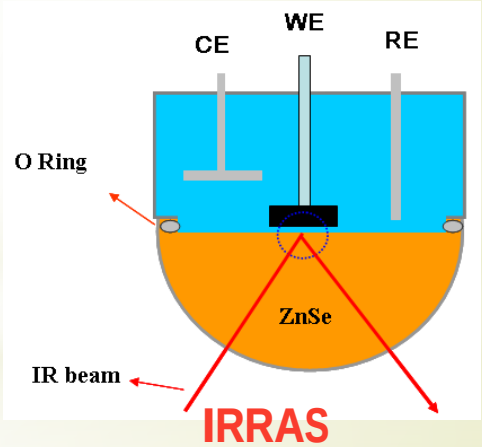
Electrochemical Activity



In situ IRRAS Study

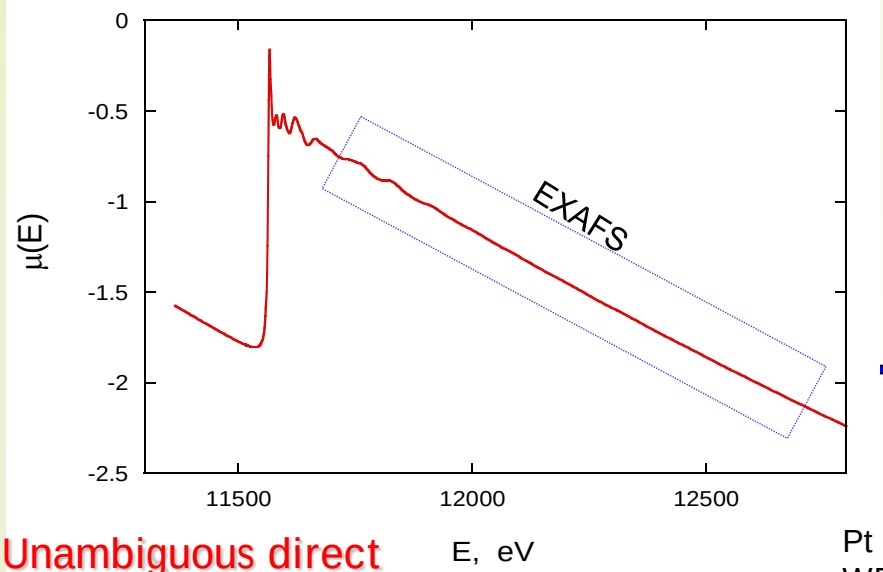




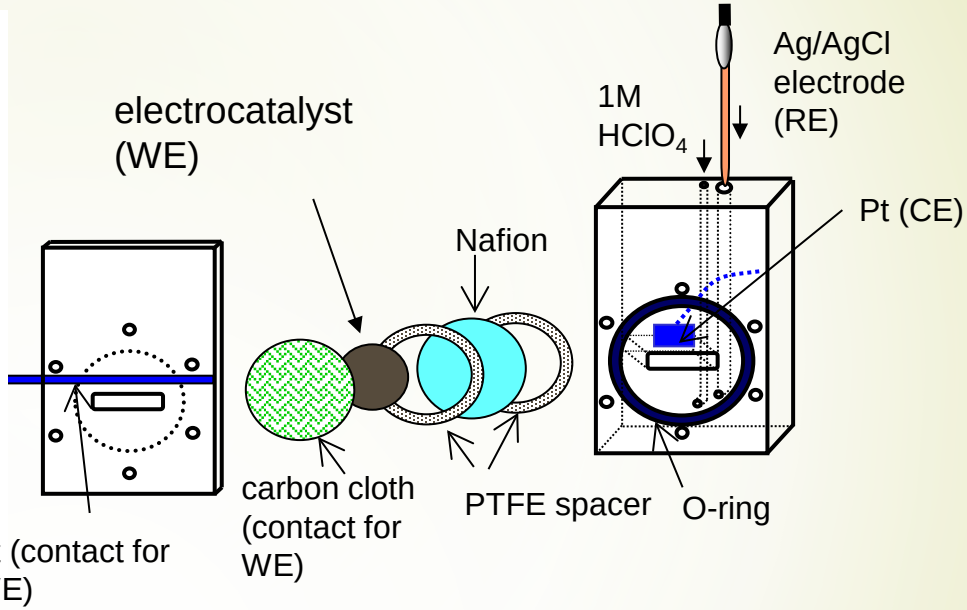


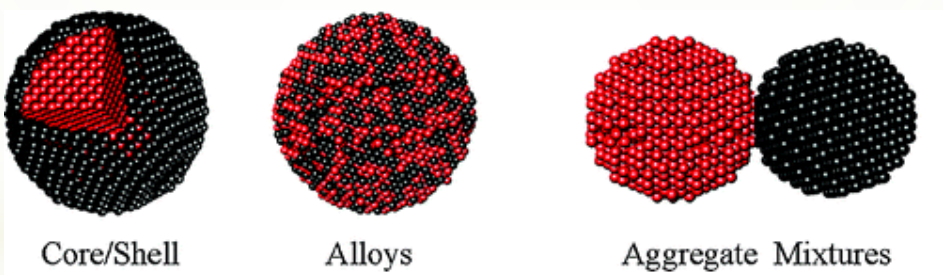
A. Kowal et al, *Nature Mat.*, **8** (2009) 325.

EXAFS: 3D structures, Coordination Numbers, Distances



Unambiguous direct structure-activity correlation with Pt MLs





Coordination numbers

Bond distances

Core/shell:
N(**Mcore-Mcore**) > N(Mshell-Mshell) ≠ 0

Alloys:
N(**M1**-M2) ≈ N(M2-**M1**) ≠ 0

Aggregate mix.
N(**M1**-M2) ≈ N(M2-**M1**) ≈ 0

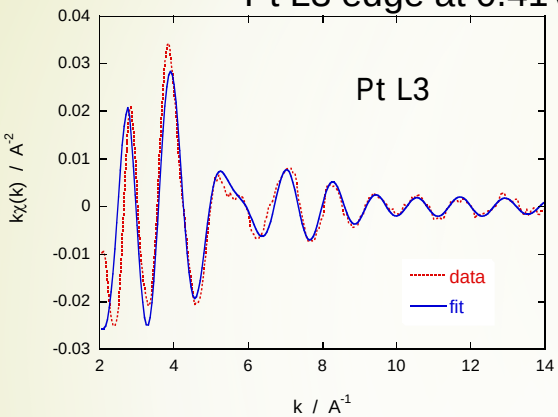
Core/shell:
d(shell-shell) ≠ d(bulk)
d(**core-core**) ≈ d(**bulk**)

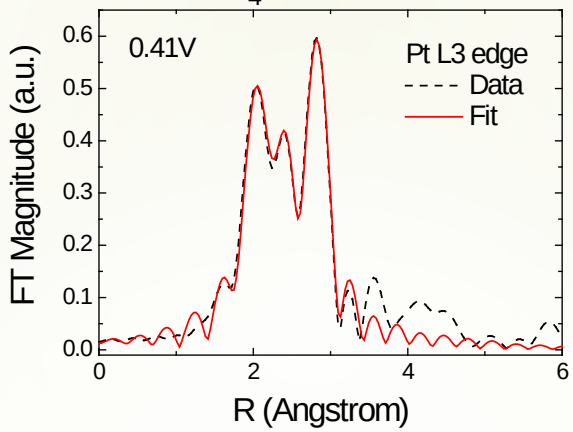
Alloys:
d(**M1-M1 bulk**) < d(**M1**-M2) < d(M2-M2 bulk)

Aggregate mixtures:
d(**M1-M1**) = **d(M1 bulk)**
d(M2-M2) = d(M2-M2 bulk)

In situ EXAFS Analysis of Pt-Rh-SnO_2

Pt L3 edge at 0.41V in 0.1 M $HClO_4$





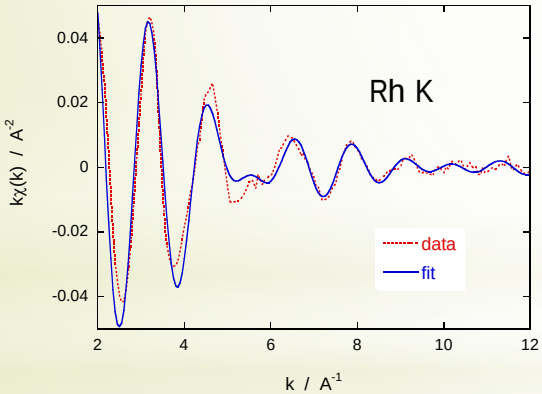
N_{Pt-Pt} = 5.1 (±1.0)
N_{Rh-Rh} = 1.9 (±0.9)

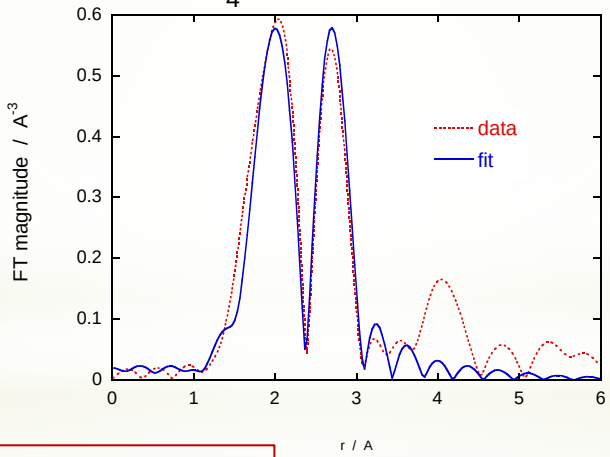
N_{Pt-Rh} = 1.7 (±1.1)
N_{Rh-Pt} = 5.5 (±1.6)

d_{Pt-Pt} = 2.740 Å (±0.012) (< Pt 2.77 Å)
d_{Pt-Rh} = 2.714 Å (±0.005)
d_{Rh-Pt} = 2.714 Å (±0.019)
d_{Rh-Rh} = 2.683 Å (±0.028) (≈ Rh 2.69 Å)

$d_{Pt-Pt} > d_{Pt-Rh} = d_{Rh-Pt} > d_{Rh-Rh}$

Rh K edge at 0.41V in 0.1 M $HClO_4$





$N_{Pt-Rh}/N_{Rh-Pt} = 0.31 \cong x_{Rh}/x_{Pt}$ from ICP (0.33) !

$N_{Pt-Pt} + N_{Pt-Rh} = 6.8$ (±1.1)

$N_{Rh-Rh} + N_{Rh-Pt} = 7.4$ (±1.6)

For solid solution:

$N(M_1M_2) / N(M_2M_1) = X(M_2) / X(M_1)$

$\Sigma_i N(M_1M_i) = \Sigma_i N(M_2M_i)$

$d(M_1) > d(M_1M_2) > d(M_2)$

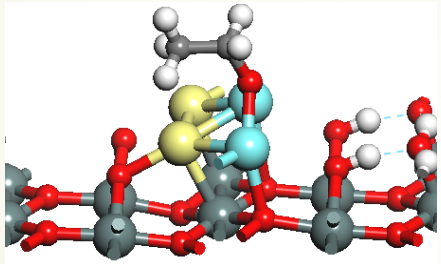
A. Frenkel, *Z.Kristallogr*, **222** (2007) 605.

