Decorated Nanoparticles in Fuel Cell Catalysis

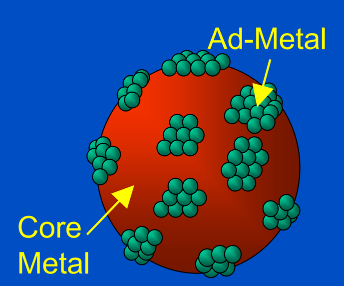
PIs: R. Masel, A. Wieckowski and P. Zelenay

University of Illinois at Urbana-Champaign and Los Alamos National Laboratory

New Catalysts for Fuel Cells

Obtained by Spontaneous Deposition

In this poster we present results of designing and characterization of new fuel cell catalysts. The method of nanoscale engineering is to build decorated nanoparticles by the use of spontaneous deposition. We produced and laboratory tested - in an electrochemical cell and in a fuel cell – some anode catalysts of improved reactivity towards electrooxidation of some specific organic fuels. The results of characterization of the catalysts by various electrochemical and surface probes give insights into mechanisms of the enhancement of methanol and formic acid oxidation. Surprisingly, on the Pt/Pd catalyst, improved reactivity for formic acid oxidation is not coupled to CO tolerance, the observation which promises new anode catalyst designs.



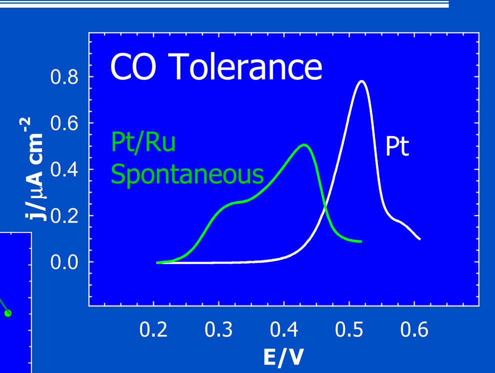
A model of a new fuel cell catalyst. The core of the particle is Pt, and admetal is introduced onto the surface by the method of spontaneous deposition. The method reduces the amount of admetal to submonolayer doses, and allows for easy control of two-dimensional admetal coverage.

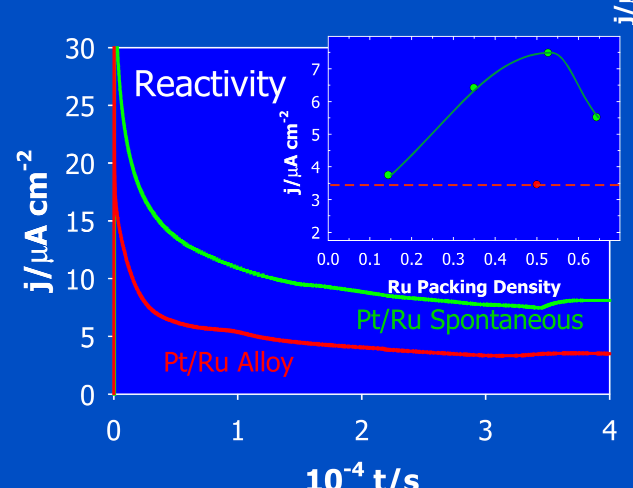
- Questions to investigate: new CO tolerant catalysts with reduced overpotentials for methanol, formic acid and hydrogen oxidation and oxygen reduction
  - Spontaneous deposition, syntheses
  - Catalyst/support (conducting polymer) interactions
  - Surface structure (nanoparticle morphology) effects
  - Electronic level considerations: Ru and Pd (Os) enhancement
  - Testing reactivity in E-cells and fuel cells new guidelines
  - Radioactive and NMR labeling (unique!)
  - Structure by in situ STM
  - Conducting polymers for O-reduction
- The synthetic approach
  - spontaneous deposition
  - other forms of electroless deposition
- New methods for catalyst characterization
- The expected outcome
  - active, robust, low noble metal load catalyst for fuel cell for both anode and cathode

