Underpotential deposition
and
galvanic replacement
for
fuel cell catalysis

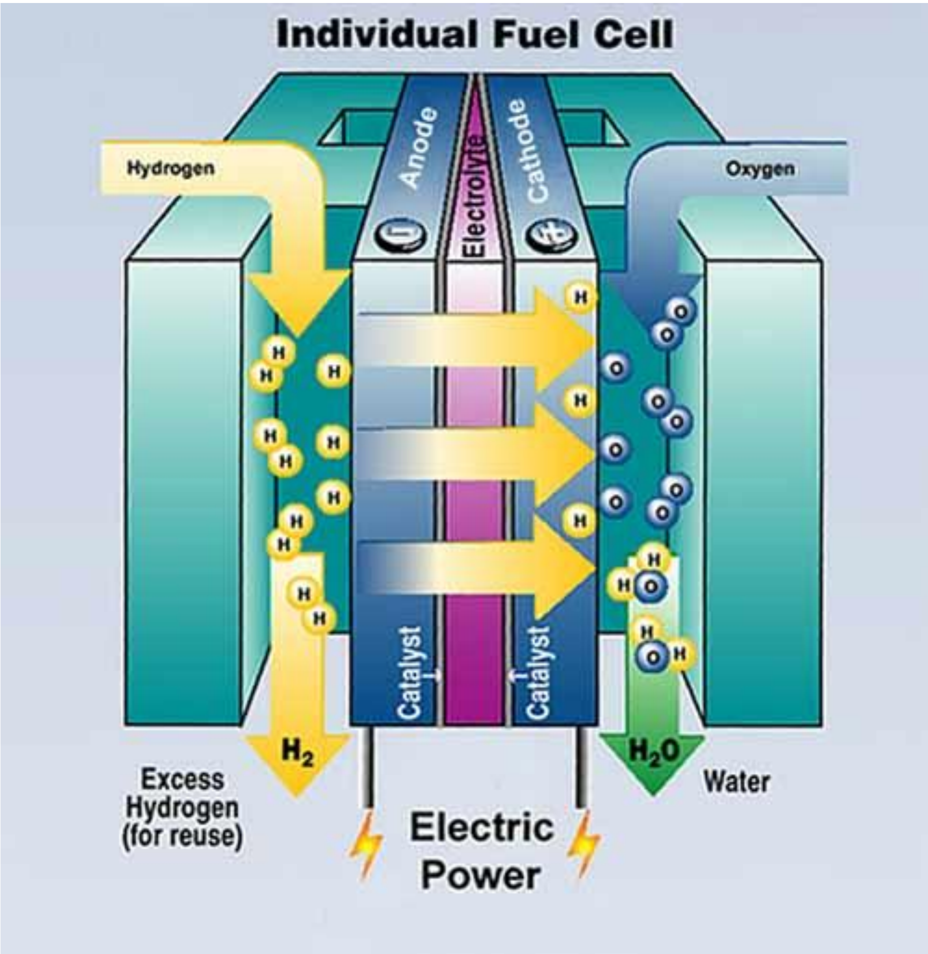
Outline

- Background
- Fuel Cell
- Underpotential Deposition (UPD) (theory)
- Galvanic Replacement (theory)
- UPD (research)
- Fuel cell improvements by UPD and GR
- Where are we now? Future work

Background of the Fuel Cell

- Fuel cell reaction discovered over 150 years ago . Chemical energy is stored in a fuel and continually supplied to the device and chemically consumed.
- In the case of PEM fuel cells, hydrogen and oxygen out of the air are reacted producing electricity, water, and heat.
- Other types include
  - Alkali with pure H2 and O2 used in the Apollo mission
  - Molten Carbonate
  - Solid oxide
- Not limited by the Carnot efficiency
- $O_2 + 2H_2 \rightarrow 2H_2O(l)$ Ideal hydrogen oxidation 1.2 V
  - Number of cells in stack determines voltage
  - Surface area of cell determines current