PtRh solid-solution-alloy nanoparticles with a diameter of 1~2 nm

A. Kowal et al, *Nature Mat.*, **8** (2009) 325.

C-C Bond Breaking on Pt-Rh-SnO_2

Ethanol adsorbed at the Rh top site of PtRh/SnO_2 through O



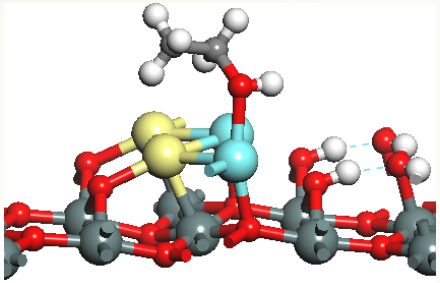
CH_3CH_2OH

-0.65

$*CH_3CH_2OH$

0.10 (1.10)

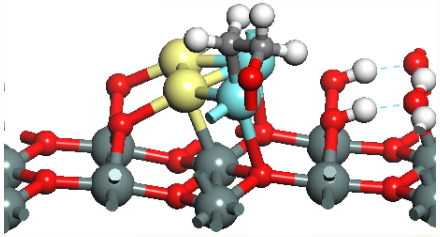
$*CH_3CH_2O + H*$



Dehydrogenation to ethoxy

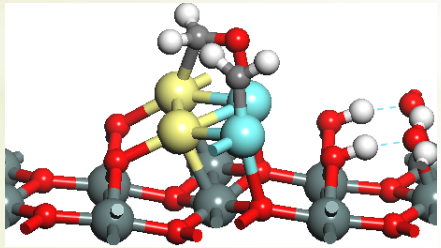
-0.27 (0.94)

$*CH_2CH_2O + 2H*$



Dehydrogenation to oxamettallacycle

0.98 (1.29)



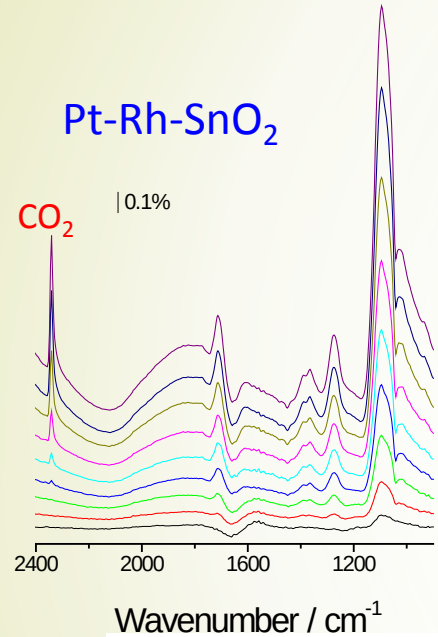
$*CH_2 + *CH_2O + 2H*$

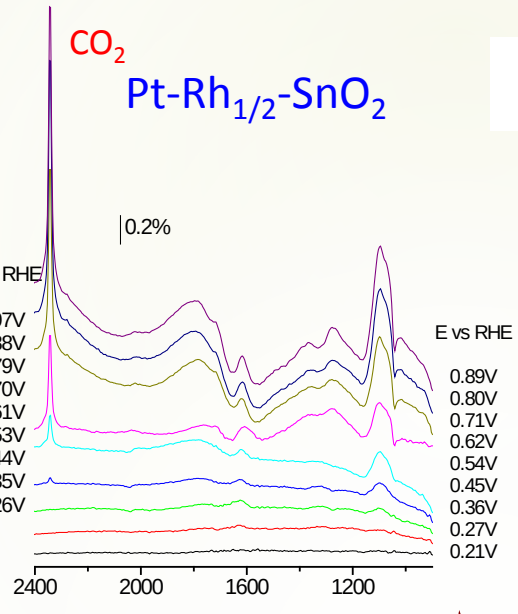
C – C bond breaking

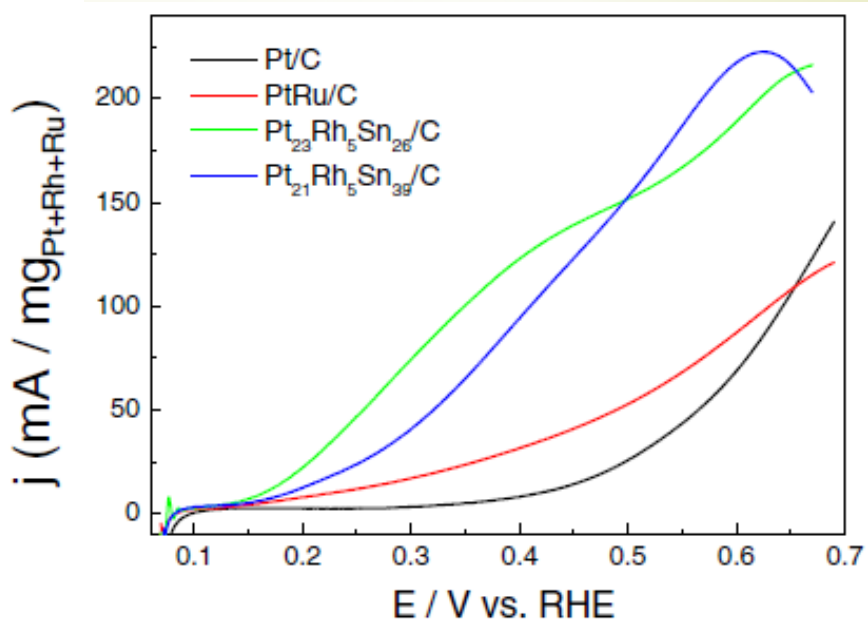
Sn;
Pt;
Rh;
C: small grey;
O;
H: small white

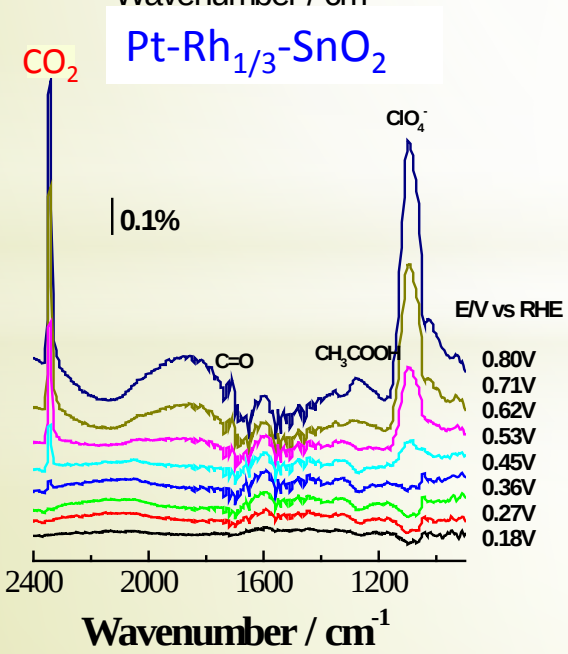
SnO_2: precludes the Rh and Pt sites to form M-OH, so they react with ethanol; provides OH to oxidize CO.
Pt: helps ethanol dehydrogenation; modifies Rh for moderate bonding to ethanol.
Rh: accomplishes the C-C bond breaking.

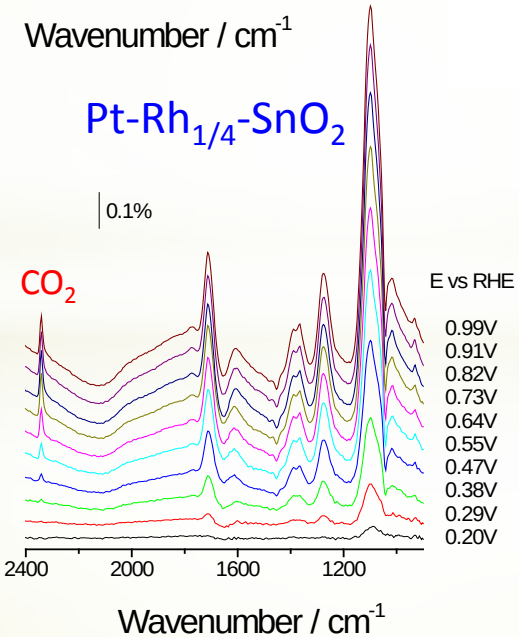
Optimizing Rh Content







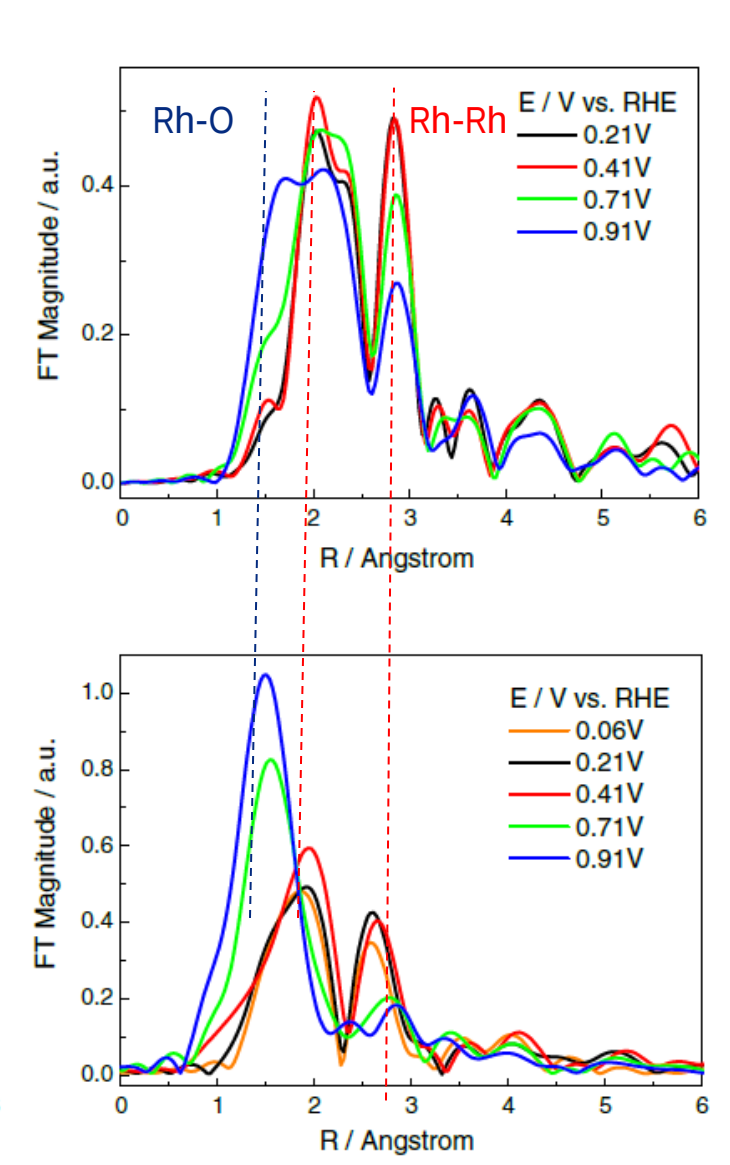




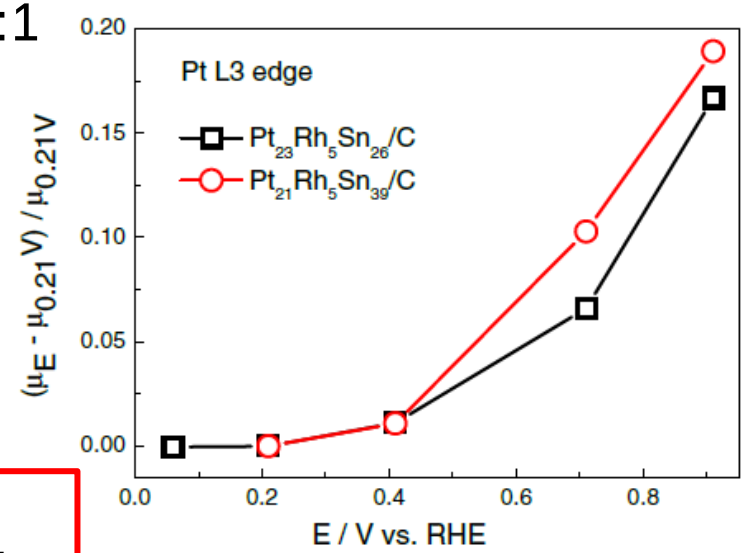
Best ratio
Pt:Rh = 3:1

M. Li et al, *Electrochim.Acta*, 104 (2013) 454.

Optimizing Sn Content

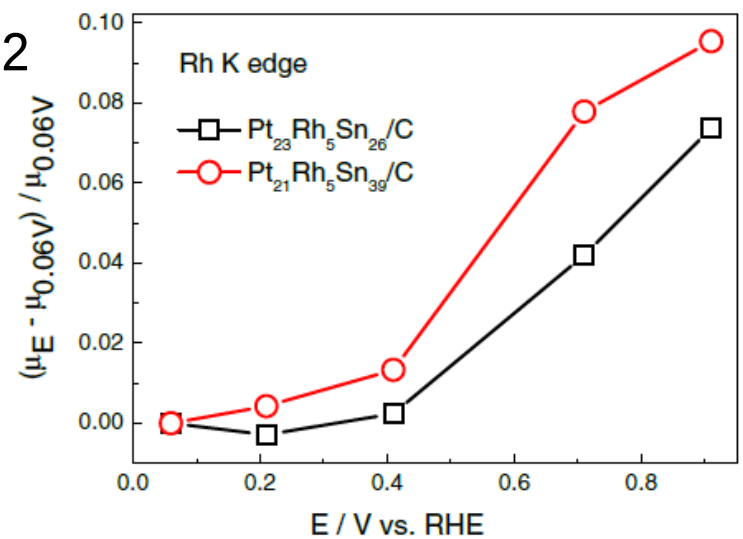


Pt:Sn = 1:1



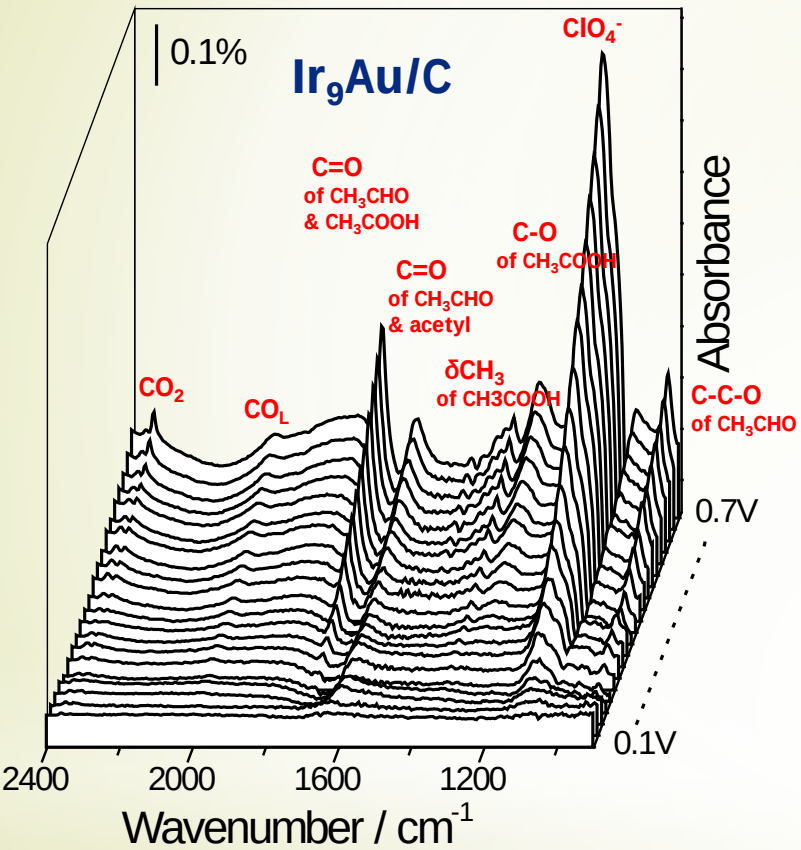
Best ratio
Pt:Sn = 1:1

Pt:Sn = 1:2



M. Li et al, *Electrocatalysis*, 3 (2012) 376.

Substitute Rh with a Cheaper Alternative?

