Basic Research Needs
For
Fuel Cells

Presentation for

DOE Hydrogen Program

Paul H. Maupin
Paul.maupin@science.doe.gov

Division of Chemical Sciences, Geosciences and Bioscience
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

May 23, 2005

Project ID #
FC51

Priority Research Areas in Fuel Cells

Electrocatalysts and Membranes

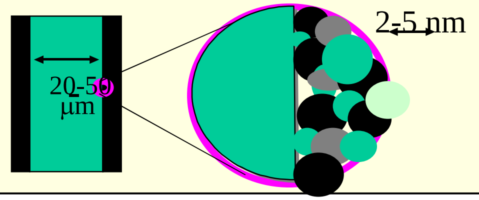
Oxygen reduction cathodes, minimize rare metal usage in cathodes and anodes, synthesis and processing of designed triple percolation electrodes

Low Temperature Fuel Cells

'Higher' temperature proton conducting membranes, degradation mechanisms, functionalizing materials with tailored nano-structures

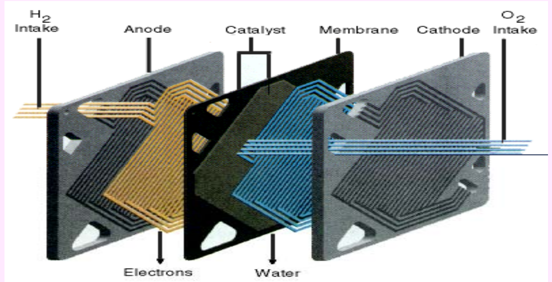
Solid Oxide Fuel Cells

Theory, modeling and simulation, validated by experiment, for electrochemical materials and processes, new materials-all components, novel synthesis routes for optimized architectures, advanced in-situ analytical tools



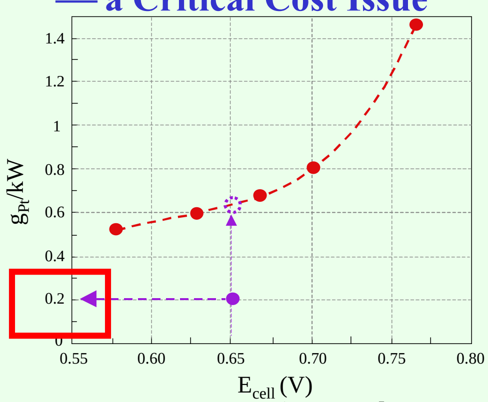
Controlled design of triple percolation nanoscale networks: ions, electrons, and porosity for gases

Internal view of a PEM fuel cell



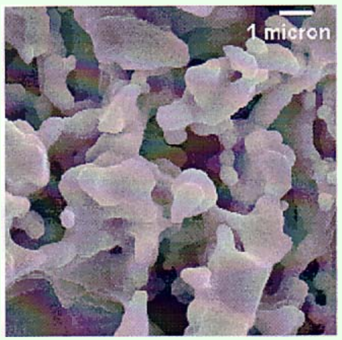
Source: T. Zawodzinski (CWSU)

Mass of Pt Used in the Fuel Cell — a Critical Cost Issue



Source: H. Gasteiger (General Motors)

