Project: LOW Pt LOADING ELECTROCATALYSTS

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H. Inoue (supported by Osaka Prefecture University)

OBJECTIVES:

1. Development of novel electrocatalysts with low Pt loading.
2. Elucidation of their catalytic action.

PROJECT TIMELINE

Project starting date: June 1, 2001

First year: Characterization of electrocatalysts and tests in MEAs.

Second year: Optimization; further improvement of CO tolerance; MEA tests; reduction of Ru loading; O_2 reduction electrocatalysts.

Third year: Characterization and MEA tests; electrocatalysts for methanol oxidation.

Success Criteria: Reduced Pt loading by more than 3 times without sacrificing the activity as compared to commercial catalysts and meeting the DOE targets.

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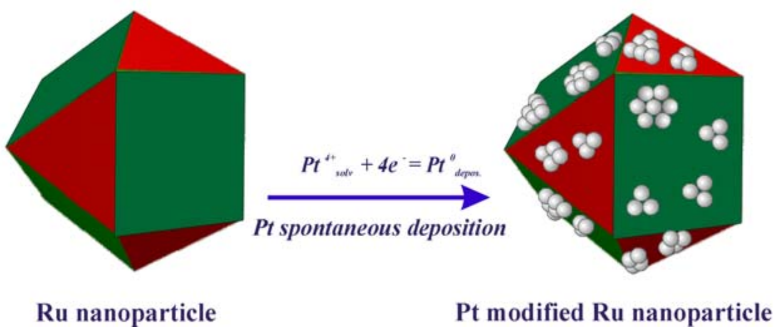
APPROACH NANOPARTICLE ENGINEERING BY SPONTANEOUS DEPOSITION: *Ru CORE* WITH *Pt SUBMONOLAYER SHELL*

Pt deposited on Ru nanoparticles spontaneously

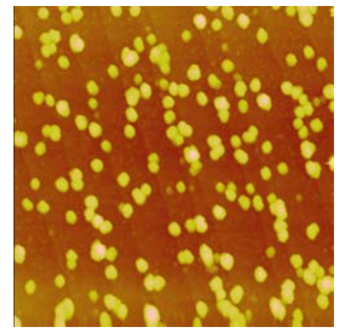


Nanoparticles used as reducing agents.
Core nanoparticles act as support and co-catalyst.
Tuning of electronic and catalytic properties by varying coverage and cluster size.
Ultimate reduction of Pt loading.

DFT calculations (Kopper et al.) and TPD data (Behm et al.) show low CO bonding strength to Pt ML on Ru(0001).

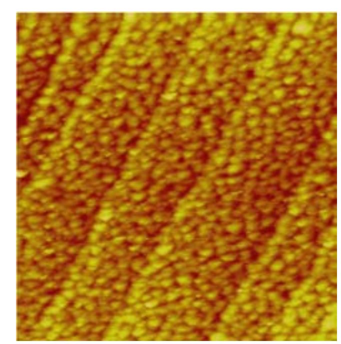
Spontaneous deposition of Pt on Ru(0001)

200nmx200nm



From 10^{-4} M H_2PtCl_6

100nmx100nm



From 10^{-2} M H_2PtCl_6

ACCOMPLISHMENTS

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- Synthesized the 1%Pt /10%Ru on C catalyst that has at least 3 times larges mass-specific activity for H_2 oxidation as compared to commercial catalysts.

- The measurements at LANL in MEA showed that it has the same activity as the commercial catalyst which contains 10 times more Pt.

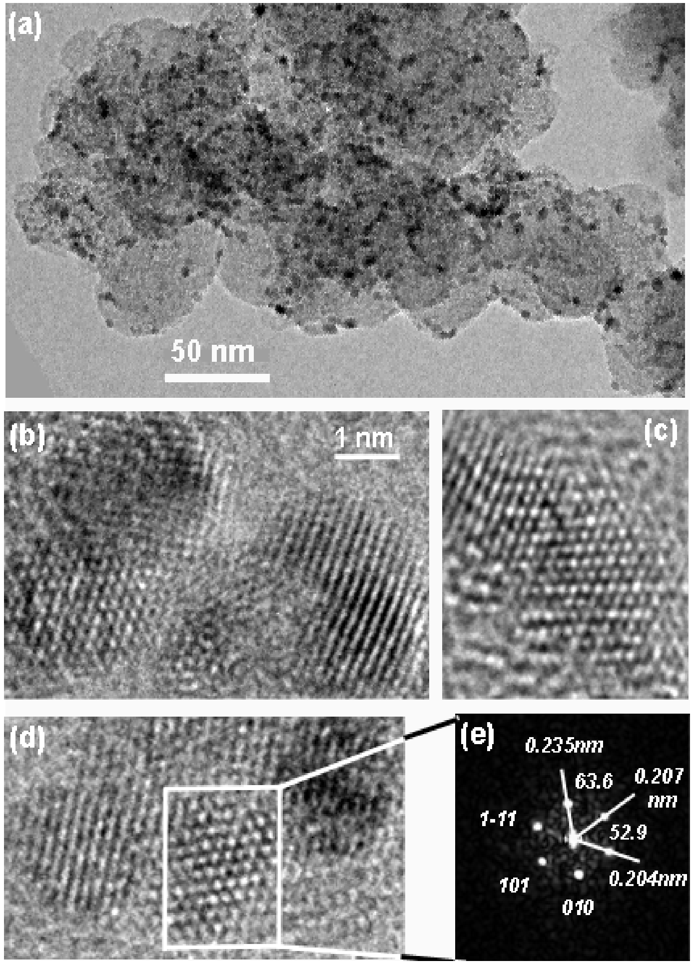
- The BNL catalyst shows higher CO tolerance in the RDE but lower in MEA measurements than the TKK catalyst (containing 10 times more Pt).