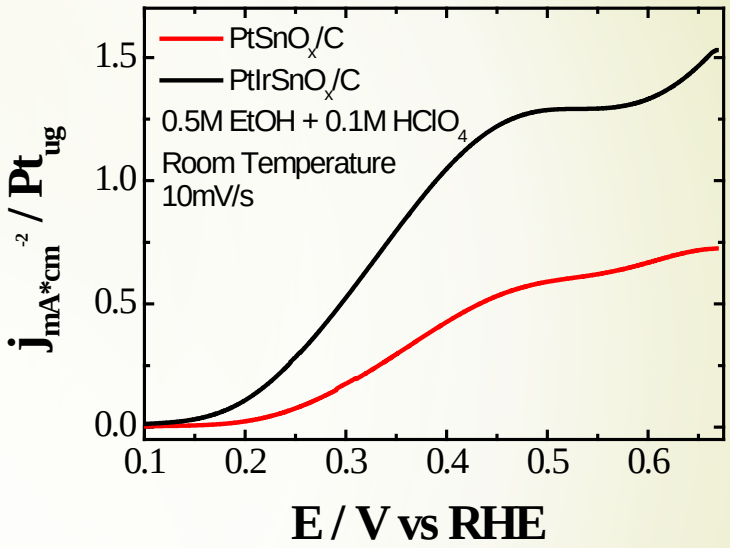


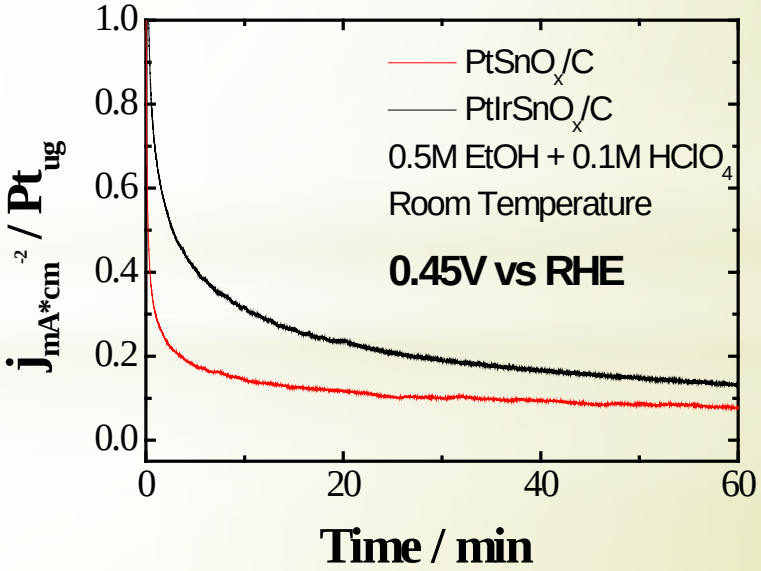
Ir oxidizes ethanol to CH_3COOH

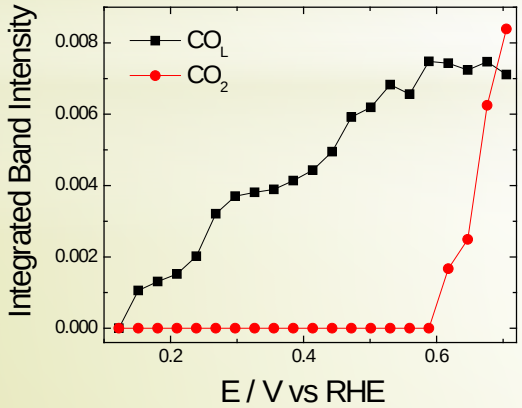
Ir_6Sn_4/C cannot split C-C bond

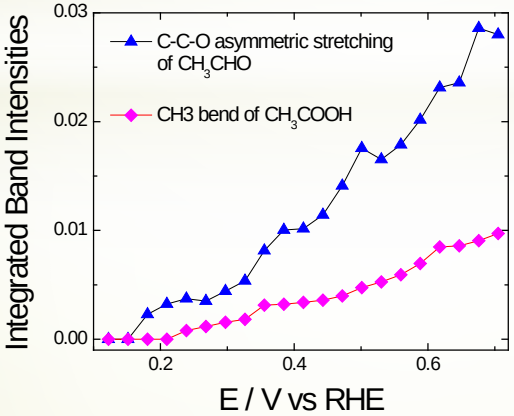
Ir_9Au/C can break C-C bond but cannot oxidize ethanol to CO_2

$PtIrSnO_2/C$ can break C-C bond and oxidize ethanol to CO_2









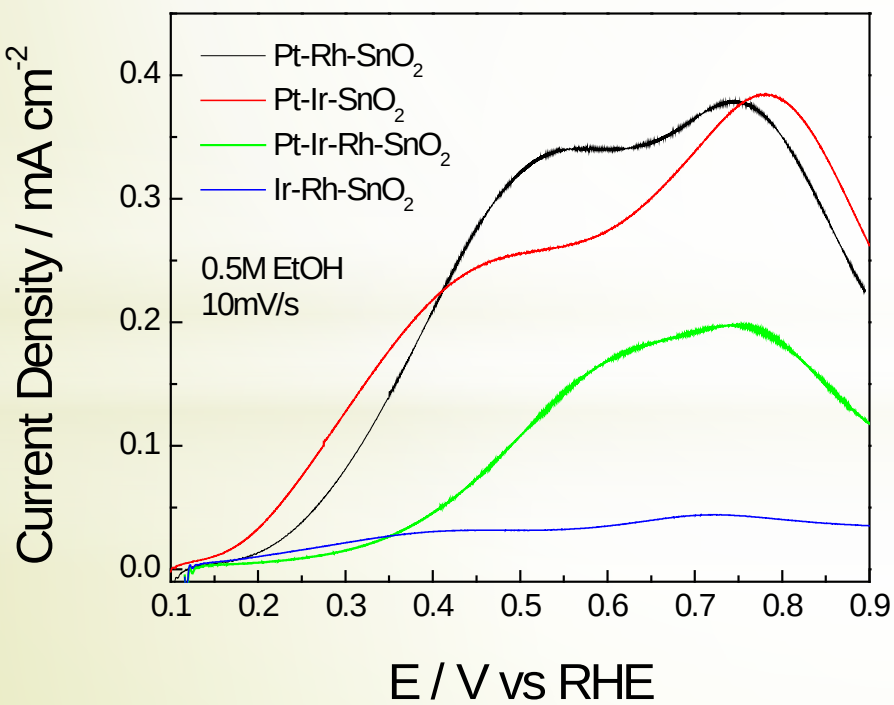
M. Li et al, JACS, 135 (2013) 132.

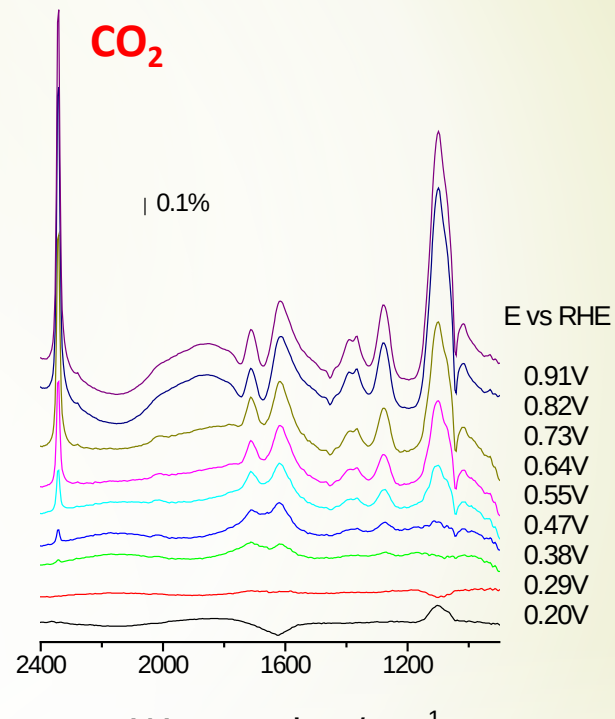
Possible Alternative: Ir-SnO_2 Catalysts

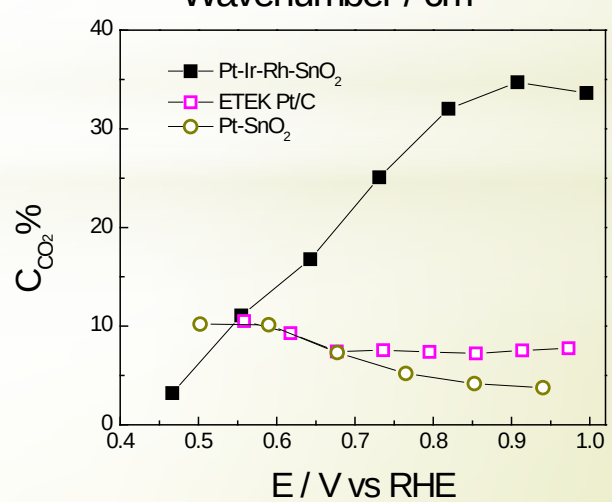
Ir-Rh-SnO_2 is inactive for ethanol oxidation.

Pt-Rh-SnO_2 activity better than Pt-Ir-SnO_2 at practical potentials.

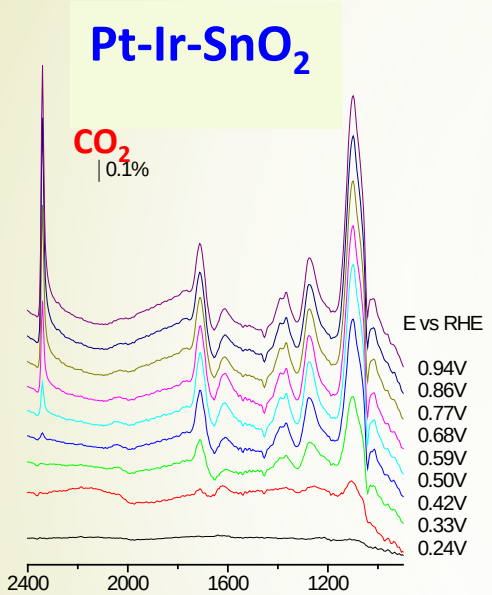
Pt-Ir-Rh-SnO_2 shows enhancement in production of CO_2.