YSZ Electrolyte for SOFCs



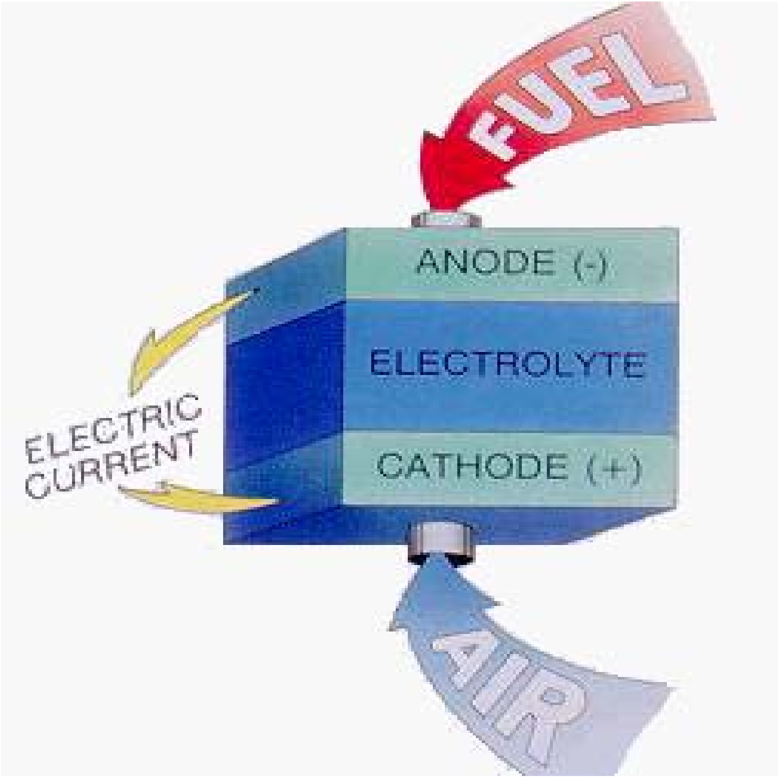
Porosity can be tailored

Source: R. Gorte (U. Penn)

High Priority Fuel Cells Research Directions

- **Nanoscale catalyst design**
- **Biological, biomimetic, and bio-inspired materials and processes**
- **Low-cost, highly active, durable cathodes for low-temperature fuel cells**
- **Membranes and separations processes for fuel cells**
- **Analytical and measurement technologies**
- **Theory, modeling, and simulation**

Basic Electrochemical Research Issues and Needs Relevant to Fuel Cells and Batteries



- Identification of participants and intermediates in electrode reactions.
- The relationship between physical structure, chemical composition and kinetics at short time scales.
- Characterization of interface structures and chemistry.
- Proton and electron transfer at electrochemical interfaces.
- Surface chemistry of electrocatalysts.
- Interface phenomena in composite electrode structures.

Program Highlights: Chemical Energy and Chemical Engineering Program

A thermodynamic guideline for the design of alloy catalysts

Balbuena, et.al. Texas A&M

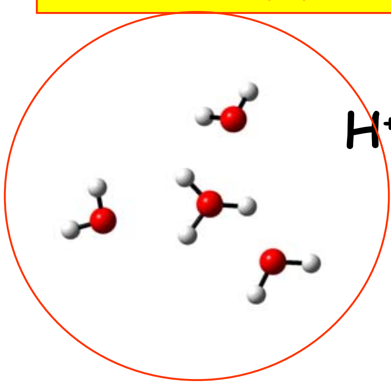
Calculations of ΔG: Gibbs Free Energy Change

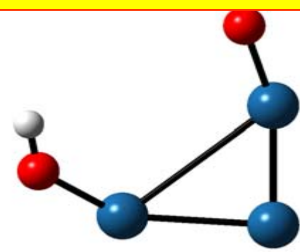
1st electron step: $O_2 + H^+ + e^- + M \rightarrow H\text{-}O\text{-}O\text{-}M$ (M: metal) (a) ΔG(a)

$H\text{-}O\text{-}O\text{-}M + M \rightarrow HO\text{-}M + O\text{-}M$ (b) ΔG(b)

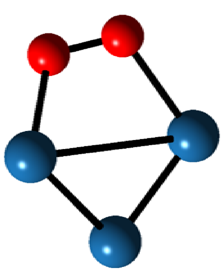
2nd–4th e-transfer steps: $HO\text{-}M + O\text{-}M + 3H^+ + 3e^- \longrightarrow 2H_2O + M$ (c) ΔG(c)

Both ΔG(a) and ΔG (c) should be highly negative for efficient catalysts.