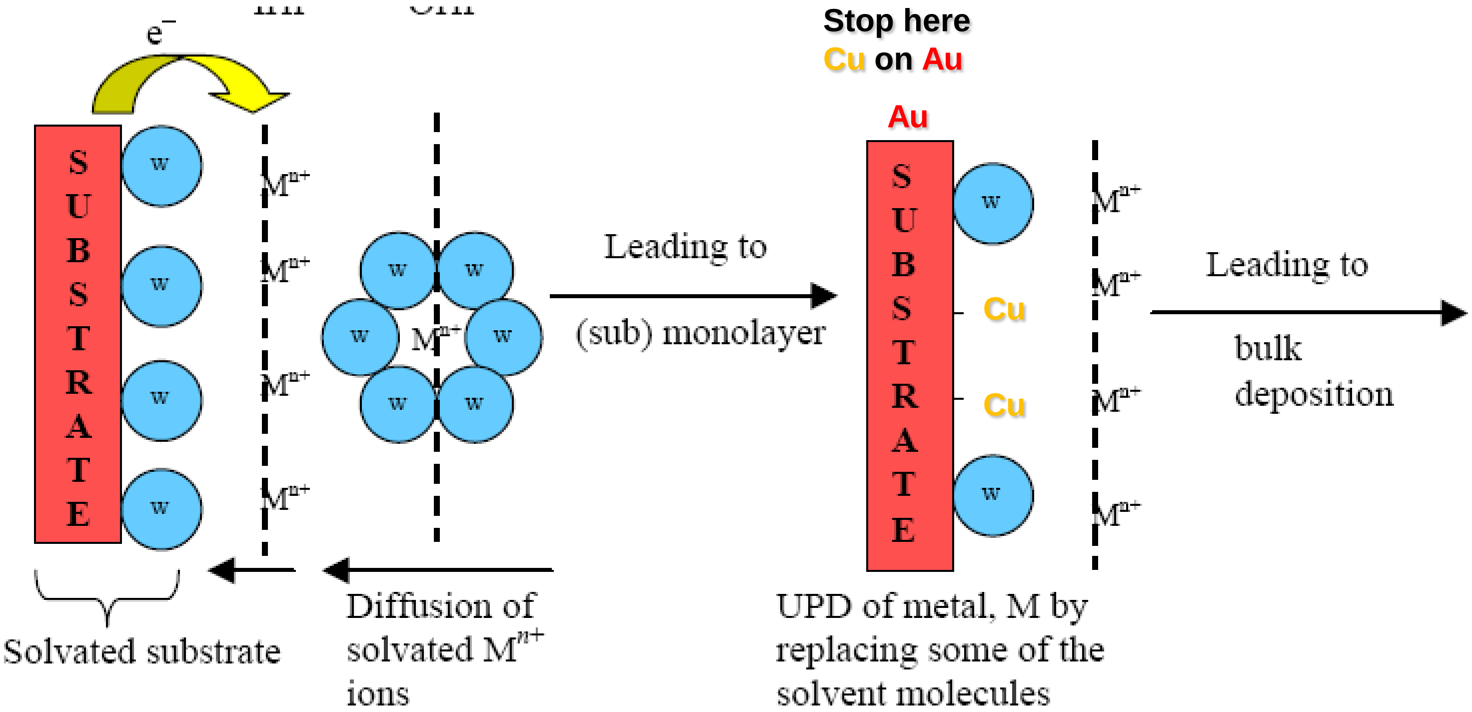
Solid polymer electrolyte membrane Fuel Cell



Fuel Cell Catalysts

- Mono/sub-mono layers of Pt on carbon support
  - Both at the Anode and Cathode
- Lower cost catalyst particles by the galvanic replacement of a monolayer of platinum on surface of a less noble metal, such as, Ag, Cu, Au, etc.
  - e.g., copper can be placed on low cost thin nanoporous Au leaf (Ehlebacher, Johns Hopkins) substrate by UPD