Pt/Ru Catalysts for DMFC Anodes

Electrochemical Cell and DMFC Testing

Electrochemical Cell Testing

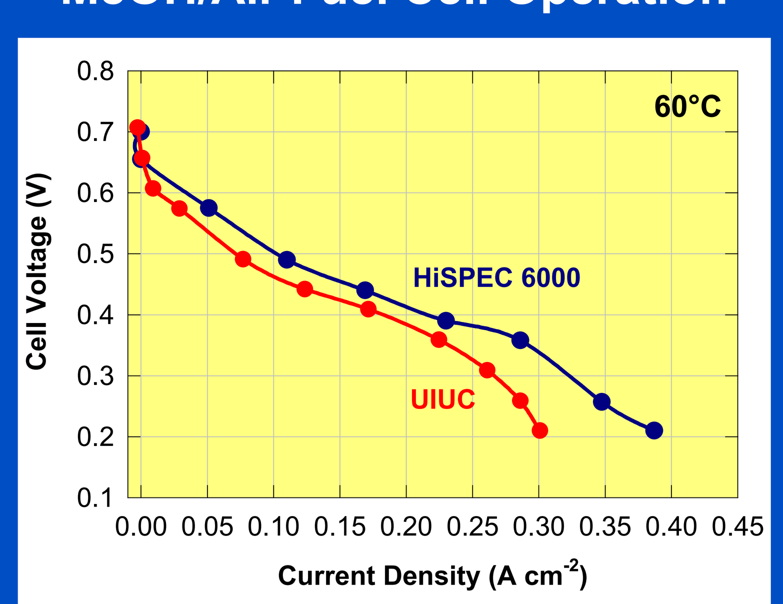




- Increased reactivity as compared to Pt/Ru alloy
- Reactivity depends on ad-atom coverage
- Improved CO tolerance [1]

Testing in DMFC

MeOH/Air Fuel Cell Operation



DMFC polarization plots for the UIUC and JM MEAs at 60°C

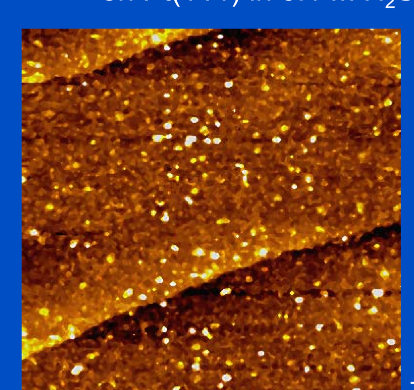
The anode catalyst from the University of Illinois at Urbana-Champaign (UIUC) was tested against Johnson Matthey (JM) HiSpec 6000 $Pt_{50}Ru_{50}$ reference catalyst in a 5 cm^2 direct methanol fuel cell (DMFC) fixture at LANL. Given the difference in BET surface area, 27 m2 g-1 and 81 m^2 g^{-1}, for the UIUC and HiSpec 6000 catalysts, respectively, the performance of the UIUC catalyst in direct-methanol fuel cell at 60°C is highly promising (surface site activity ca. 3x higher for our catalyst).

Pt/Ru Catalysts

Microscopic Examination of the Deposits

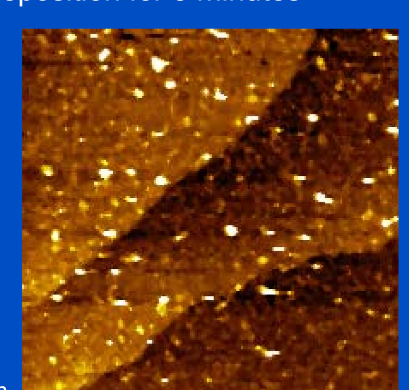
Manipulation of Ru Islands via Potential Control

In Situ STM Imaging of Ru Deposition on Pt(111) in 0.1 M H_2SO_4—1 deposition for 3 minutes

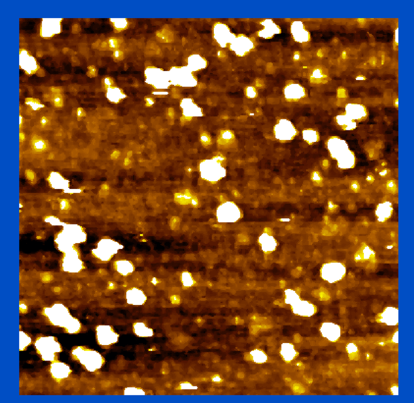


70 x 70 nm

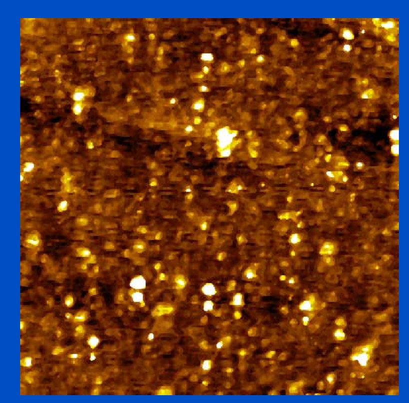
Initial surface @ 0.46 V vs. RHE
Coverage= 19%
90% monolayer,
10% bilayer
Island size 1-3 nm



