Catalysis in Polymer Electrolyte Membrane Fuel Cells

Fundamentals and Current Research

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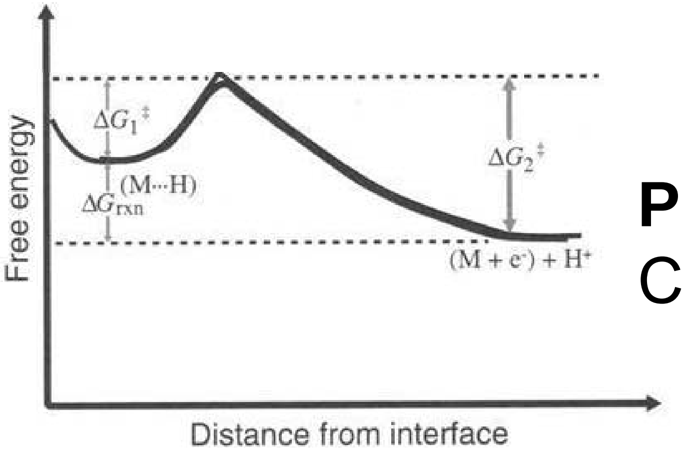
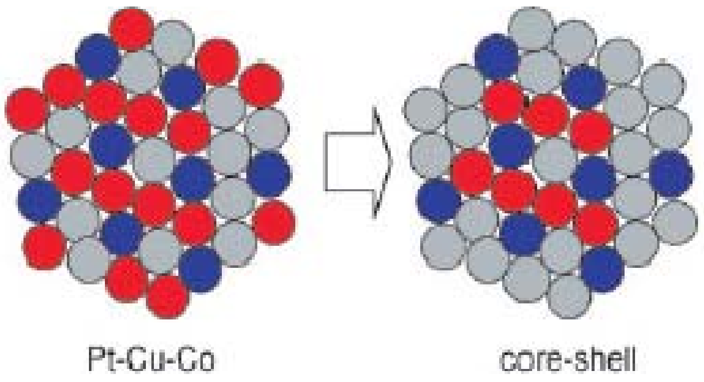
MSE 395
June 5, 2008

Overview



Part I: Fundamentals of Catalysis in Fuel Cells



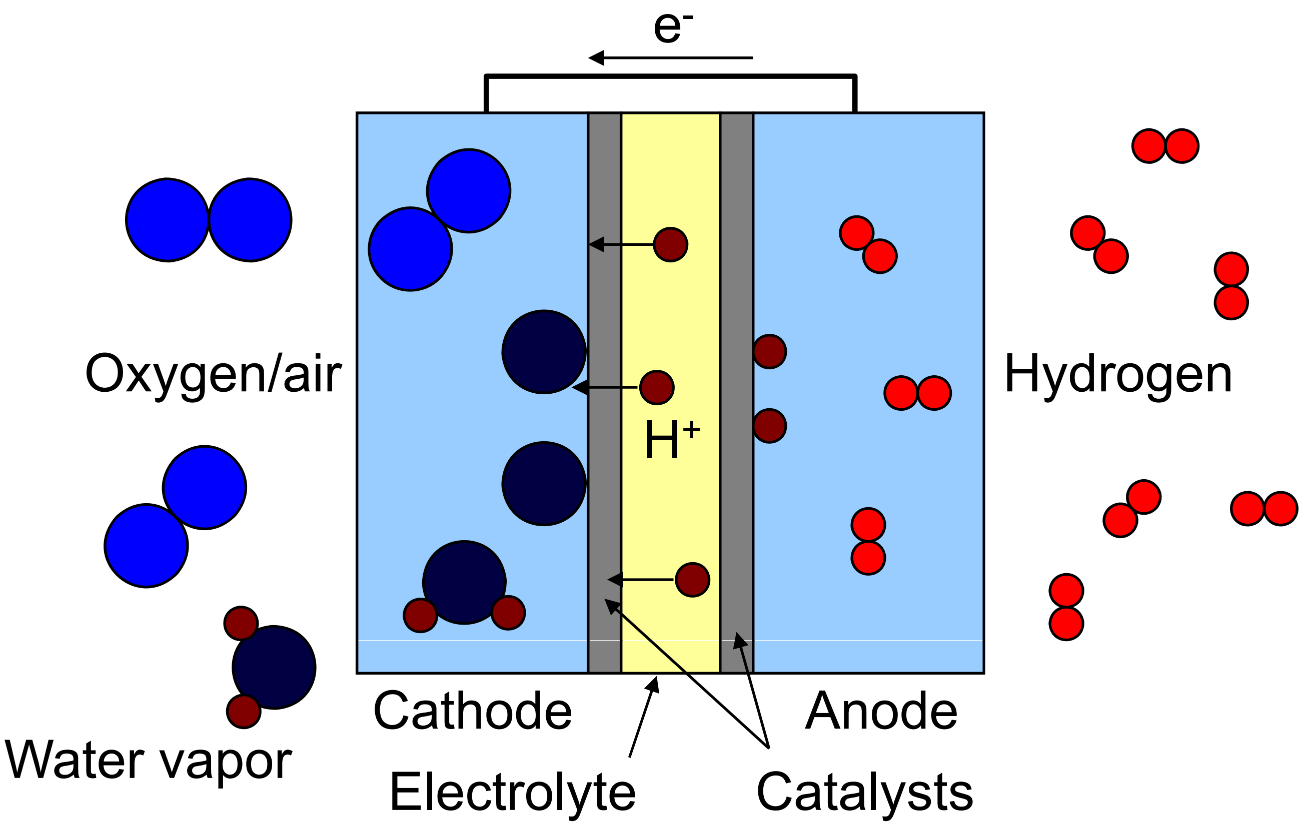
Part II: Current PEMFC Catalyst Research