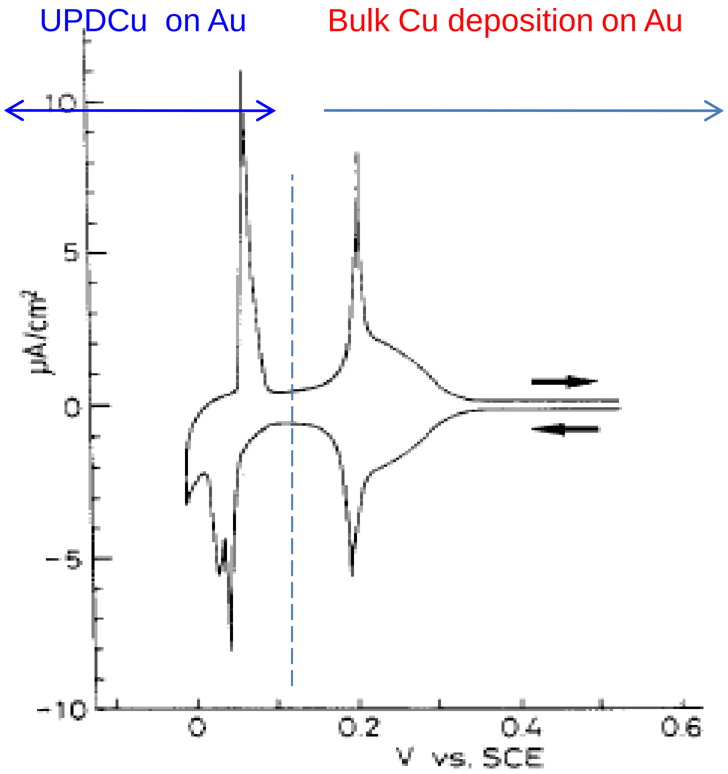
UPD (UnderPotential Deposition)


Stop here
Cu on Au

The deposition of a metal monolayer on a dissimilar metal substrate at a potential anodic (more positive) of the Nernst potential, Er, for bulk deposition where $E^r = E^0 - (RT/zF)\ln[1/(a\mathrm{Me}^{z+})]$

- Adatom has higher affinity for substrate than like atoms
- UPD of Cu on Au occurs at 0 to 0.46 V (-0.24 to +0.22 vs SCE)
- bulk deposition occurs at +0.24 V
- E^o being +0.34 V vs Standard Hydrogen Electrode