Surface moved to 0.96 V vs. RHE
Coverage= 18%
80% monolayer,
20% bilayer
Island size increases to 2-5 nm



Second Deposition at 0.46 V
- 23% coverage
  - 50% monolayer
  - 30% 2 monolayers
  - 20% 3 monolayers or higher
- 3-5 nm island size



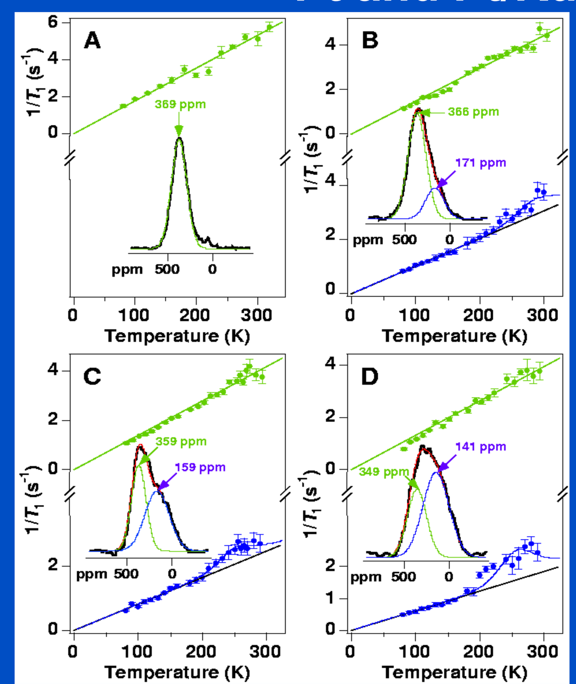
Resulting surface at 0.46 V after being held at 0.96 V
- 23% coverage (97% monolayer)
- 0.5-2 nm island size

In the images above, we examine the role of electrode potential on the island size using EC-STM. Upon increasing the surface potential to 0.93 V vs RHE, the island size increases due to the oxidation of the Ru islands [2]. Much higher Ru dispersion is achieved when the potential is returned to 0.46 V!

Pt/Ru Catalysts

Examination by EC-NMR

^{13}C NMR of CO on nanoparticle Pt and Pt/Ru electrodes



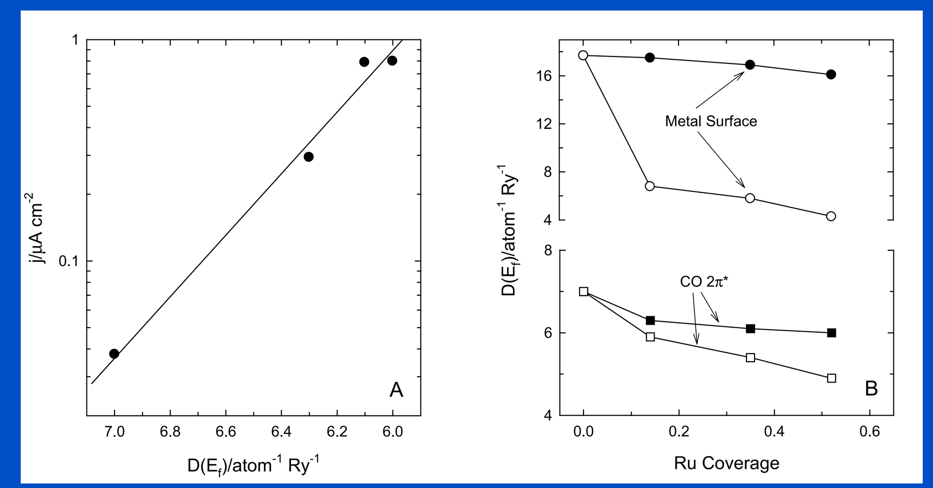
- ^{13}C NMR relaxation follows the Korringa behavior, T_1T = const., characteristic of metals.
- On Pt black/Ru sample, it deviates from Korringa and exhibits an additional diffusion component:

$$T_1^{-1} = aT + 2(\Delta\omega)^2\tau/(1+\omega_0^2\tau^2)$$

- The activation energy obtained from ^{13}C relaxation data shows that presence of Ru on Pt surfaces enhances CO diffusion, which may kinetically facilitate CO oxidation [3].