Loadings in anode: 18μg Pt/cm^2 + 180 μg Ru/cm^2
DOE Target for 2004: 300 μg/cm^2 for anode and cathode

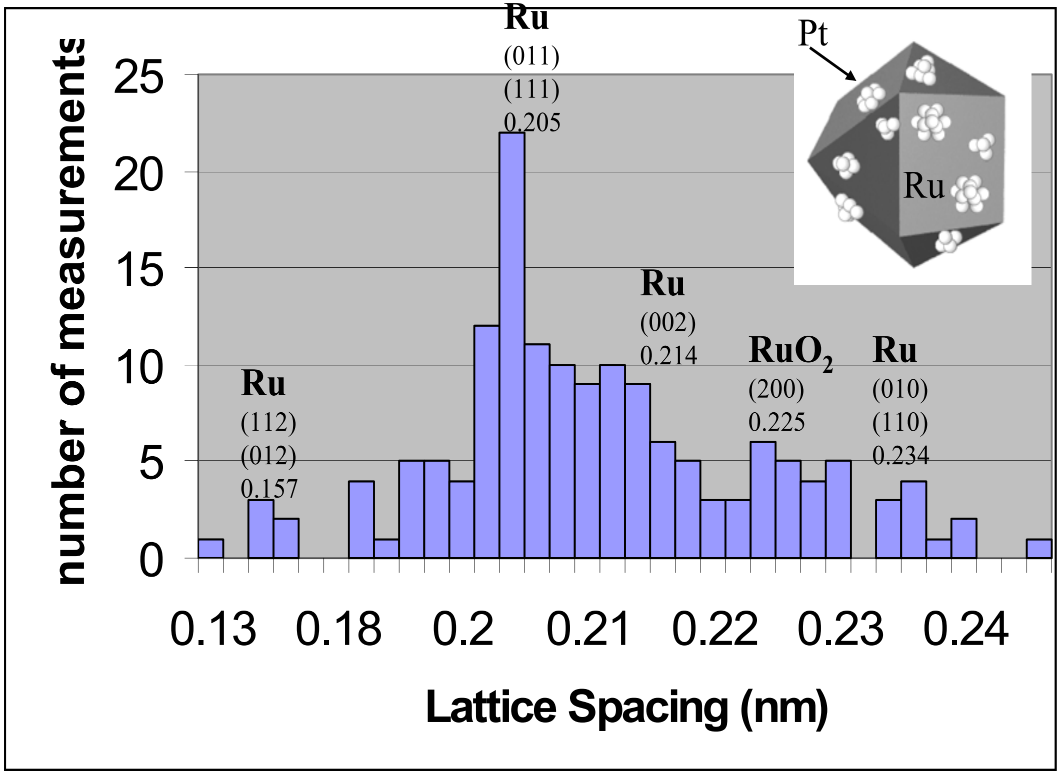
- Demonstrated the possibility of having a catalyst for O_2 reduction with a monolayer Pt coverage on Ru approaching the activity of supported Pt.

- Developed a synthesis of carbon-supported W nanoparticles with D. Mahajan, BNL, to be used as a core for the Pt or Pt/Ru shell (replacement for Ru).