Cyclic voltammetry



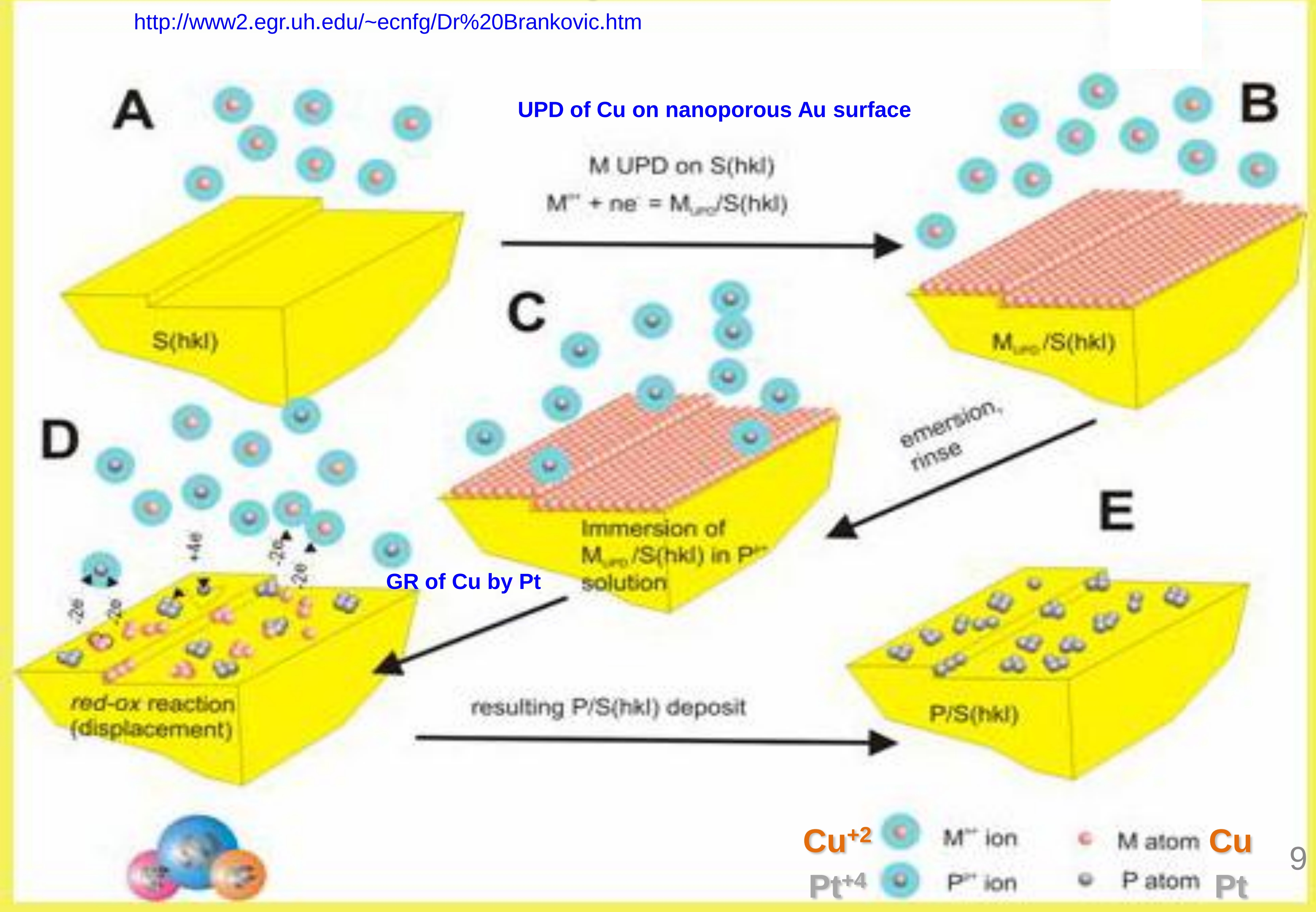
UPD first occurs at steps, grain boundaries and other high energy surfaces. Usually use the (111) crystal orientation for the substrate

Galvanic replacement

- Spontaneous redox process
  - Cu atoms are oxidized by the more noble Pt cation which is reduced there by replacing the Cu atom on the surface
    - $E^{Pt+4/Pt} > E^{Cu+2/Cu}$
    - Therefore $\Delta G = -nF\,E$ is favorable
    - Only supports ½ mono layer of Pt (Pt^{4+}, Cu^{2+})
  - Galvanic series (most noble to least)
    - Palladium
    - Platinum
    - Gold
    - Copper
    - Lead
    - Zinc
  - Substrate must be more noble than replacement metal