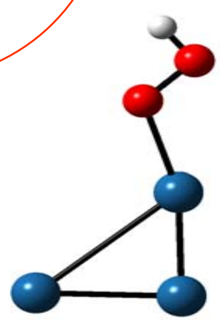




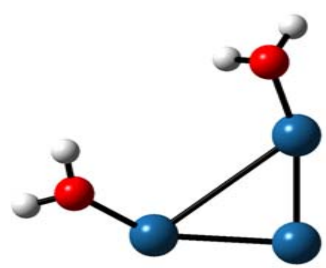
HO-M +O-M



M…O_2



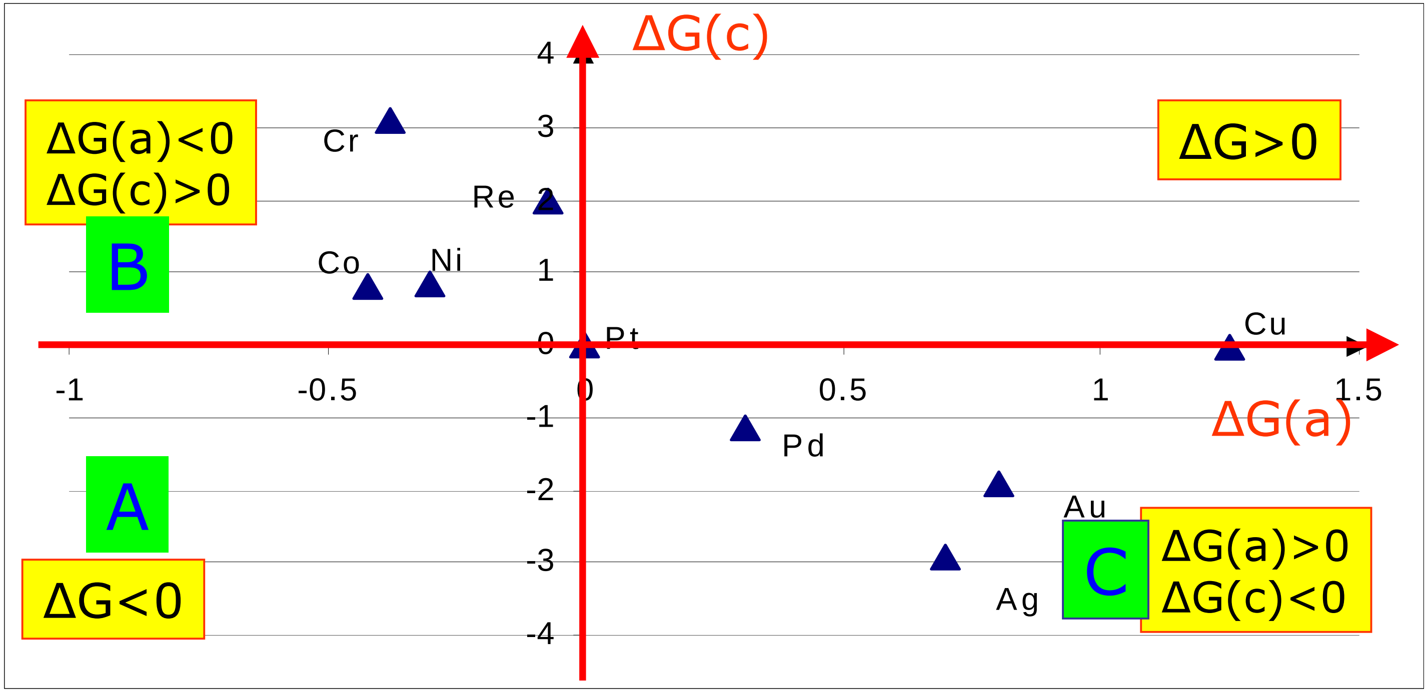
M-OOH



$2H_2O$…M

6	7	8	9	10	11
24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag
74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au

Plots of Relative ΔG: very interesting correlations



Pt: $5d^9 6s^1$
Co: $3d^7 4s^2$
Ni: $3d^8 4s^2$
Pd: $4d^{10}$
Cu, Ag, and Au:
$nd^{10}(n+1)s$ (n=3-5)

- Why no any other metals work as well as Pt catalyze the ORR?