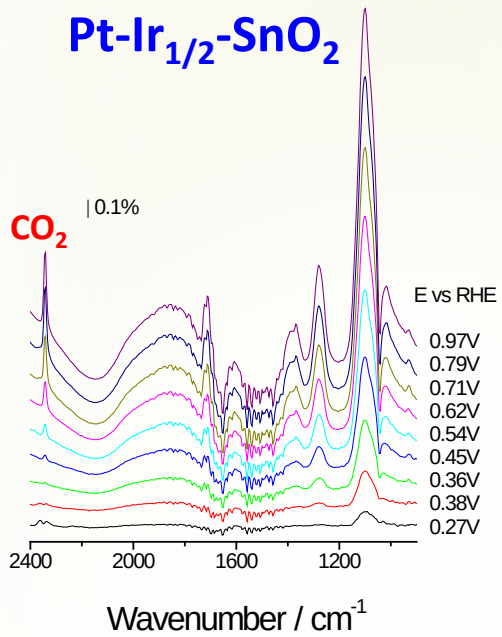


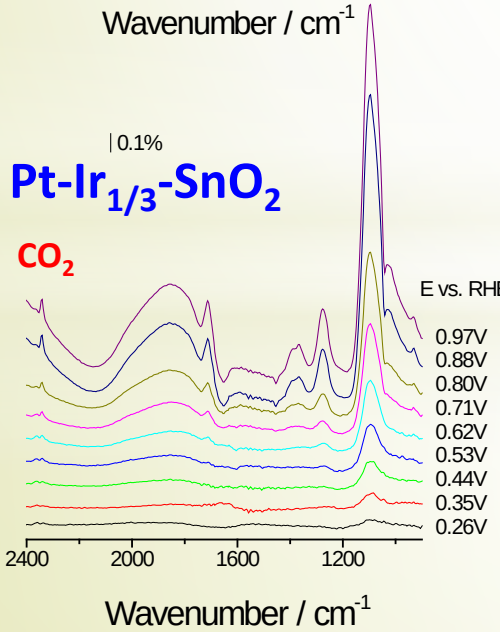


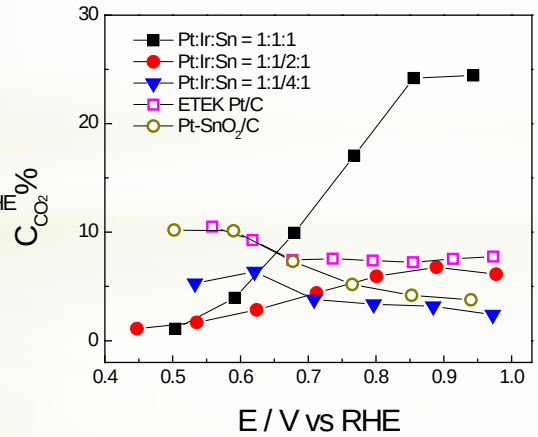


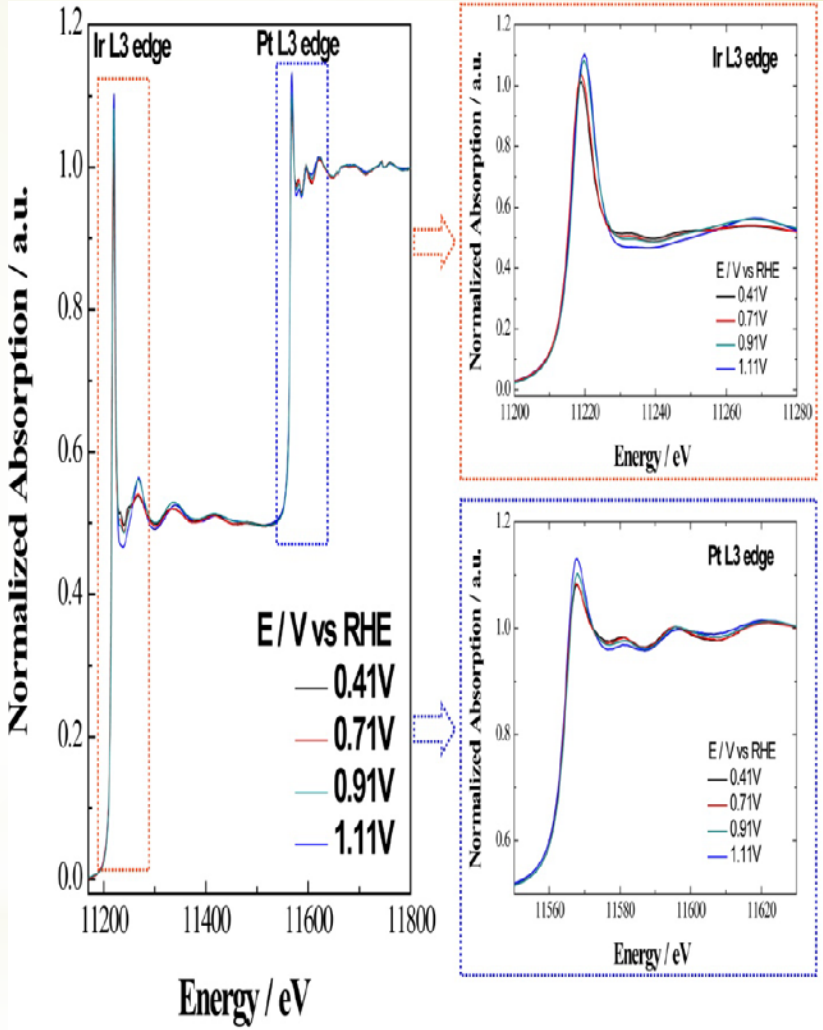
Optimizing Ir Content in Pt-Ir-SnO_2











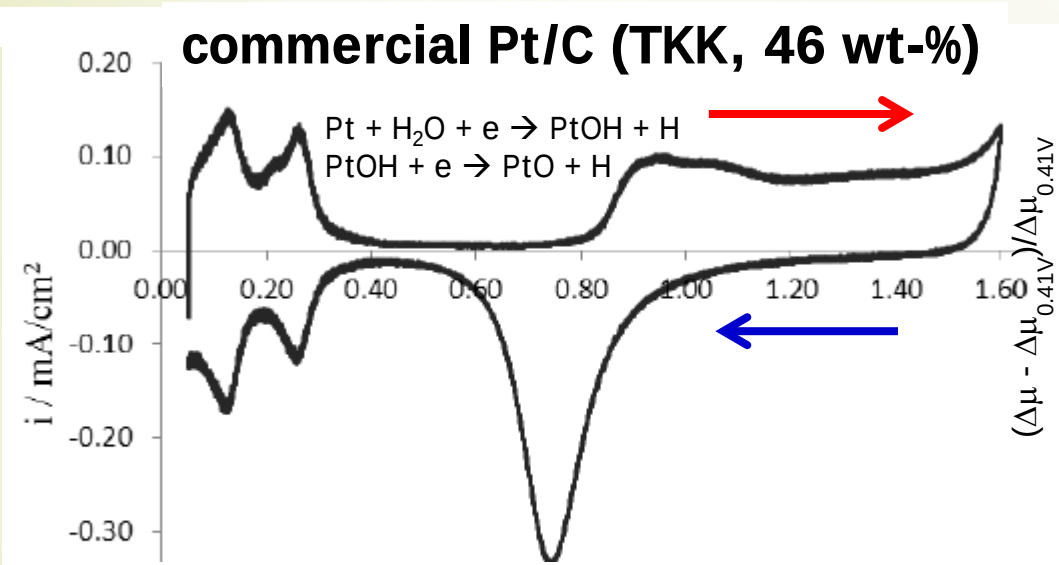
SnO_2 keeps Pt and Ir in metallic state below 0.7 V

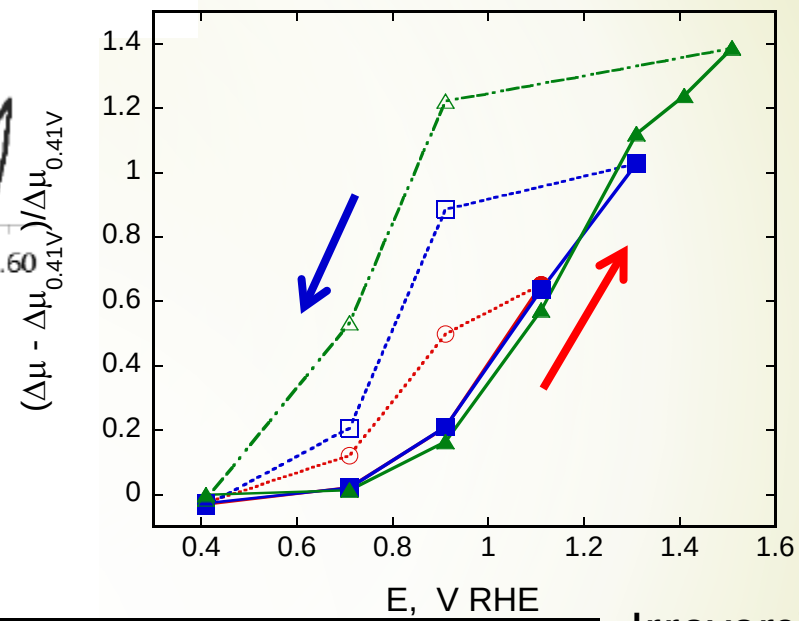
M. Li et al, JACS, 135 (2013) 132.

Anode Side Summary: EtOH Oxidation on Pt-Rh-SnO_2

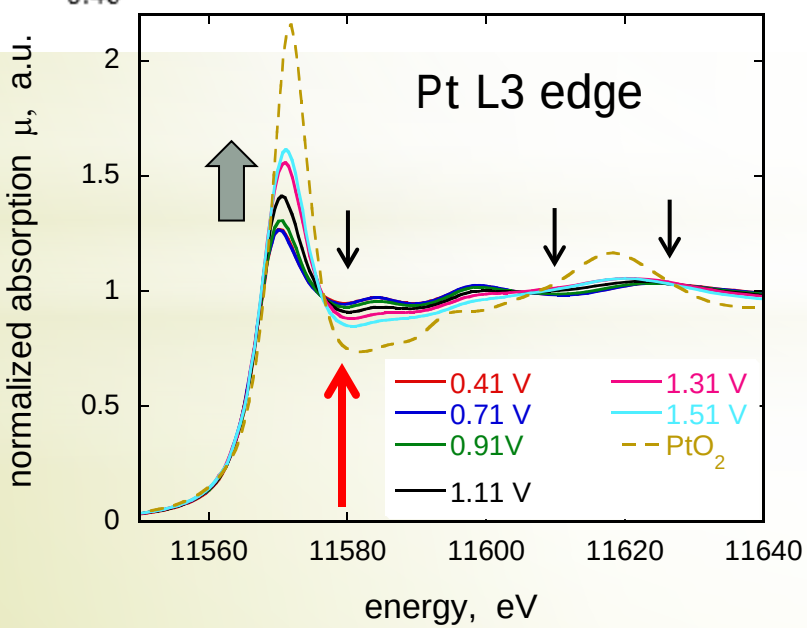
* Ternary Pt-Rh-SnO_x electrocatalysts show unprecedented activity for ethanol oxidation and produce large amount of CO_2.
* The optimized catalyst composition is Pt / Rh / Sn = 1 / (1/3) / 1.
* Cheaper alternatives seem possible, by substitution of Rh with Ir.
* Binary Au-Ir catalyst splits C-C bond but cannot oxidize ethanol to CO_2.
* Ternary Ir catalysts can split the C-C bond and oxidize ethanol to CO_2.
* Key component requirements:
  - i) component to provide OH for CO oxidation while suppressing oxidation of other constituent(s);
  - ii) component to facilitate a strong adsorption of ethanol to split C- C bond.