UPD and Galvanic Replacement

http://www2.egr.uh.edu/~ecnfg/Dr%20Brankovic.htm



UPD of Cu on nanoporous Au surface

GR of Cu by Pt

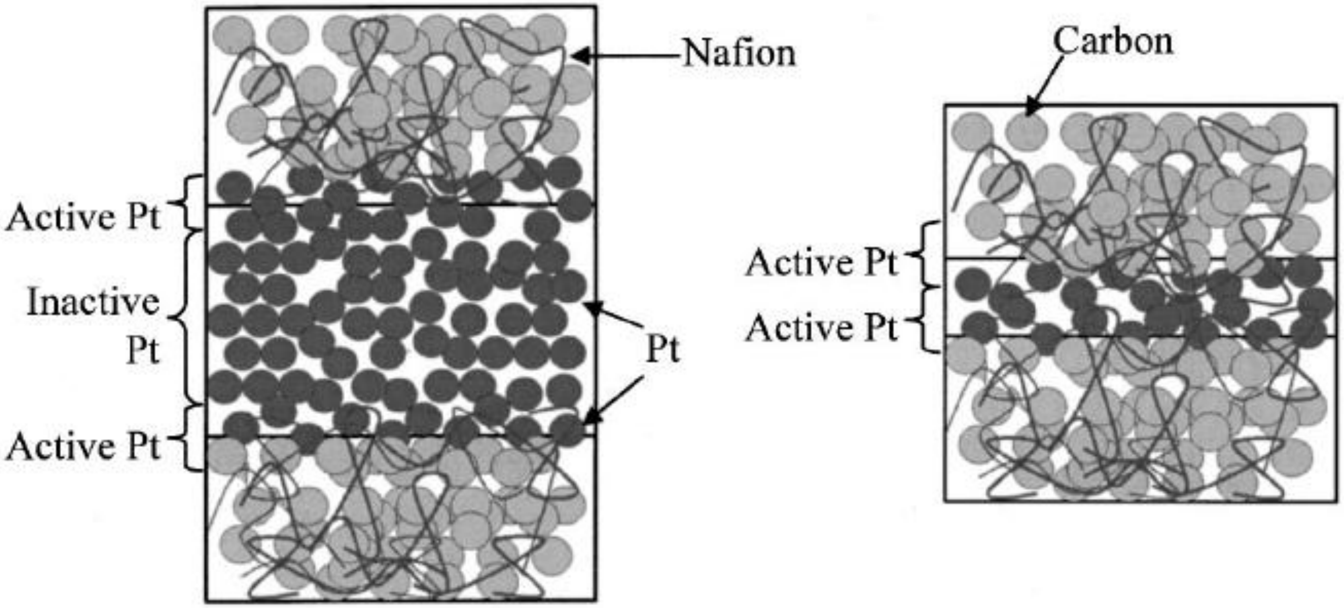
Research on Current Difficulties with Fuel Cells
$$$

- Cost too much **$$$**…
- need to
  - **Reduce Pt loading**
  - **Increase Pt surface area available for reaction**
  - **Need more robust catalysts**

- But catalysts become clogged with impurities
  - Reduction of the O_2 on Pt-catalyzed cathode is easily made inefficient
    - Carbon Monoxide from fuel reforming, sulfur and phosphorus compounds from electrolyte reduce performance – use more fuel **$$$**
    - Cathode – slow oxygen reduction reaction (ORR) – requires more Pt than anode side running on *pure* hydrogen $$$
    - Anode – slow hydrogen oxidation kinetics (HOR) on anode due to CO poisoning from fuel reforming – so anode now requires more Pt than cathode side $$$

Cost Consideration/Efficiency

- Amount of Pt used will only be surface active



Haug, A. et. al. Increasing Proton Exchange Membrane Fuel Cell Catalyst.Effectiveness Through Sputter Deposition. *Journal of The Electrochemical Society*, 149 3 A280-A287 A284 2002

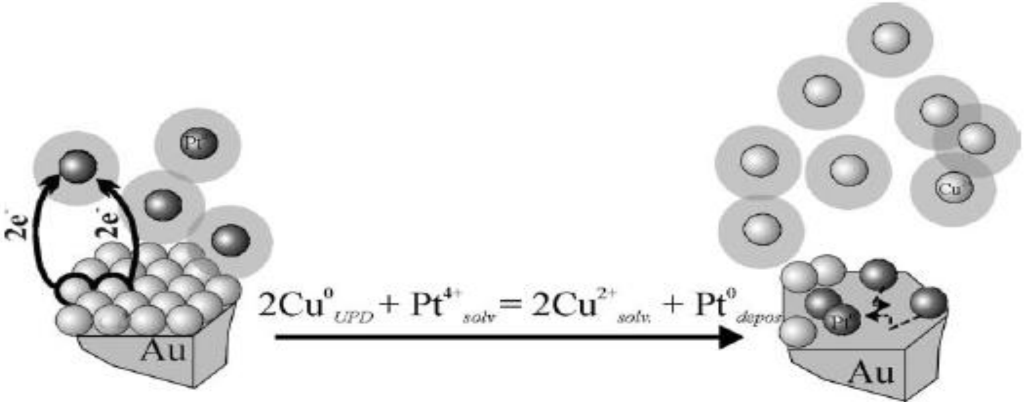
Thinner gas diffusion layers and smaller catalysts on smaller supports