TEM PICTURES OF Ru NANOPARTICLES WITH A Pt SUBMONOLAYER ON A CARBON SUBSTRATE

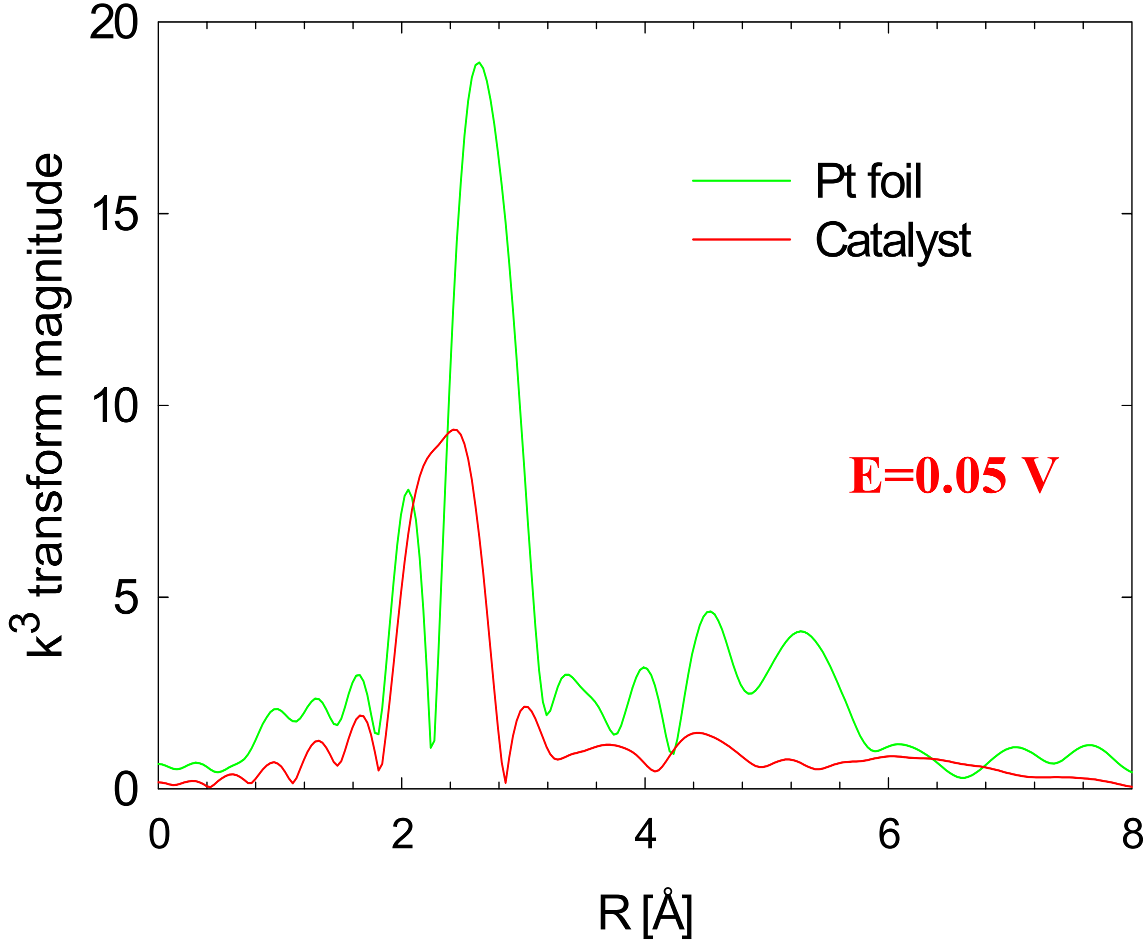


Lattice Spacing Distribution



Particle size increased from ~2 nm to ~2.5 nm after Pt deposition

In situ EXAFS OF $Pt_{1/8ML}$ ON Ru NANOPARTICLES



Pt coordinated with 4 Ru

Pt - Ru distance: ~ 2.69 Å (as in the alloy)

No larger Pt islands!

In collaboration with Balasubramanian and McBreen

Approaching limiting value for Pt dispersion. A truly full catalyst utilization possible.