The concepts in Part I are applicable to all fuel cells, while Part II concerns only PEMFCs.

Part I

Fundamentals of Catalysis in Fuel Cells

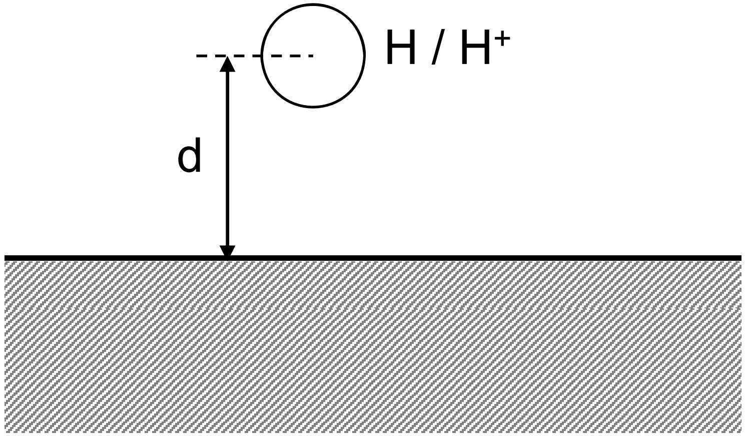
Fuel Cell Structure

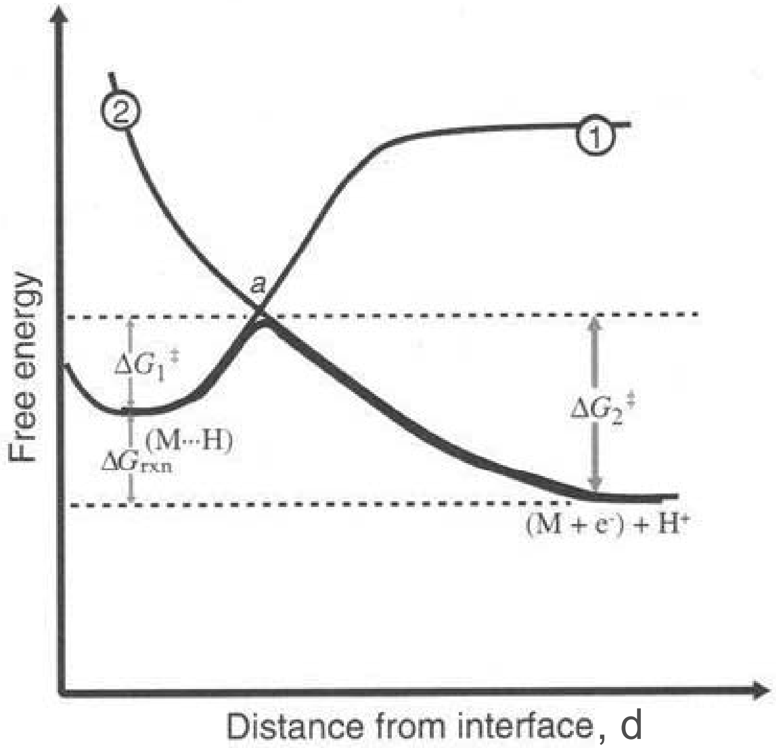


A fuel cell separates two halves of an electro-chemical reaction to convert H_2 to electricity.