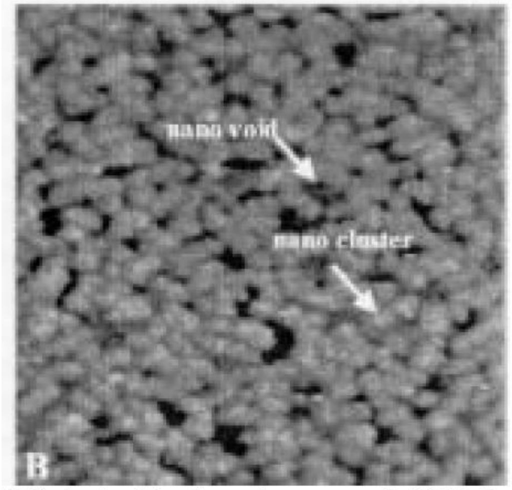
Reason to Go Smaller

- More exposed catalyst so more cost efficient triple phase boundary
  - (electrolyte, electrode, catalyst)
- Increased surface area – more reactive area
- Benefits from nanoparticle catalysts
  - higher activity from strain
  - a greater percent of noble atoms are on the surface.
    - Bulk atoms - 12 neighbors
    - Surface atoms – 6 to 9 neighbors

UPD/GR Submonolayer Formation

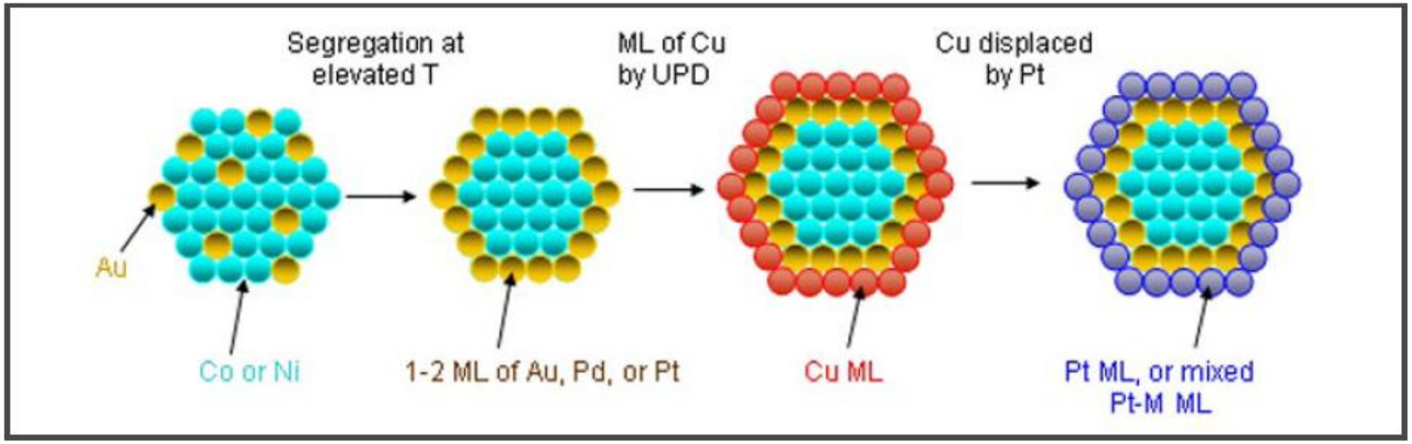
- Replacement (irreversible redox of Cu UPD on Au(111))
- Pt(4+) – submonolayer
- Pd(2+) – monolayer
- Ag(1+) – bilayer
- No preferential deposition on steps or defect sites like other deposition methods.