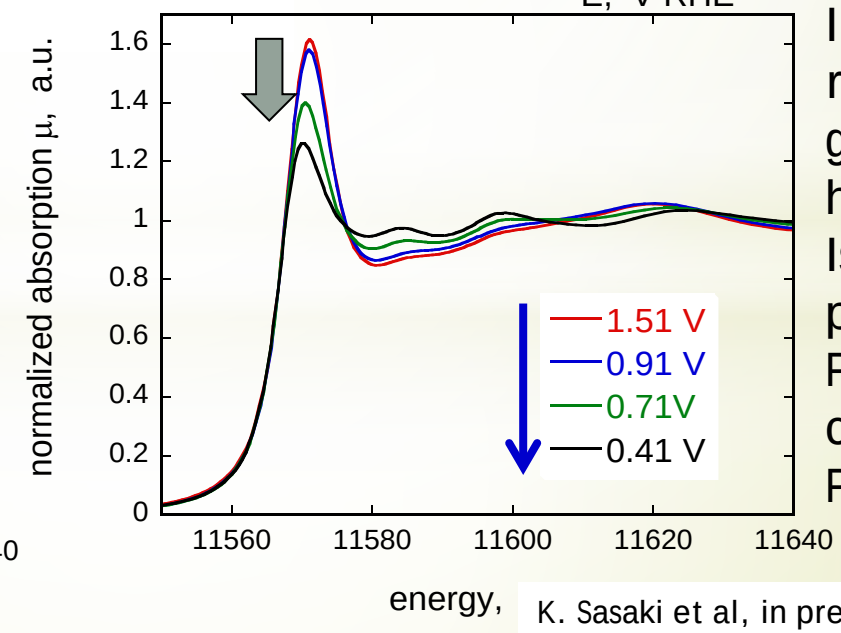
Cathode side: Oxygen Reduction on Pt/C





White line intensity follows oxidation

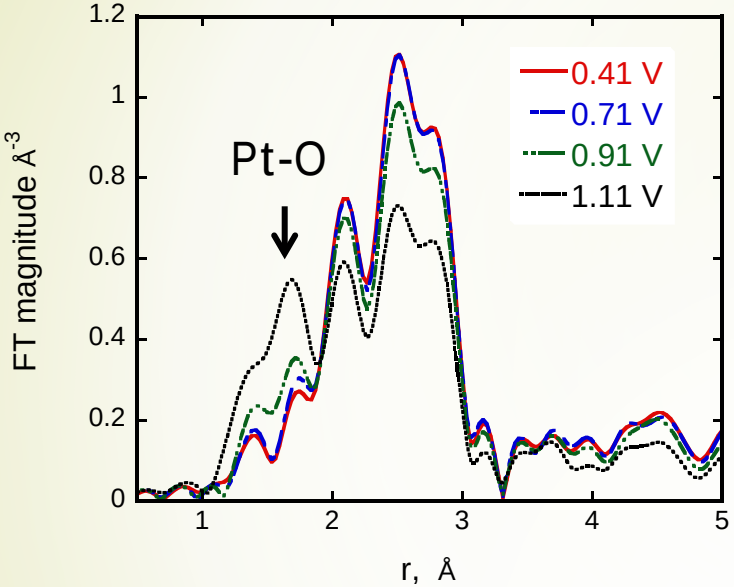


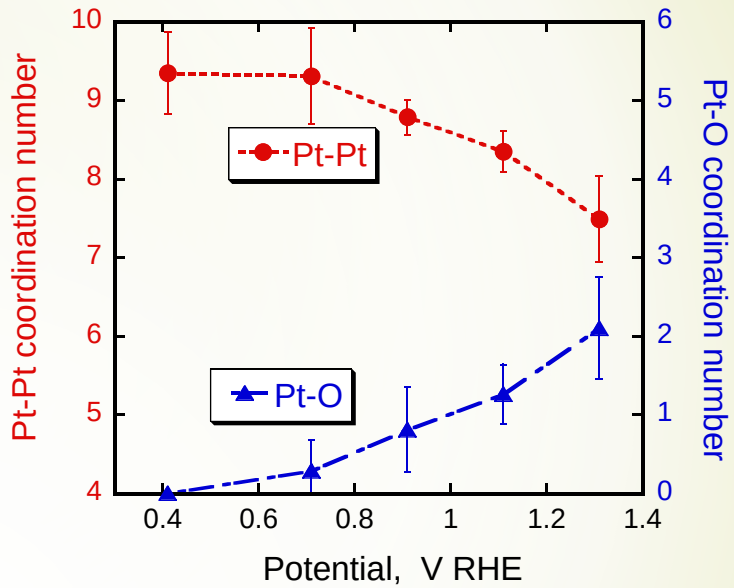


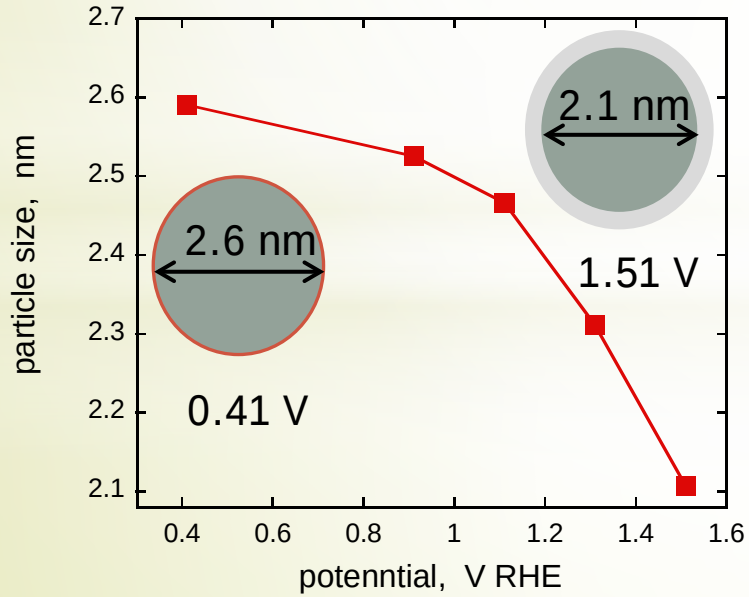
Irreversible reduction gives hysteresis; Isosbestic points with Pt/C and commercial PtO_2

K. Sasaki et al, in preparation.

In Situ XAS and XRD of Carbon-Supported Pt/C







XAS

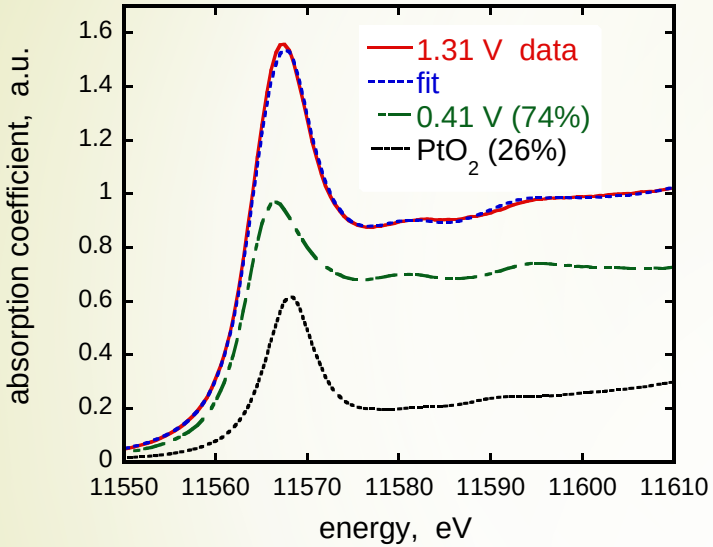
- Pt-O peak increases with potential
- Pt-Pt & Pt-O CNs: *ca* 2.5 nm diameter Pt at 0.41 V and the formation of 1~2 monolayer oxide growth with increasing potentials

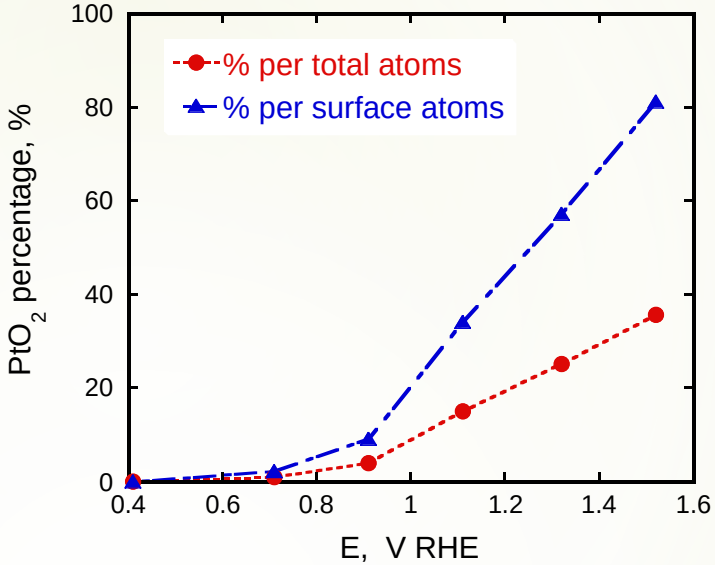
XRD

- Pt peaks decrease with E; no PtO_2 peaks
- Particle size decreases from 2.6 (at 0.41 V) to 2.1 nm at 1.51 V): 0.9 monolayer Pt oxidized

In Situ XANES of Carbon-Supported Pt/C

Liner Combination Fitting (LCF)





Ratio of surface atoms (N_s) to total atoms (N_t) is a function of particle size.

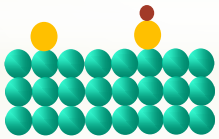
(Benfield, J Chem Soc Farad Trans.1999, 88, 1107)

- N_s/N_t = 0.44 for 2.6 nm NPs
- 81% of surface atoms oxidized at 1.51 V

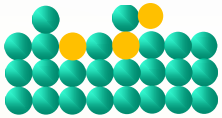
Δμ technique (Rameker *et al*)

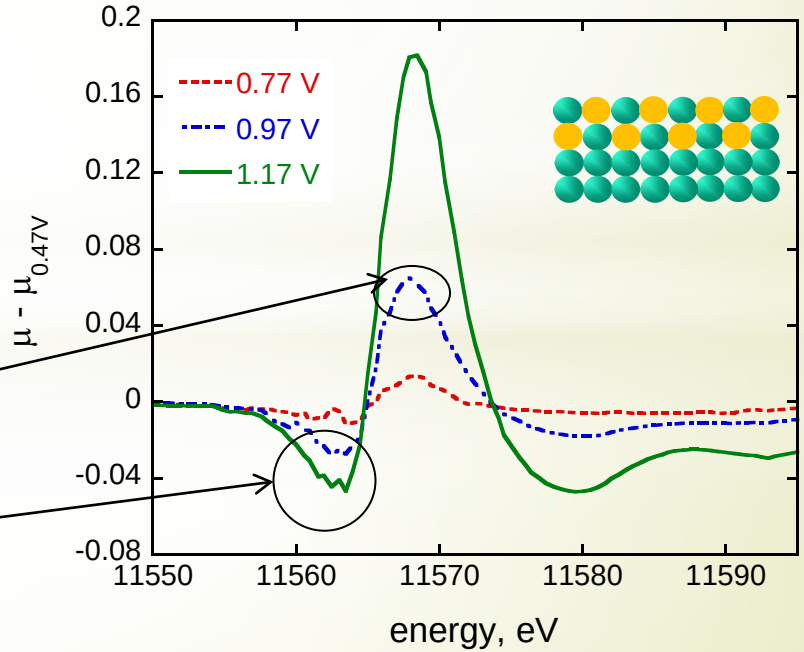
$\Delta\mu$ (= μ - $\mu_{0.41V}$)

O(OH) in atop site of Pt (0.77 V)



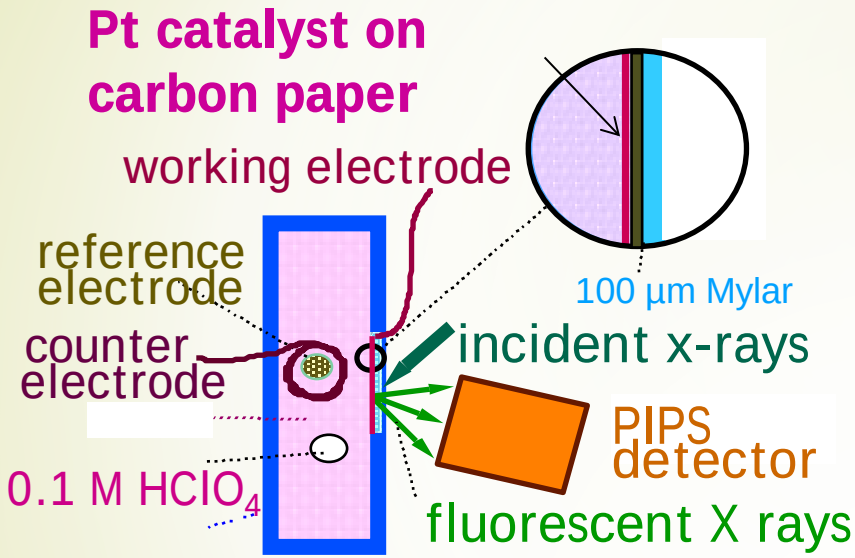
The formation of subsurface O (place-exchanged with Pt) above 0.97 V