Case Study: Hydrogen Oxidation

$$H_{(ads)} \rightarrow H^{+} + e^{-}$$

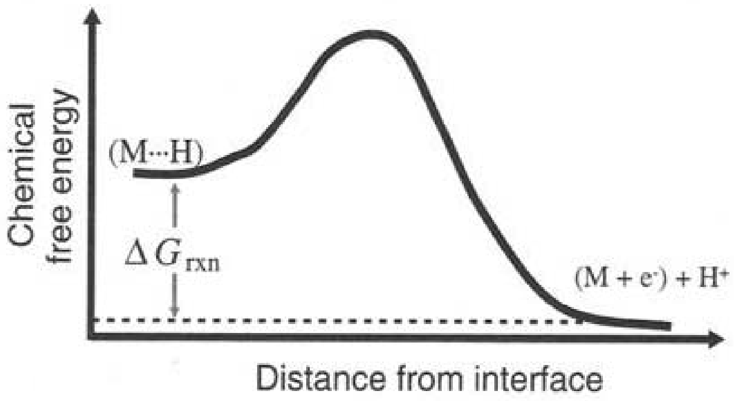




R. O’Hayre et al. Fuel Cell Fundamentals. Hoboken, NJ: John Wiley & Sons, 2006, pgs. 237–240.

Reactants must overcome an energy barrier – the activation energy – to convert into products.

At Thermodynamic Equilibrium



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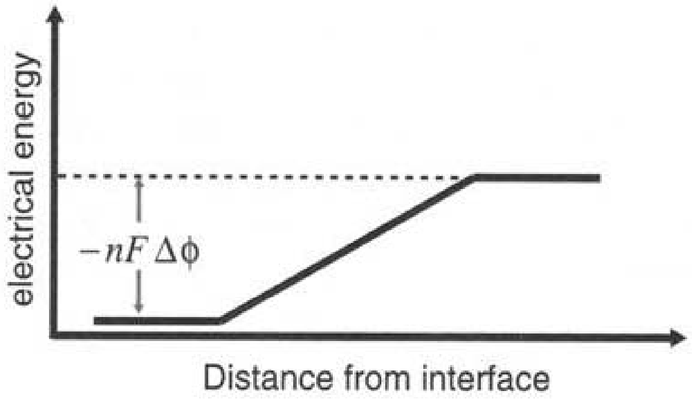

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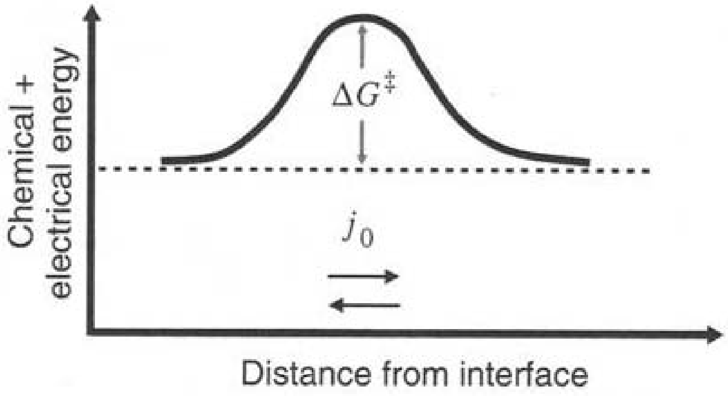
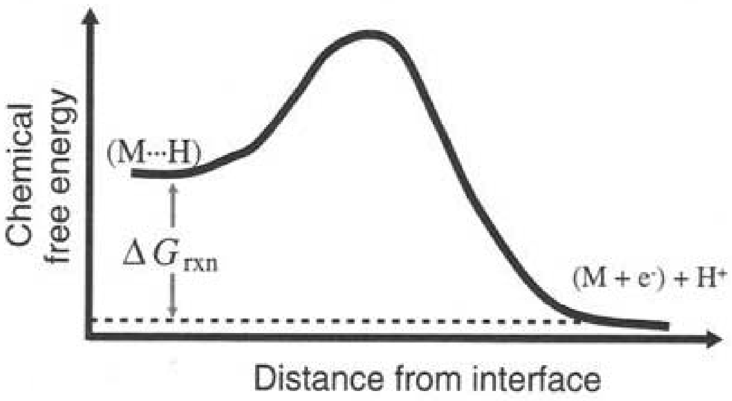


$$j_0 \propto \exp\left(\frac{-\Delta G}{RT}\right)$$

R. O'Hayre et al. Fuel Cell Fundamentals. Hoboken, NJ: John Wiley & Sons, 2006, pgs. 237–240.

The forward and reverse reaction rates eventually reach a dynamic equilibrium with current density j_0.