Brankovic, S et al. Metal Monolayer Deposition by replacement of metal adlayers on electrode surfaces. Surface Science 474 (2001) L173-179.

Tailored Platinum Monolayer on Non-Noble Metal-Noble Metal Core-shell Nanoparticles Electrocatalysts for O2 Reduction



Model for the synthesis of Pt monolayer catalysts on non-noble metal-noble metal core-shell nanoparticles

- Induced strain on the monolayer from a proper shell – more active Pt monolayer
- Use of non-noble core and noble shell, cheaper
- Fractional amount of Pt and another noble metal gives higher activity than current carbon-supported Pt electrocatalysts

J. Zhang, F. Lima, M. Shao, K. Sasaki, J. Wang, J. Hanson, and R. Adzic, Platinum Monolayer on Nonnoble Metal-Nobel Metal Core-Shell Nanoparticle Electrocatalysts for O2 Reduction," *J. Phys. Chem. B*, **109**, 22701-22704 (2005).

Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters

- Dissolution/loss of active surface of Pt Cathode is quick due to cycling potentials
- Au Galvanic replacement of Cu monolayer (UPD) on Pt surface.
- **Au clusters stabilize Pt metal surface under highly oxidizing conditions and suppress Pt dissolution during ORR/potential cycling without decreasing its activity/kinetics**
- 30 – 40% coverage of Pt by Au
- **Stabilization due to d-orbital coupling with Au – thus lower energy state**

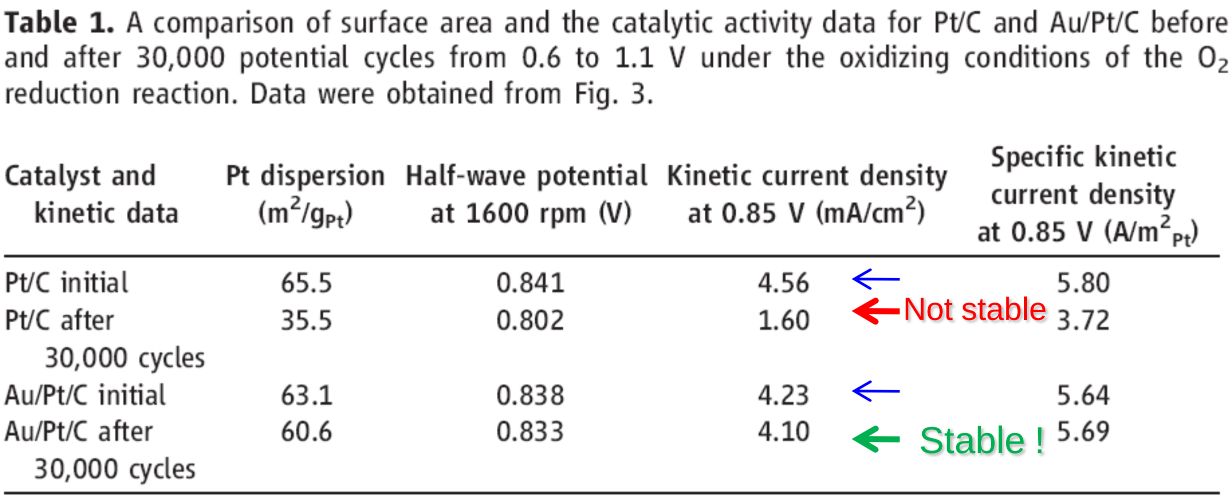


Table 1. A comparison of surface area and the catalytic activity data for Pt/C and Au/Pt/C before and after 30,000 potential cycles from 0.6 to 1.1 V under the oxidizing conditions of the O_2 reduction reaction. Data were obtained from Fig. 3.

Catalyst and kinetic data	Pt dispersion (m^2/g_{Pt})	Half-wave potential at 1600 rpm (V)	Kinetic current density at 0.85 V (mA/cm^2)	Specific kinetic current density at 0.85 V (A/m^2_{Pt})
Pt/C initial	65.5	0.841	4.56	5.80
Pt/C after 30,000 cycles	35.5	0.802	1.60	3.72
Au/Pt/C initial	63.1	0.838	4.23	5.64
Au/Pt/C after 30,000 cycles	60.6	0.833	4.10	5.69

Pt only

Not stable

Pt on Au

Stable !