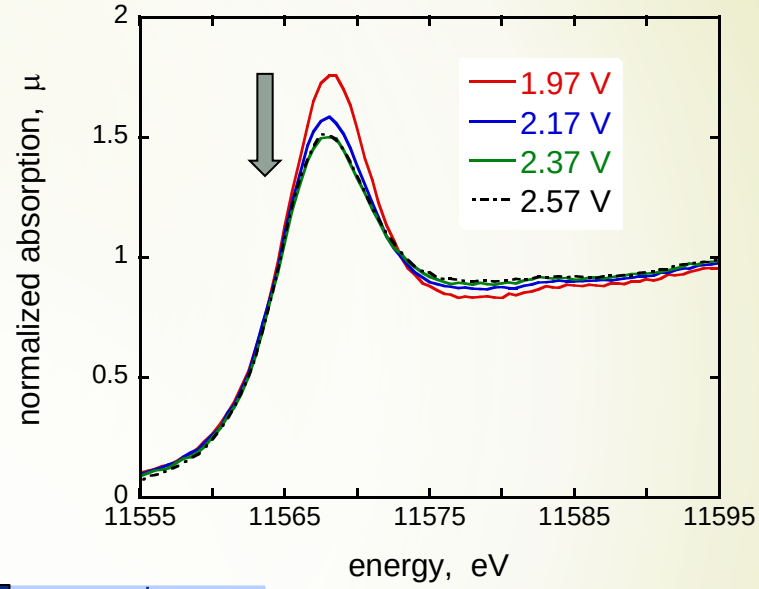


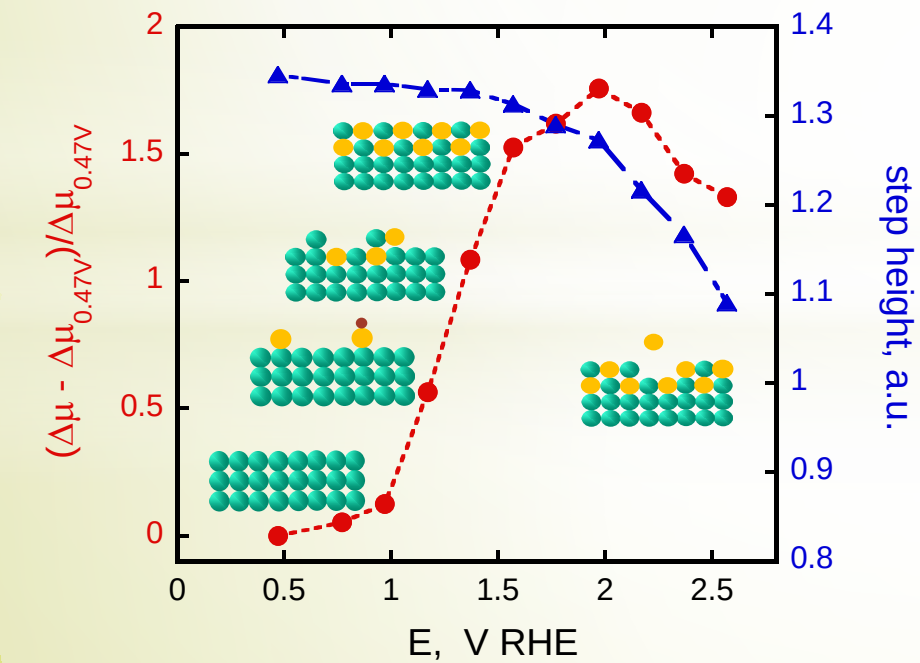


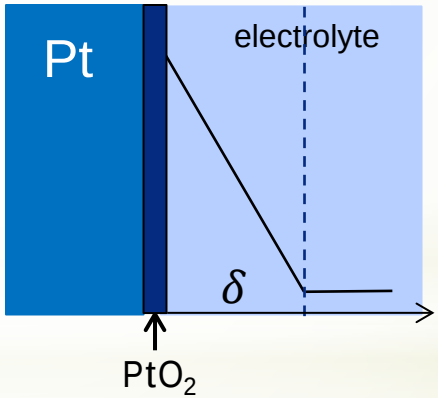
(Arruda, et al, JPCC, 2008, 112, 18087; Teliska, et al, JPCB 2005, 109, 8076)

In situ XAS Cell for Higher Potentials









$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$[H^+] = \sim 5$ M

$PtO_2 + 2H^+ \rightarrow PtO + H_2O$

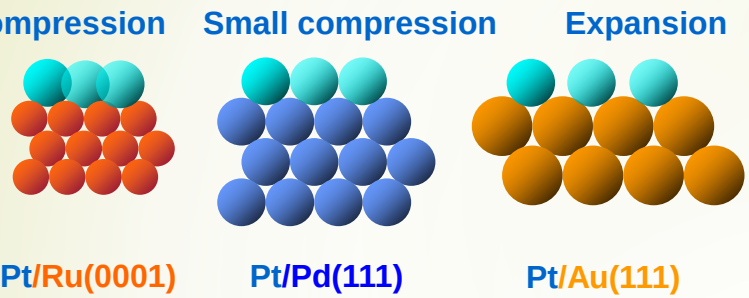
$PtO + 2H^+ \rightarrow Pt^{2+} + H_2O$

Decrease of Pt step height → loss of Pt

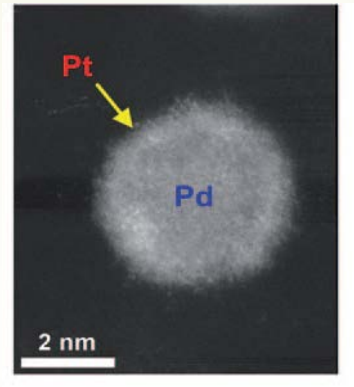
- ❑ Detachment of Pt NPs by vigorous O_2 evolution and/or carbon corrosion
- ❑ Dissolution of Pt oxide

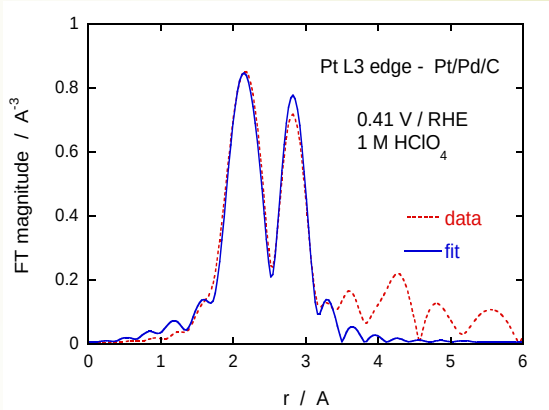
K. Sasaki et al, in preparation.

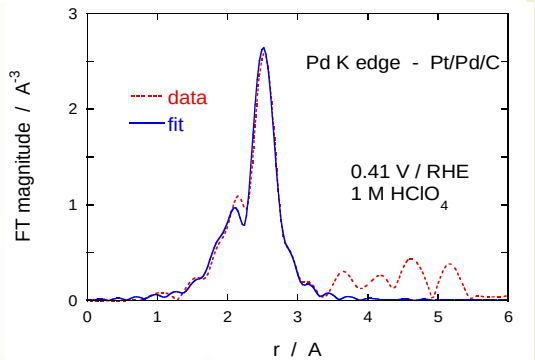
Pt Monolayer Electrocatalysts for O_2 Reduction



Adzic et al, Top. Catal. 46 (2007), 249







Unique Features of XAS characterization

Pt ML catalysts: signal reflects the changes of the top Pt layer that takes part in reaction

Unambiguous direct structure-activity correlation with Pt MLs

Fit Pt L3 and Pd K data (at 0.41 V) concurrently with constraints:

$N_{Pt\text{-}Pd} = (x_{Pd}/x_{Pt})*N_{Pd\text{-}Pt}$ & mole ratio x_{Pd}/x_{Pt}=3.1 from ICP

$N_{Pt\text{-}Pt}$ = 5.8 (±0.8)

$N_{Pt\text{-}Pd}$ = 2.7 (±0.7)

$R_{Pt\text{-}Pt}$ = 2.729 Å (±0.005) (< 2.744 Å Pt/C < 2.772 Å Pt)

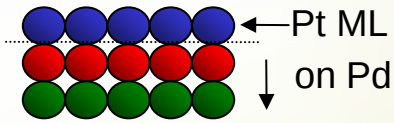
(A.Frenkel, Z. Kristallogr. 222 (2007) 605)

Montejano-Carrizales et al, NanoStruct. Mater., 8 (1997) 269.
McBreen, Mukerjee, Fuel Cell Handbooks, 895

Pt ML on Pd(111)

$N_{Pt\text{-}Pt}$ = 6

$N_{Pt\text{-}Pd}$ = 3



Cubo-octahedron

(111) + (100) + edges

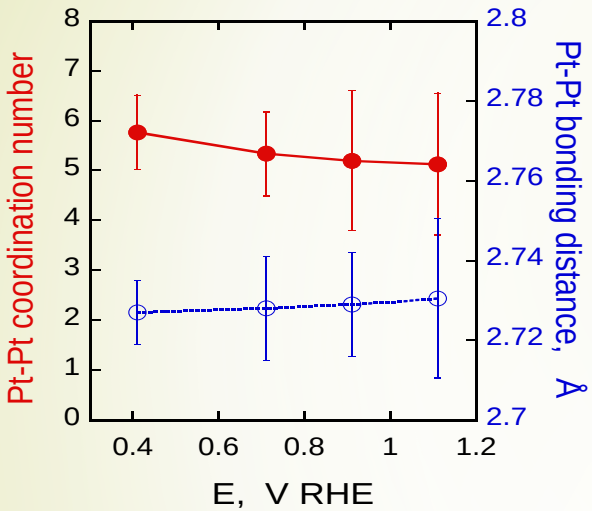
For ϕ4.5 nm particle,

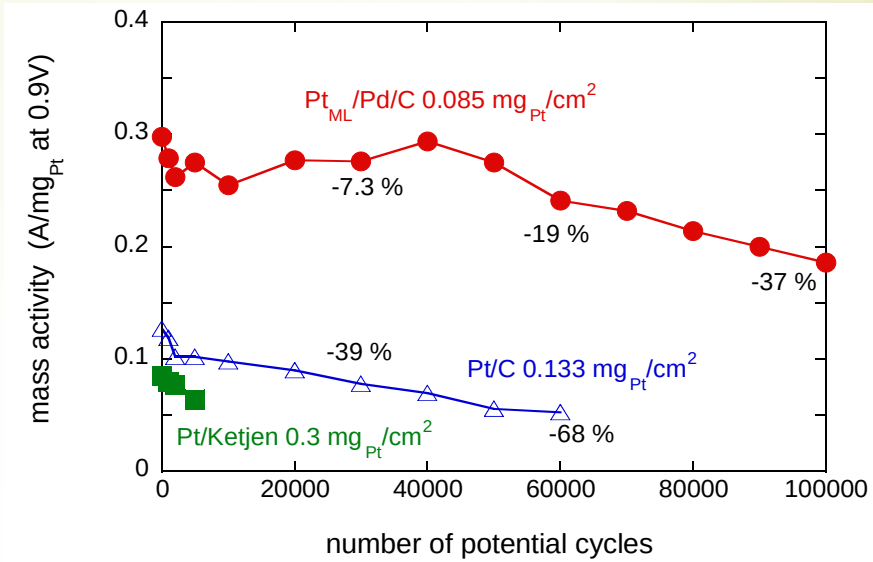
$N_{Pt\text{-}Pt}$ = ~5.2

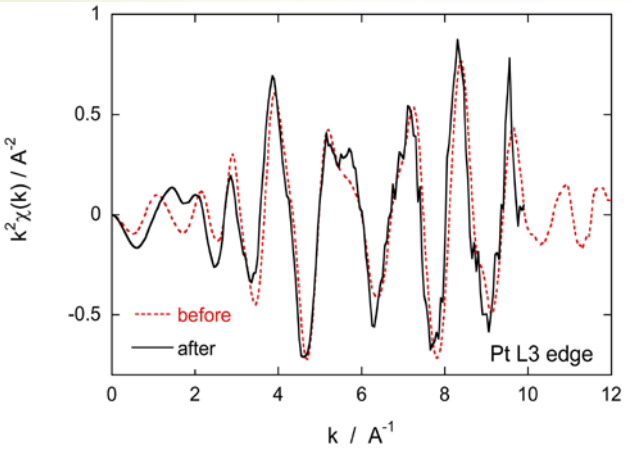
$N_{Pt\text{-}Pd}$ = 3.2

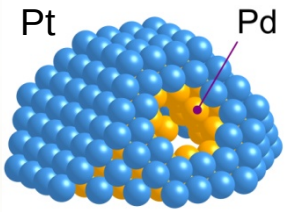
Formation of Pt ML & the contraction in Pt bonding verified

In Situ XAS of Pt / Pd Core-Shell Nanoparticles









- Oxidation of Pt monolayer is retarded compared with Pt/C
- N_{Pt-Pt} and R_{Pt-Pt} are fairly constant with potentials
- Pd preferentially forms PdO (or PdOH) at pinholes or defects on Pt ML, which prevents Pt oxidation
- Further oxidation of Pd at the defects and/or O penetration through Pt ML.