CHARACTERIZATION OF ELECTROCATALYSTS IN A THIN FILM RDE: H_2 and H_2/CO OXIDATION

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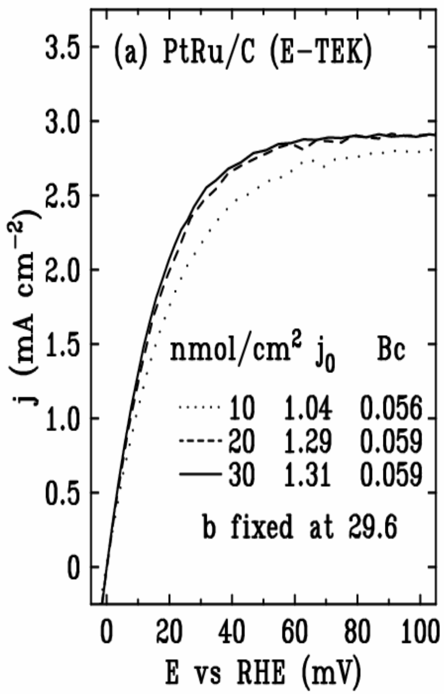
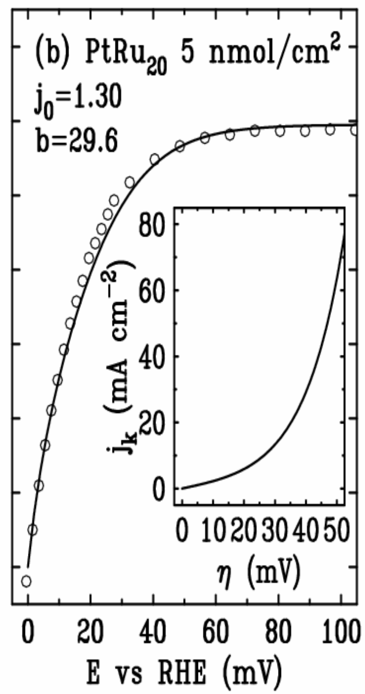
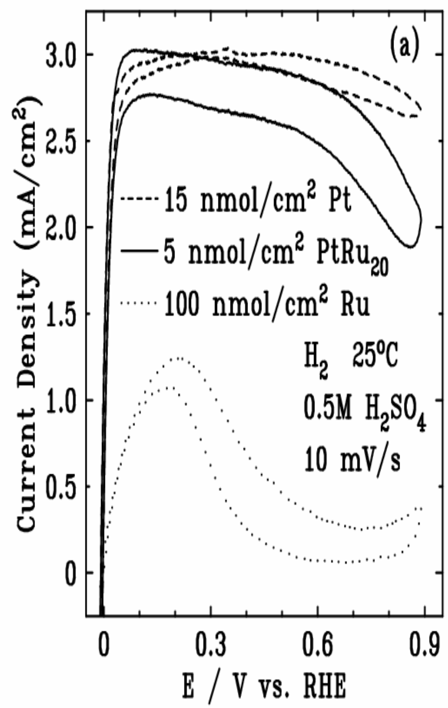
$$j(\eta,\omega) = \frac{j_0 \exp(2.3\,\eta/b)}{1 + j_0 \exp(2.3\,\eta/b)/Bc\sqrt{\omega}}$$

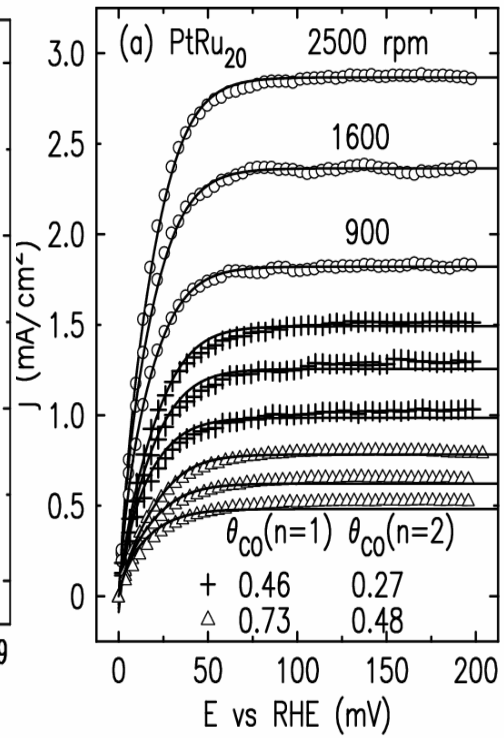
$$j(\eta,\omega) = \frac{j_0\,(1-\theta_{CO})^n \exp(2.3\,\eta/b)}{1 + j_0\,(1-\theta_{CO})^n \exp(2.3\,\eta/b)/Bc\,(1-\theta_{CO})^n\sqrt{\omega}}$$

Kinetic parameters determined by nonlinear fitting of the entire polarization curve









No Nafion® film needed to make a thin-film RDE!