Catalyst	Activation Energy
Pt	7.8 kcal/mol
Pt/Ru	4.9 kcal/mol

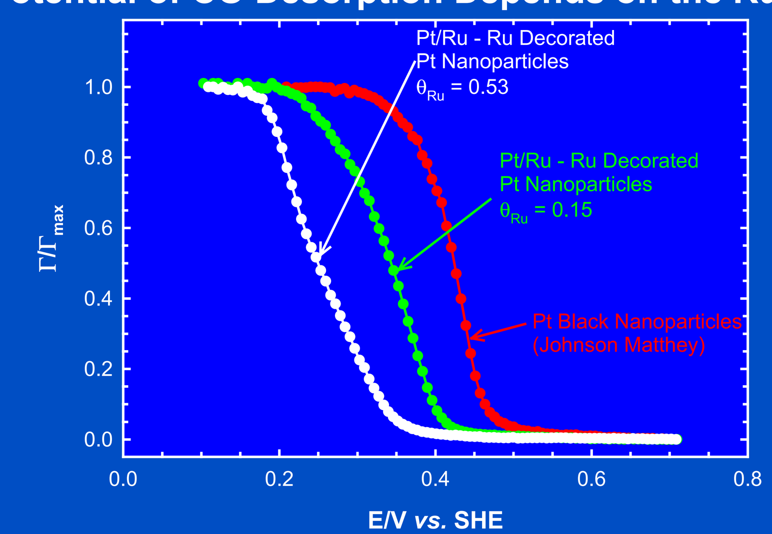
Correlation Between the 2π*-LDOS and Methanol Oxidation Current Density



Pt/Ru Catalysts

Examination by Radioactive Labeling

The Potential of CO Desorption Depends on the Ru Coverage

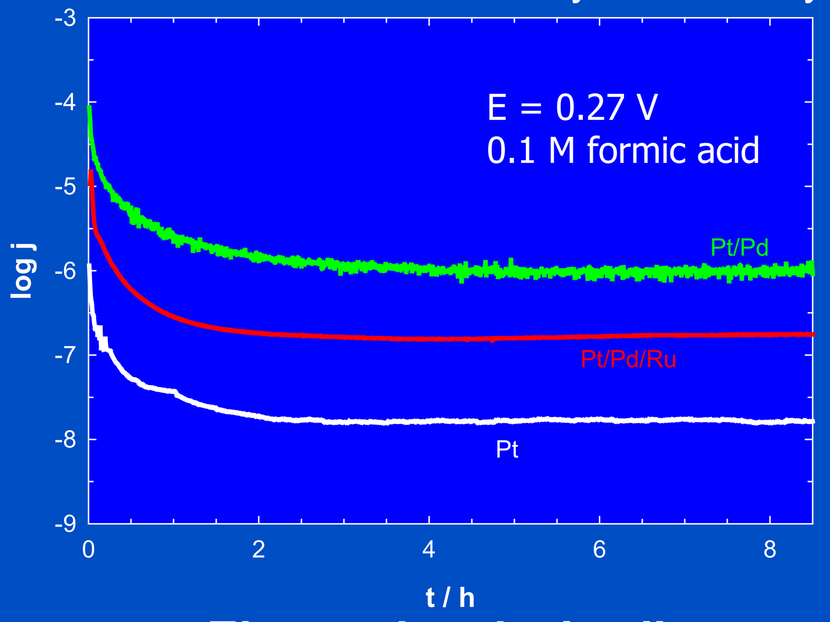


- Quasi steady-state: slow potential scan of 0.1 mV/s
- CO adsorbed from 0.01 M methanol (C-14) solution in 0.1 M H_2SO_4 at -0.1 V then methanol removed from the solution