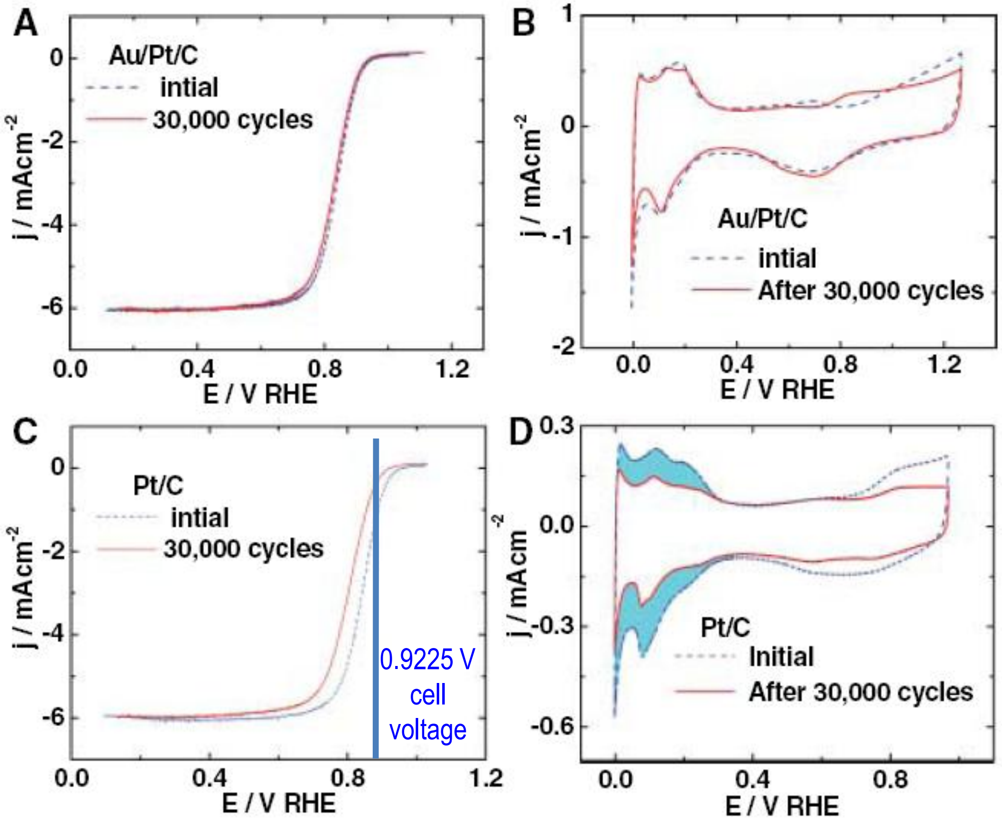
Zhang, J. Sasaki, K, Sutter, E., Adzic, R. Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters. Science (2007) 315, 220.

Experimental Validation

- Despite 1/3 coverage of Pt by Au, ORR activity is unchanged
  - Au oxygen activation
  - Au – CO oxidation
- Shaded region is lost Pt Area
- Loss in half-wave potential /activity

Pt on Au

Pt only



0.9225 V cell voltage

Concluding Remarks on Fuel Cells

- Electrode catalysis is still the most pressing fuel cell problem
- UPD and GR are being used to minimize noble metal deposition to a mono or submonolayer
- Even so the best catalyst, Pt, remains too expensive
  - Pt is such a cost-inefficient catalyst that most research seems to be direct towards its alternatives.
- US DoE sought a conversion efficiency goal of 75% for H_2 - O_2 fuel cell by 2010 …
  - 0.9225 V cell voltage (75% efficiency) under load was close with optimized electrodes using Pt deposited by UPD/ GR methods

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