COMPARISON OF H_2 OXIDATION ON THREE ELECTROCATALYSTS

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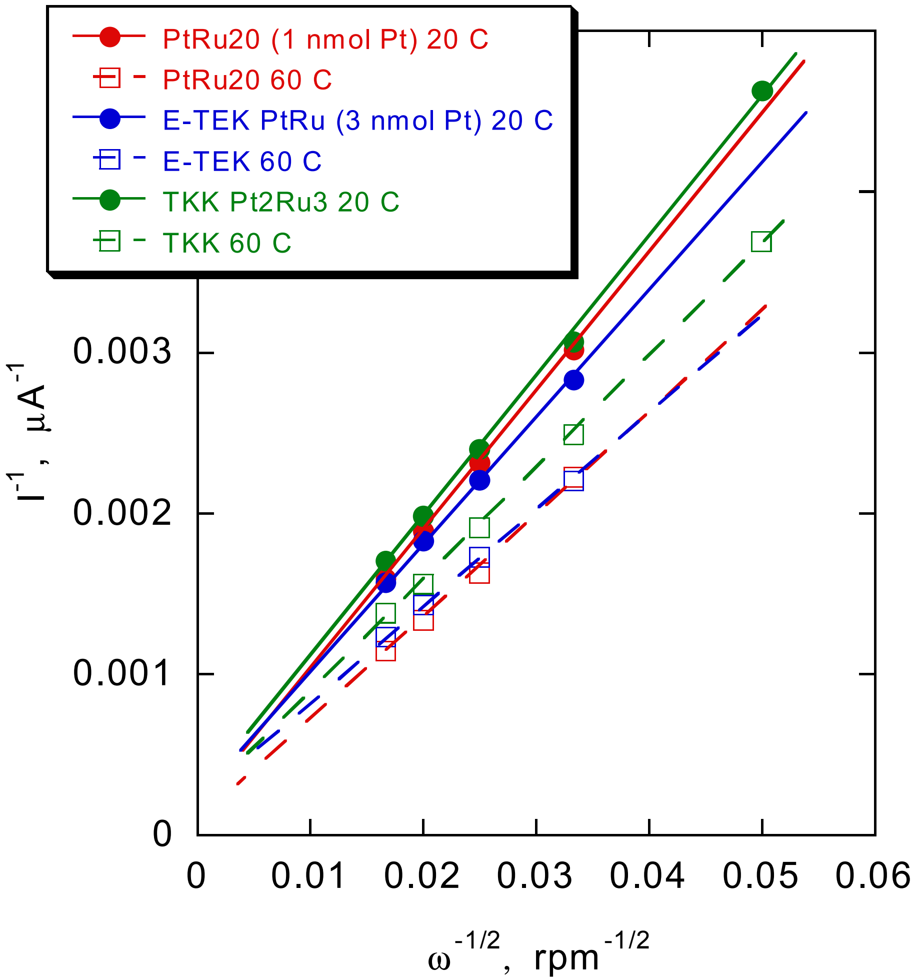
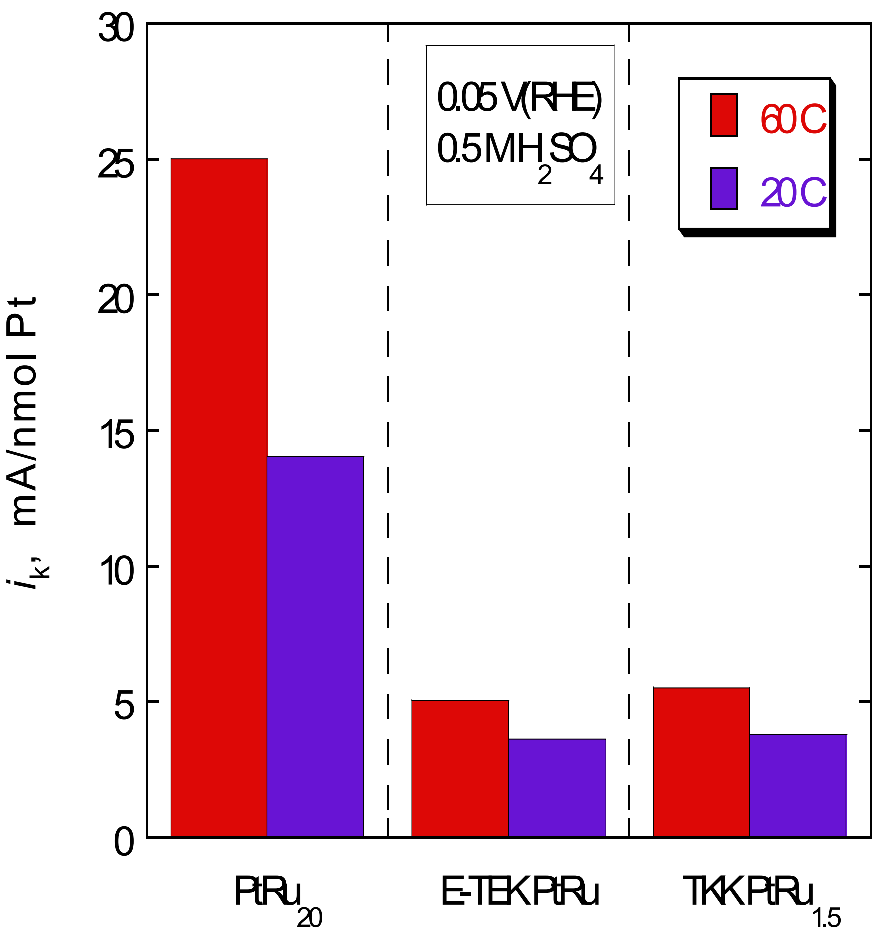
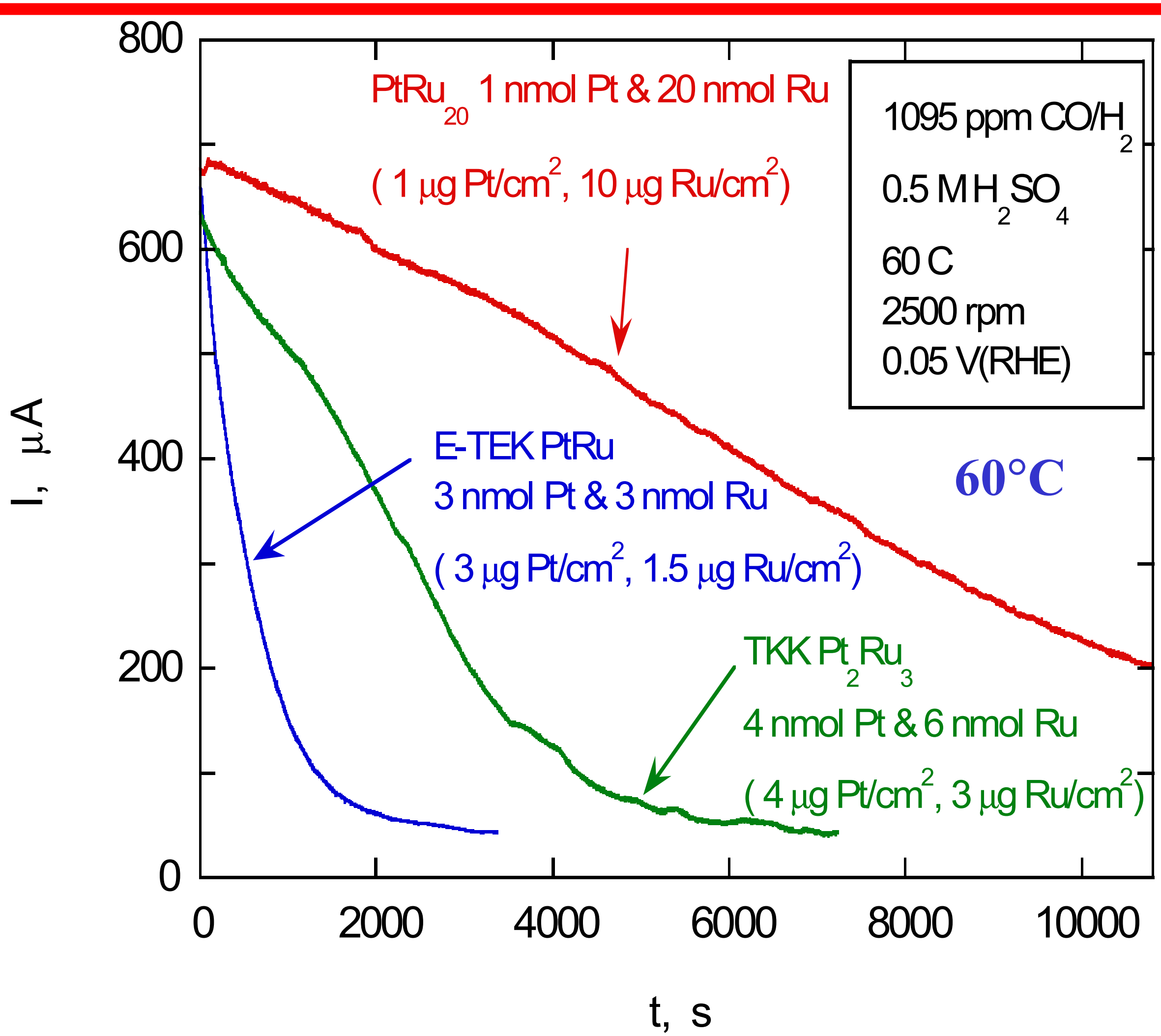