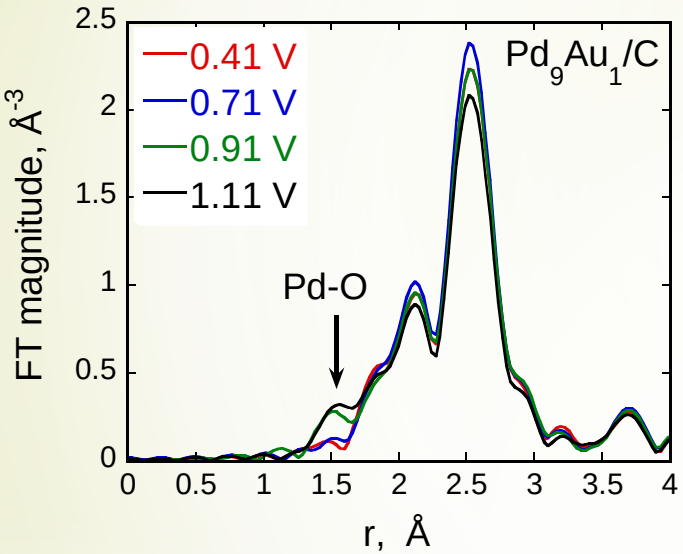
❖ The structure of Pt shells was almost retained after the MEA test

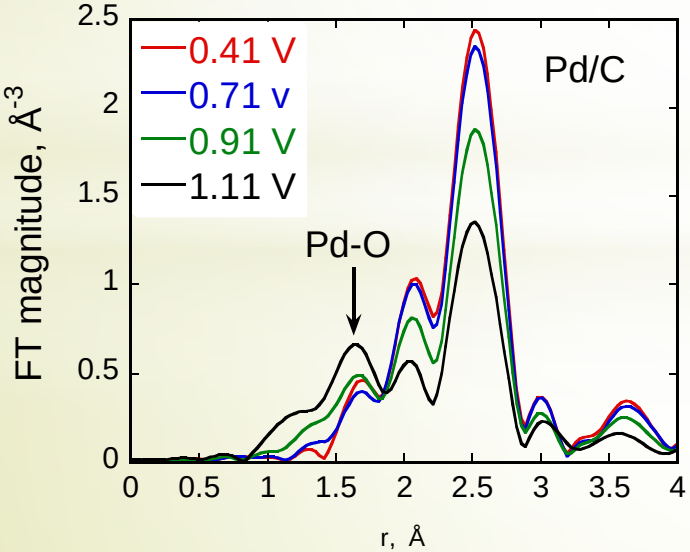
Significant losses of Pd core after the cycle test (STEM-EELS, EDX)

K. Sasaki, et al, *ACIE*, 46 (2010) 8602

In Situ XAS of Pd_9Au_1/C Nanoparticles

Alloying Pd with a small amount of Au to increase the stability (Pd:Au = 9:1)





Fit Pd K and Au L3 data (at 0.41 V) concurrently

N_{Au-Au}	2.3 (±1.6)	Au-Au	2.771 Å
N_{Au-Pd}	8.1 (±1.1)	Au-Pd (= Pd-Au)	2.760 Å
N_{Pd-Pd}	9.2 (±0.4)	Pd-Pd	2.756 Å
N_{Pd-Au}	0.9 (±0.1)		

For an ideal AB solid-solution alloy NPs with the mole ratio x_A/x_B (Frenkel, Z. Kristallogr. 222 (2007) 605)

(i) $N_{A-A}/N_{A-B} = x_A/x_B$

$N_{Au-Au}/N_{Au-Pd} = 0.28 : x_{Au}/x_{Pd} = 0.16$

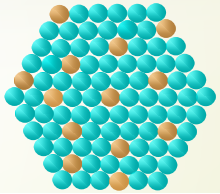
$N_{Pd-Pd}/ N_{Pd-Au} = 10.1 : x_{Pd}/x_{Au} = 9.0$

(ii) $N_{A-M} = N_{B-M}$

$N_{Au-Au} + N_{Au-Pd} = 10.4 : N_{Pd-Pd} + N_{Pd-Au} = 10.1$

The fitting result indicates the formation of Pd-Au solid-solution nanoparticles.

Both the XANES indicate possible electronic interaction between Pd and Au



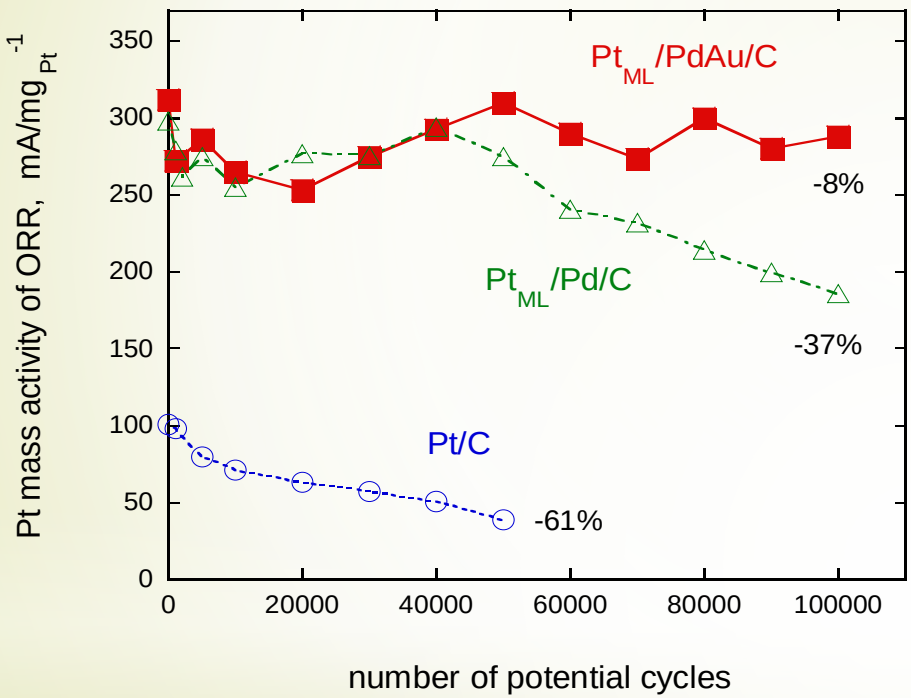
Pd

Au

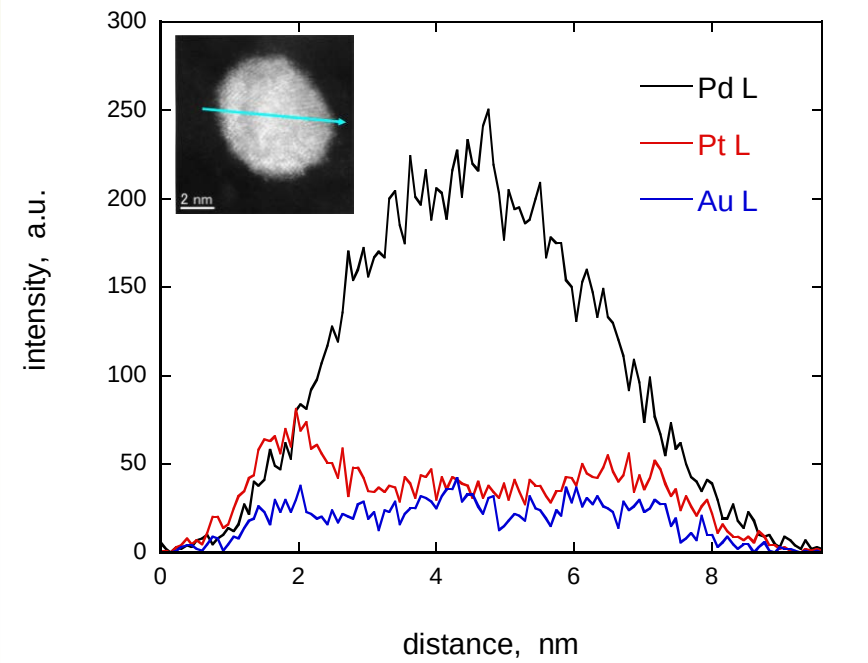
K. Kuttiyiel, et al, *Electrochim.Acta*, 110 (2013) 267

MEA Test of Pt Monolayer on PdAu Alloy Core

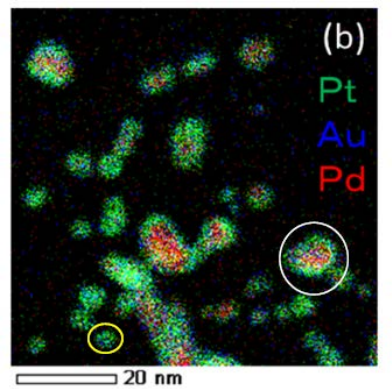
MEA stability test with potential cycling between 0.6 V and 1.0 V



The structure of Pt shell on PdAu core was retained after the 100k cycle test



Stability: $Pt_{ML}/Pd_9Au_1 > Pt_{ML}/Pd > Pt$

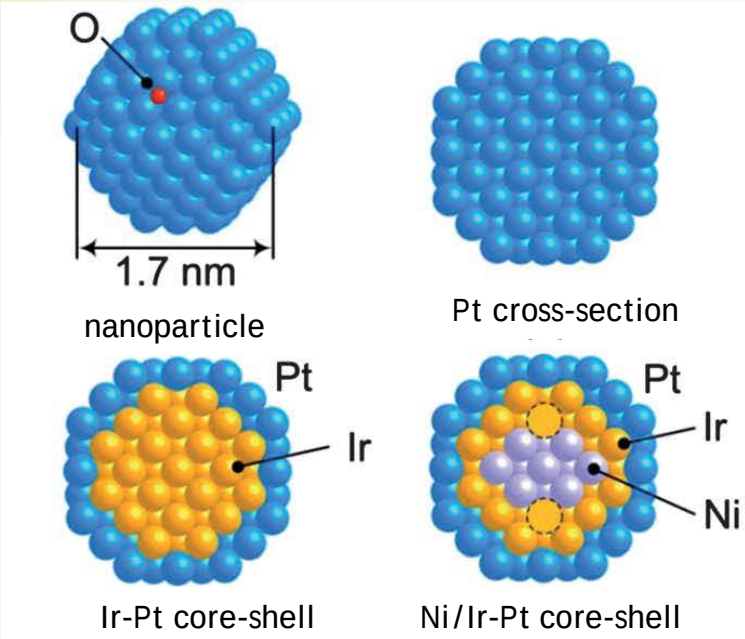


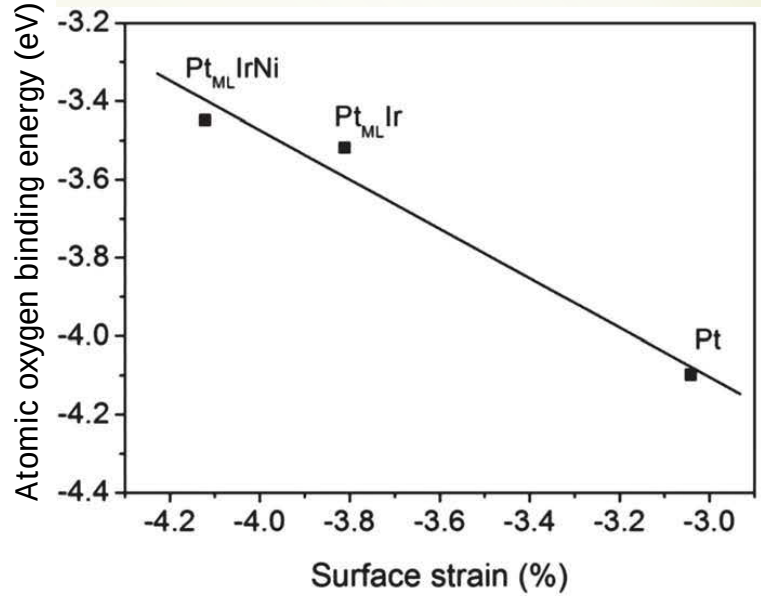
STEM/EDS elemental maps after 20k cycle test between 0.6V-1.4V

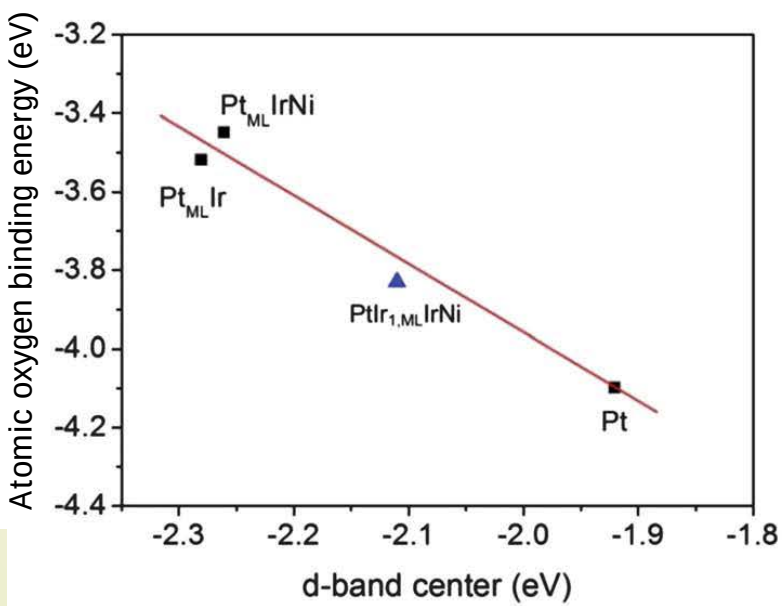
For relatively large particles, the core-shell structure is clearly retained under the hash condition.