Away from Equilibrium



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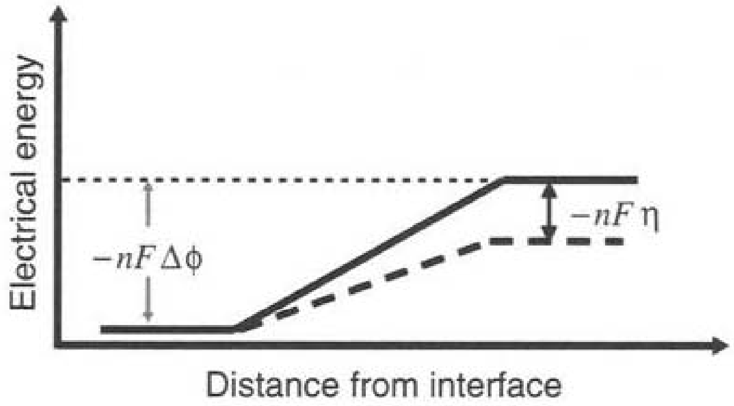

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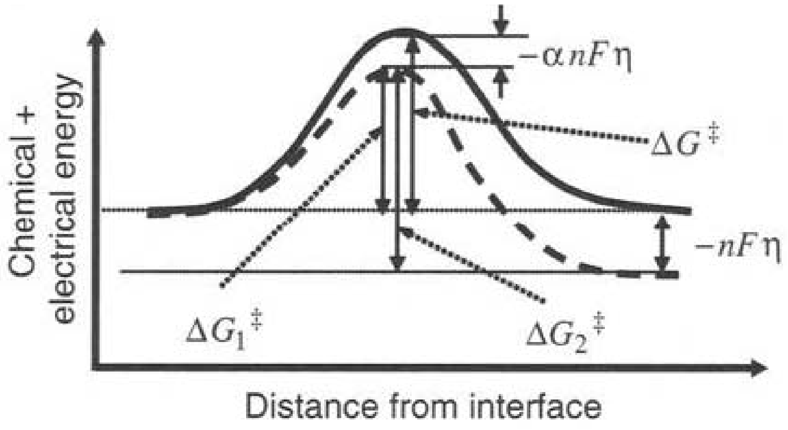
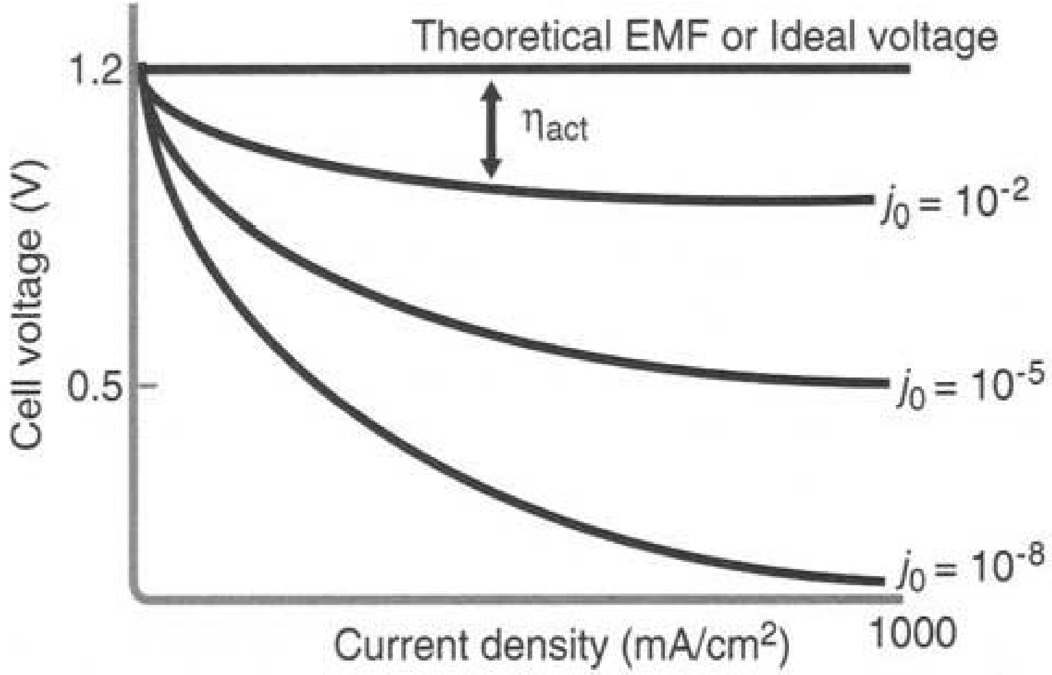


$$j = j_0\left[\exp\left(\frac{\alpha nF\eta}{RT}\right) - \exp\left(\frac{-(1-\alpha)nF\eta}{RT}\right)\right]$$

R. O'Hayre et al. Fuel Cell Fundamentals. Hoboken, NJ: John Wiley & Sons, 2006, pgs. 237–240.

An activation overpotential, η, is necessary to produce a net current.