COMPARISON OF THREE ELECTROCATALYSTS FOR CO TOLERANCE



$\theta_{CO(Pt,Ru\ hex)} = 0.75$

CO coverage from stripping charges

θ_{CO}

0.5

0.63

0.79

Lower Pt-CO bond strength and an efficient CO spillover to RuOH are likely cause of enhanced CO tolerance.

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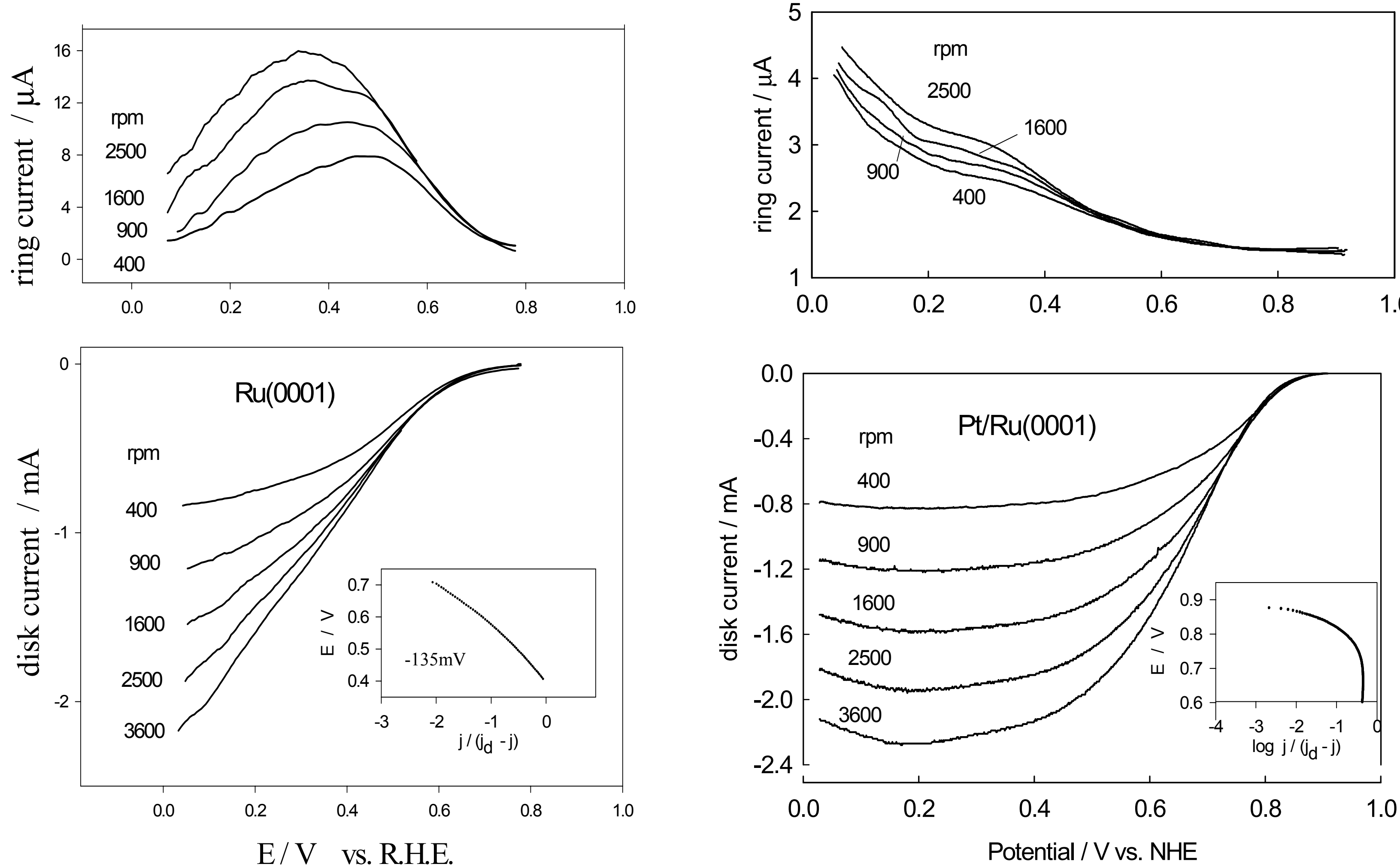
O_2 REDUCTION ON BARE and 1.5 ML Pt-COVERED Ru(0001) IN 0.05M H_2SO_4



EXAFS (J. McBreen et al.) showed a lower PtOH formation on Pt in PtRu alloy than on bare Pt. DFT calculation (Kopper et al.) also suggest lower PtOH formation in Pt ML on Ru.

O_2 REDUCTION ON BARE and $Pt_{1.5ML}$-MODIFIED $Ru(0001)$ and $Ru(10\bar{1}0)$, and $Pt_{1/2ML}Ru/C$