New Pt/Pd Catalysts for Formic Acid Fuel Cell Anode

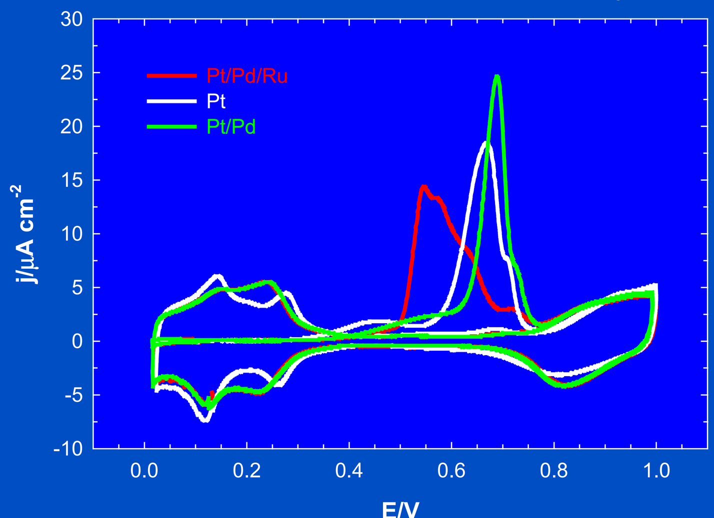
Electrochemical Cell and Fuel Cell Testing

Electrochemical cell: reactivity and stability testing



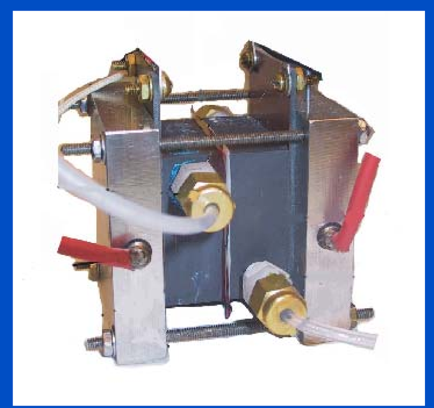
Electrochemical cell:

CO tolerance of the new catalysts

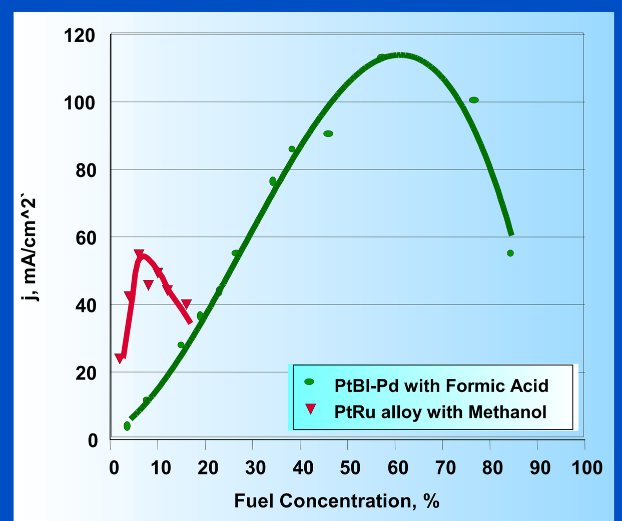


Surprisingly, the enhancement in formic acid oxidation by the admetal addition does not correlate with the threshold for CO oxidative stripping (the CO tolerance). The Pt/Pd catalyst requires the highest potential to remove the CO, yet it is the most active!

Testing in Fuel Cell



A fuel cell using our catalyst developed in UIUC



The formic acid fuel cell using Pt/Pd anode catalyst produced currents up to 120 mA/cm^2 and power output up to 50 mW/cm^2 at 60 C. Open circuit potential is about 0.72 V [4].

Acknowledgements:

Contribution to these projects by P. K. Babu, T. Barnard, C. Johnston, H. S. Kim, M. McGovern, C. Rice, P. Waszczuk, and Y. Zhu is highly appreciated. This work is supported by DOE under the grant DOE LANL 30167010139, and by DARPA under US Air Force grant F33615-01-C-2172.

Selected References:

1. Waszczuk, P.; Solla-Gullon, J.; Kim, H. S.; Tong, Y. Y.; Montiel, V.; Aldaz, A.; Wieckowski, A.; "Methanol electrooxidation on platinum/ruthenium nanoparticle catalysts", *J. Catal.* **203**, 1, (2001).
2. Crown, A.; Johnston, C.; Wieckowski, A.; "Growth of ruthenium islands on Pt(hkl) electrodes obtained *via* repetitive spontaneous deposition", *Surf. Sci. Lett.*, **506**, L268, (2002).
3. Tong, Y.; Kim, H. S.; Babu, P. K.; Waszczuk, P.; Wieckowski, A.; Oldfield, E.; "An NMR investigation of CO tolerance in a Pt/Ru fuel cell catalyst", J. Am. Chem. Soc. **124**, 468-473, (2002).
4. Rice, C.; Ha, S.; Masel, R. I.; Waszczuk, P.; Wieckowski, A.; "Direct formic acid fuel cells", *J. Power Sources*, in press.