- ΔG strongly correlates with metal electronic configuration:
  B: vacant valence *d* orbitals, ΔG(a)<0 and ΔG(c)>0
  C: fully occupied valence d orbitals, ΔG(a)>0 and ΔG(c)<0.

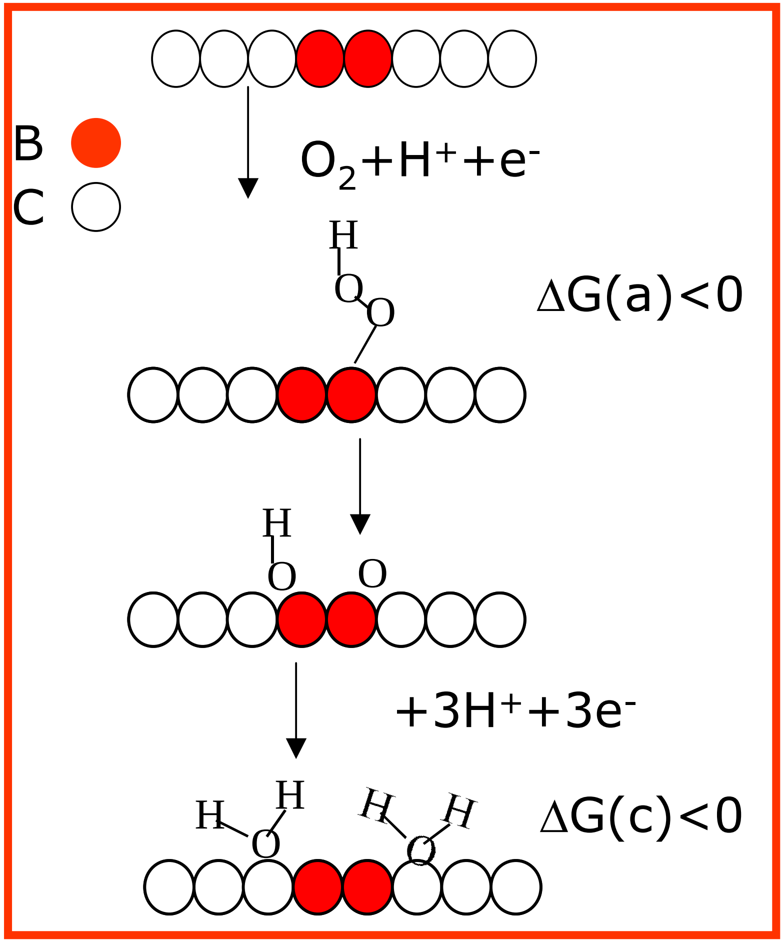
- A thermodynamic guideline to design alloy catalyst: couple one metal in area B (ΔG(a)<0) with another metal in area C (ΔG(c)<0) => BC_3 (bimetallic clusters).

A Thermodynamic guideline for the design of alloy catalyst for ORR

Principle:
B (metal in area B, $\Delta G(a)<0$)
+ C (metal in area C, $\Delta G(c)<0$)
➔BC_3 ($\Delta G(a)<0$, $\Delta G(c)<0$)

Examples: $Co\text{-}Pd_3$ (Ag, Au), $Ni\text{-}Pd_3$ (Ag,Au), and so on; (need to be further characterized!!)

A couple of bimetallics that work as established by experimentalists, such as Pt-Ni (25% Ni), Pt-Co (25% Co)*, could also be explained by the present guideline.