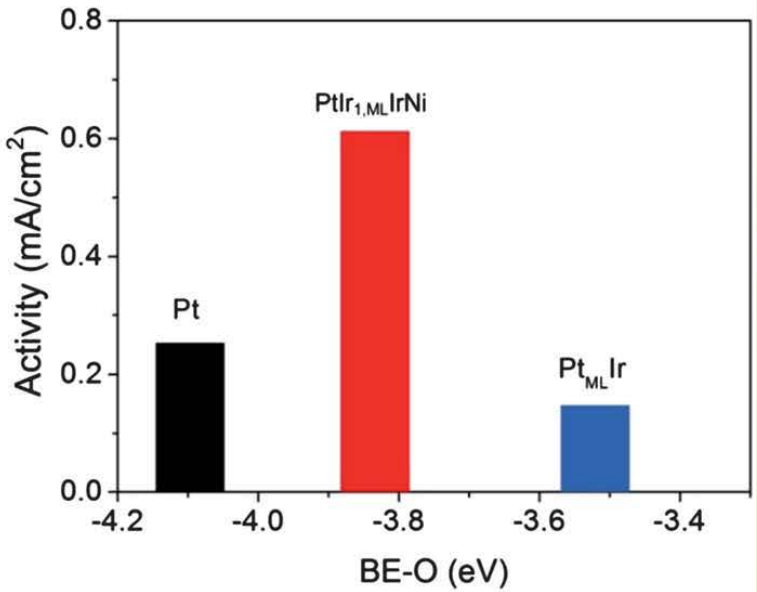
K. Sasaki et al, *Nat. Comm.*, 3 (2012) 1115

Pt/Ir-Ni Core-Shell Nanoparticles

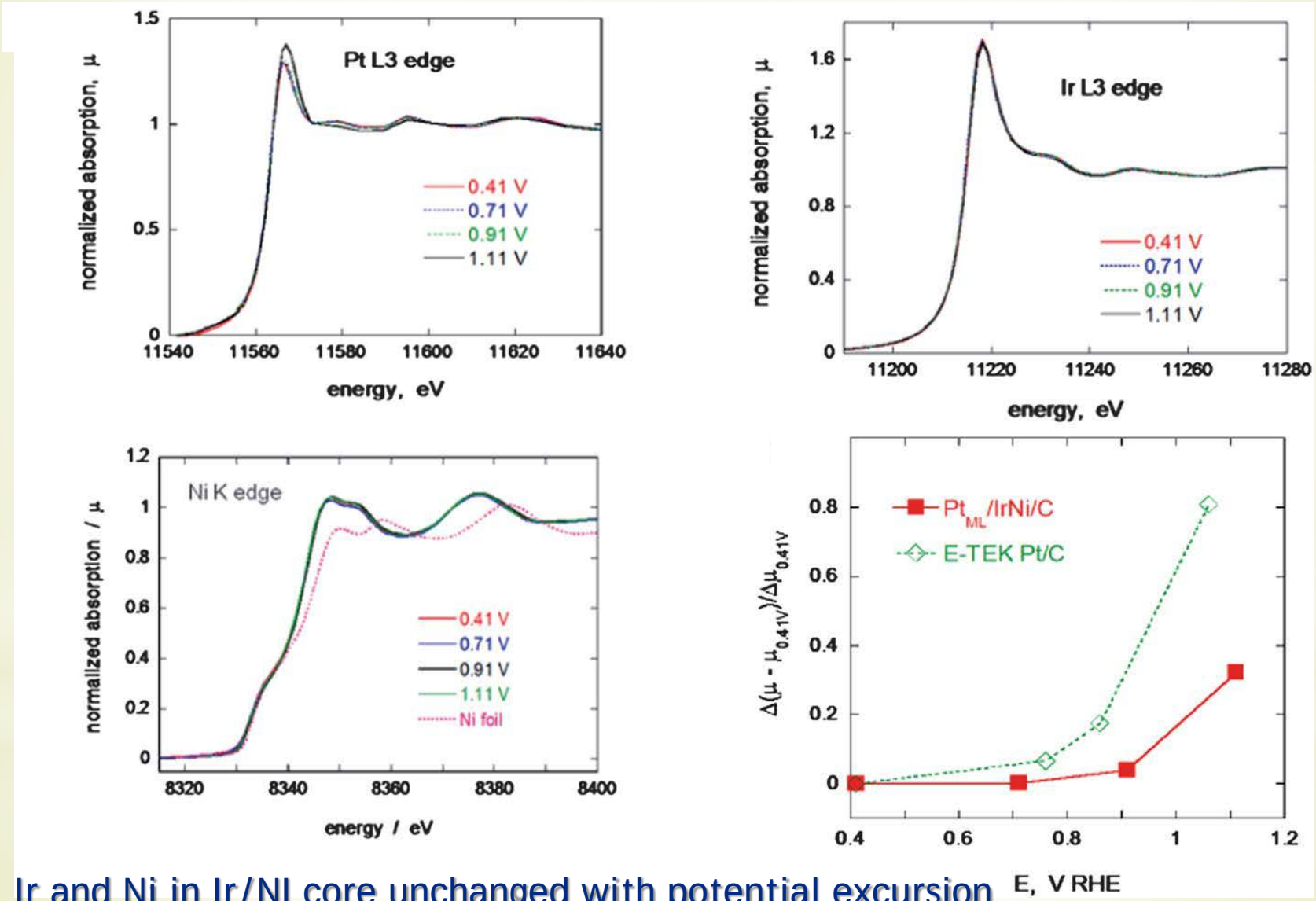








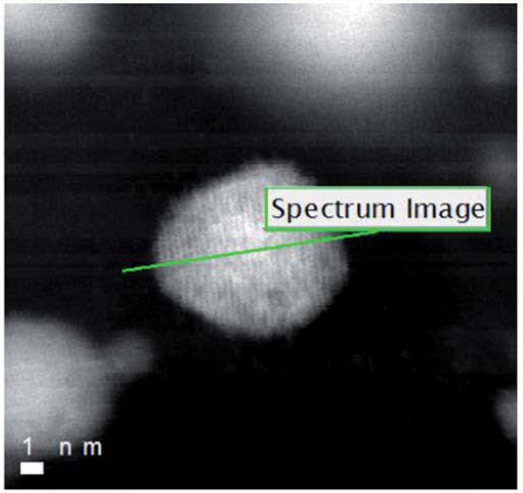
In Situ XAS Pt/Ir-Ni Core-Shell Nanoparticles

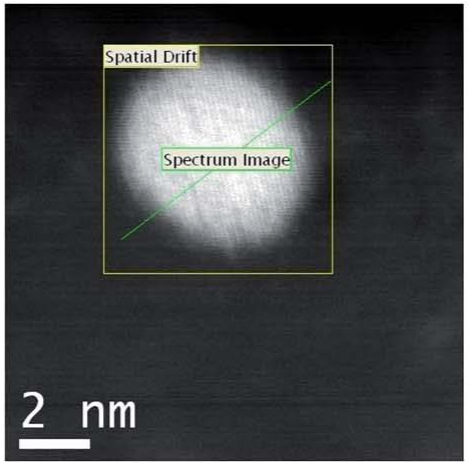


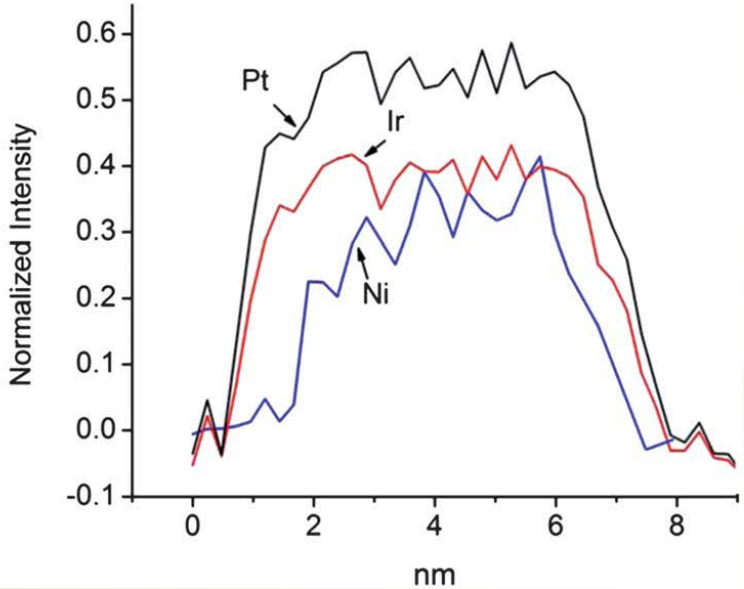
- Ir and Ni in Ir/NI core unchanged with potential excursion
- Pt monolayer shell completely covers the Ir/Ni core.

K. Kuttiyiel, et al, *Energy Environ. Sci.*, 5 (2012) 5297

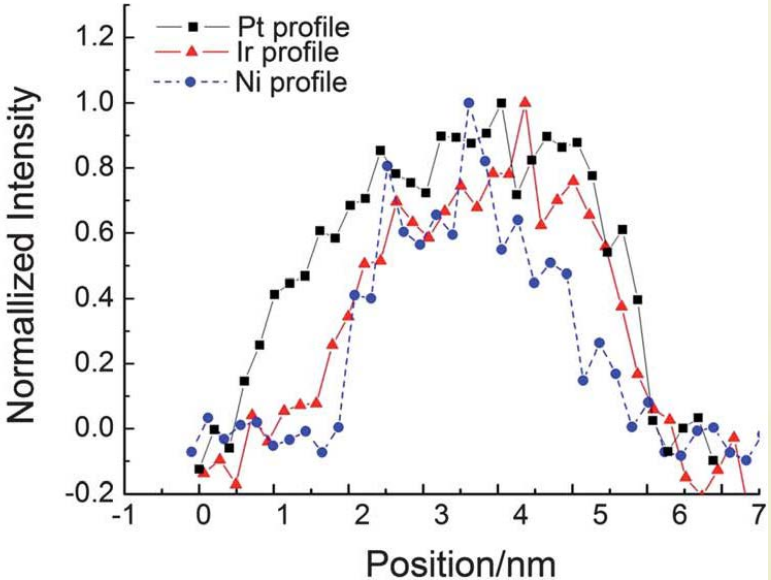
MEA Test of Pt/IrNi Core-Shell Nanoparticles







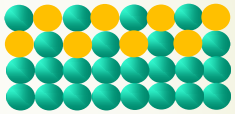
Freshly prepared nanoparticle



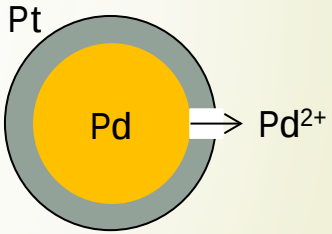
After 50,000 potential scans between H_2 and O_2 evolution.

Cathode Side Summary: O_2 Reduction on Pt/C, Pt_{ML}/M and Pt_{ML}/M_1M_2 Nanoparticles

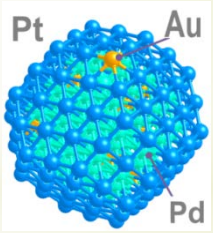
- Monolayer Pt atoms on the surface form a PtO_2-like oxide layer for Pt/C catalyst up to 1.5 V. At higher potentials the Pt oxide layer may dissolve under the OER



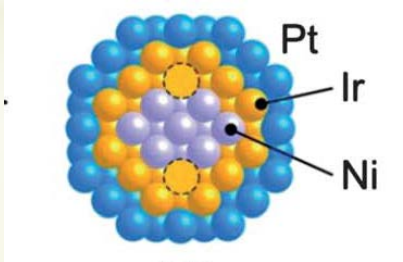
- The Pt shell is protected by sacrificial Pd dissolution in PtML/Pd core-shell nanoparticles



- Alloying Pd core with a small amount of Au further increases the stability of Pt monolayer catalysts



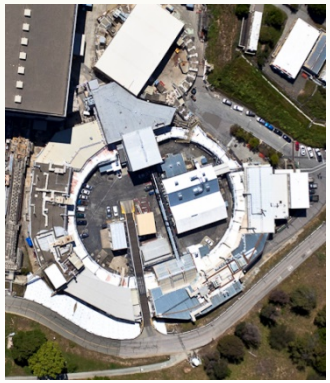
- PtML/Ir/Ni retains its structure even after 50,000 scans
- The Pt monolayer electrocatalysts approach offer a uniquely attractive possibility for the practical applications of PEM fuel cells.

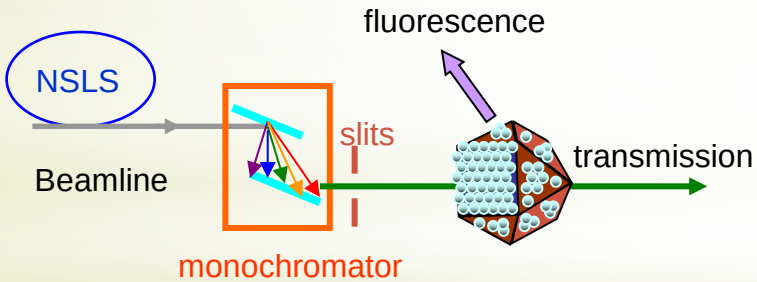


Summary and Outlook for XAFS/Electrochemistry

- *In situ* XAFS is indispensable tools to characterize and rationalize degradation of Pt nanoparticle and Pt monolayer electrocatalysts.

We expect limited access for our studies at **one** beamline at SSRL over next 1 - 2 years…





Thanks to:
DOE,
Sayed Khalid,
Steve Ehrlich and
Anatoly Frenkel

We had access to **three** beamlines at NSLS I that closed on Sept. 30, 2014.

…until **two** XAS beamlines open at NSLS II in 2016 for brighter future in XAFS/electrochemistry!

Thank You!