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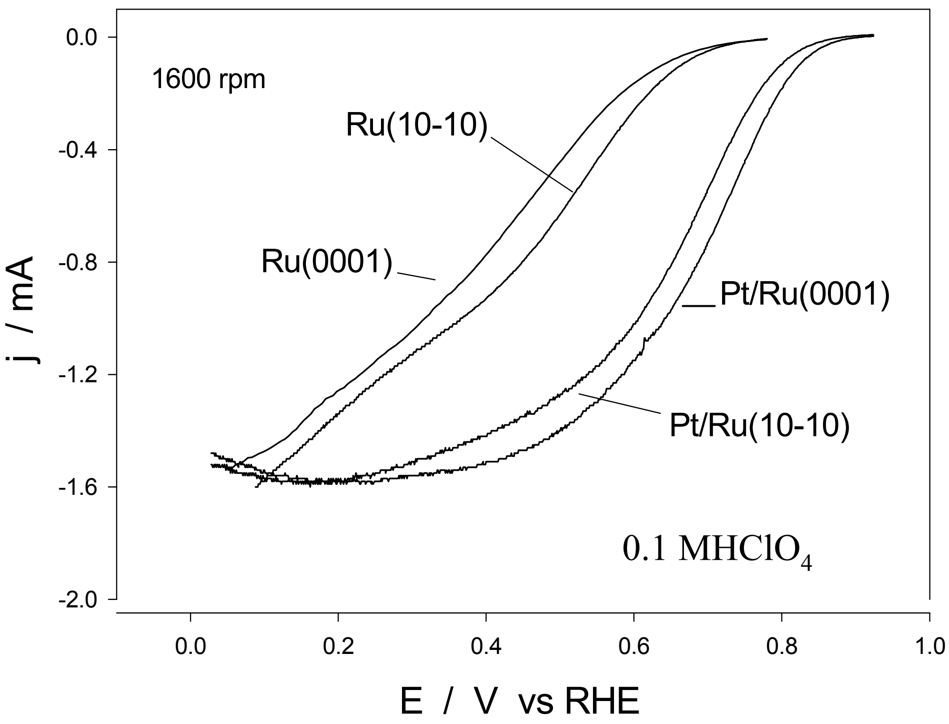
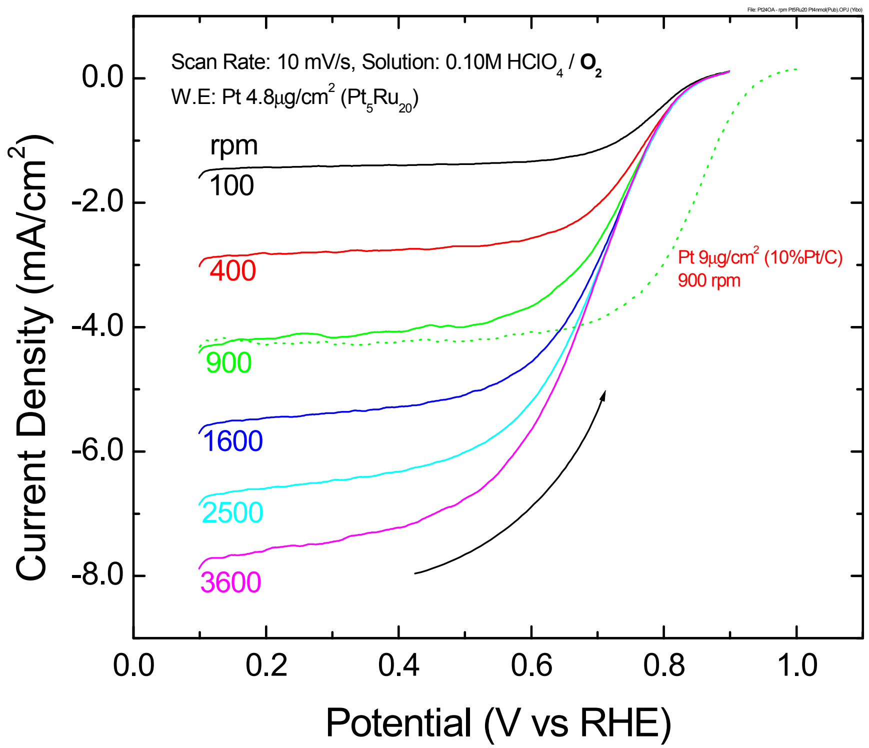




Interaction with Catalysts Manufacturers :

Initial contacts with E-TEK, and Microcoating Technologies Inc. and FCC & I Inc.

Other Collaboration:

Los Alamos National Laboratory

Answers to the previous review:

"..Ru is expensive.." - the effort to make the W or other metal core/ Pt or Pt-Ru shell electrocatalyst by the same approach is underway. (Currently, Pt is seven times more expensive that Ru)

"..MEA tests at LANL.." – First tests done.

FUTURE PLANS

Improvement of the Pt/Ru catalyst:

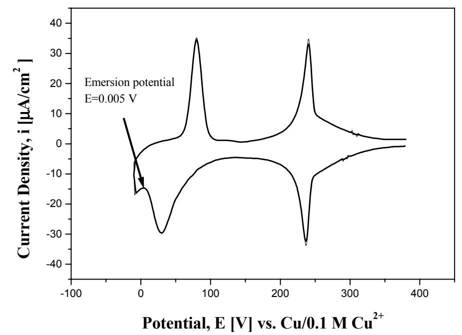
1. Optimization of the Pt submonolayer/Ru electrocatalyst for MEAs.
2. Codeposition of submonolayers of Pt and other noble metals (surface combinatorial synthesis)

Replacement of Ru

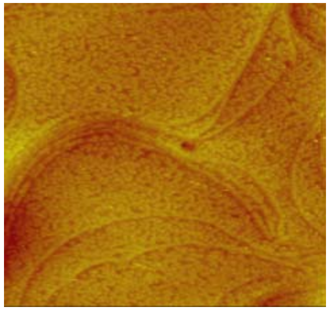
1. Pt or Pt and Ru on W or other valve metal nanoparticles by spontaneous deposition
2. Pt or Pt and other noble metals on Au nanoparticles by replacing Cu adlayer

Au nanoparticles active for CO oxidation in gas phase (Haruta; Goodman et al.)

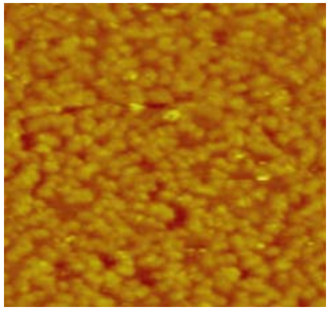
DEPOSITING Pt MONOLAYER ON Au(111) BY REPLACING THE Cu UPD ADLAYER



320x320 nm



105x105 nm



No step edge effects