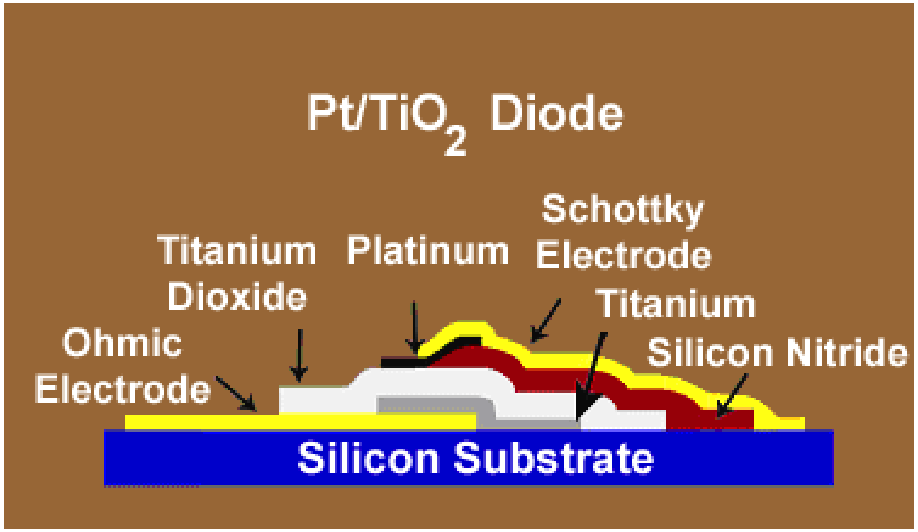


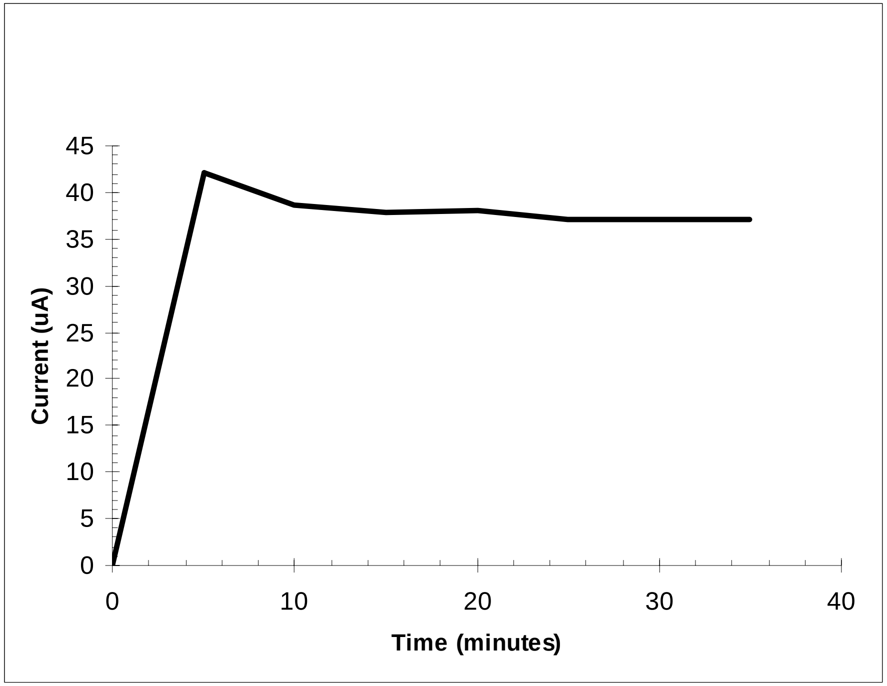
Ross, P. N.,et al., J.Phys. Chem. B, 106, 11970-11979, (2002) Program Highlights: Catalysis and Chemical Transformations

Hot electron flow induced by exothermic chemical reactions

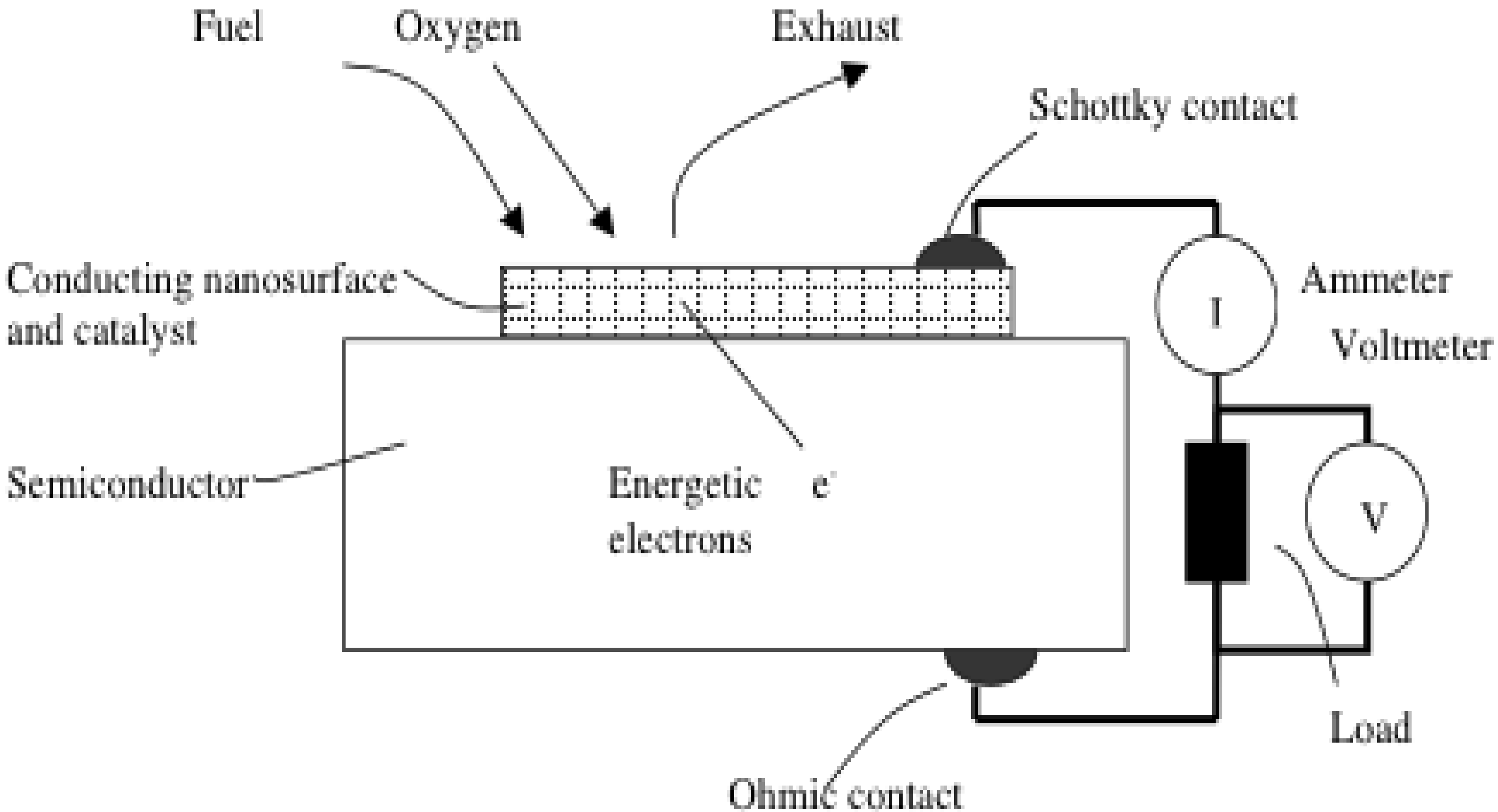
Gabor A. Somorjai et.al., LBNL and UC Berkeley

Hot Electron Current Produced by Carbon Monoxide Oxidation at 80 ºC over the Pt/TiO_2 Catalytic Nanodiode





Schematic representation of hot electron generation by exothermic catalytic reactions using a nanodiode



Exothermal catalytic chemical reactions considered for Energy Conversion by Nanoscience

Oxidation of carbon monoxide,

Hydrogenation of ethylene

Oxidation of ammonia

Oxidation of hydrogen

Oxidation of methanol

Oxidation of methane

..and etc.

3.14 mm2 Pt 5.8 nm thick, 150 nm TiO_2