The Butler-Volmer Equation



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Catalysts are necessary to maximize j_0, allowing for operation at high current densities.

Part II

Current PEMFC Catalyst Research

PEMFC Catalyst Goals

Current PEMFCs use Pt catalysts which have two noteworthy problems:

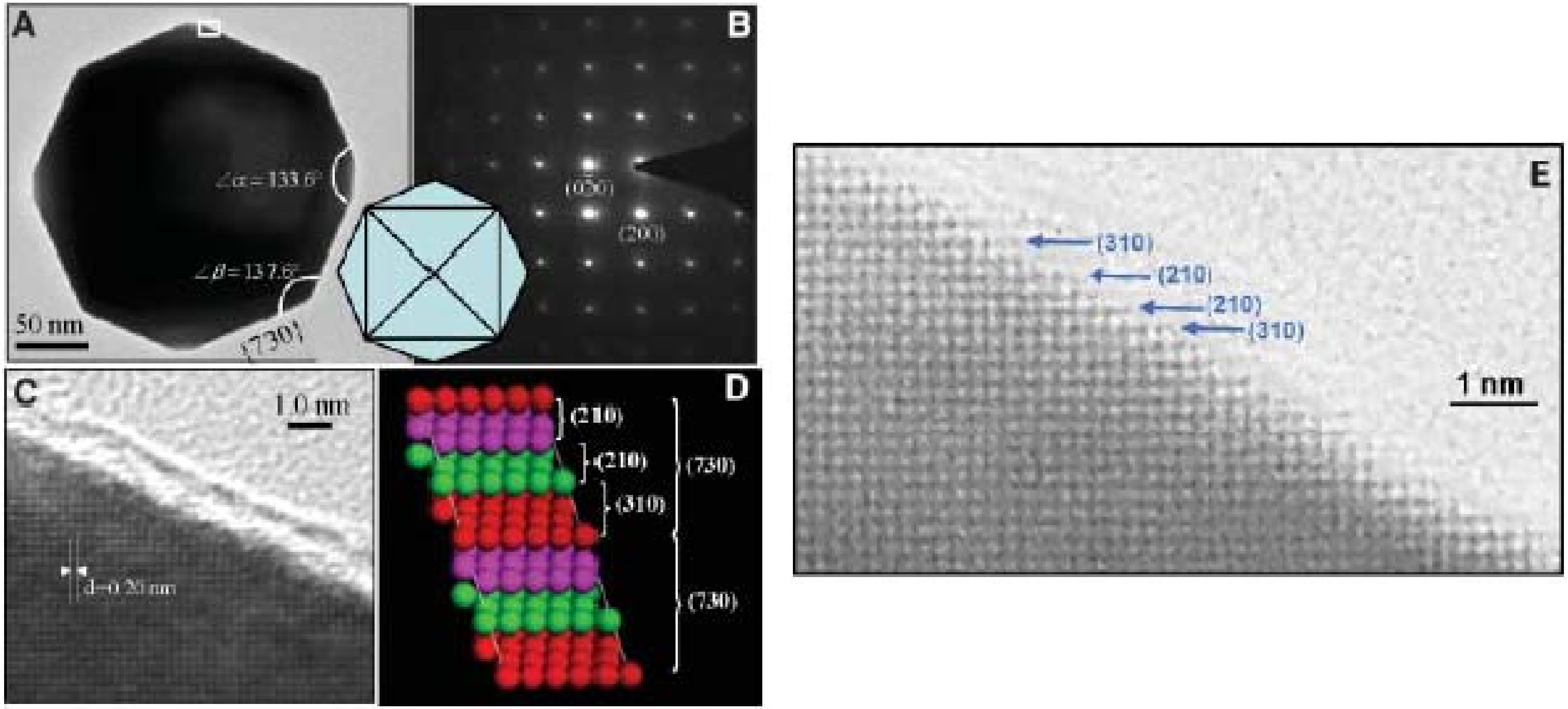
Cost – New PEMFC catalysts must use 4x less Pt*

*U.S. Department of Energy. Hydrogen Posture Plan (2006), pg. 5.

Poisoning – Contaminants/electrolyte solution must not poison the catalyst.

Most current PEMFC catalyst research focuses on modifying Pt catalysts to meet these goals.

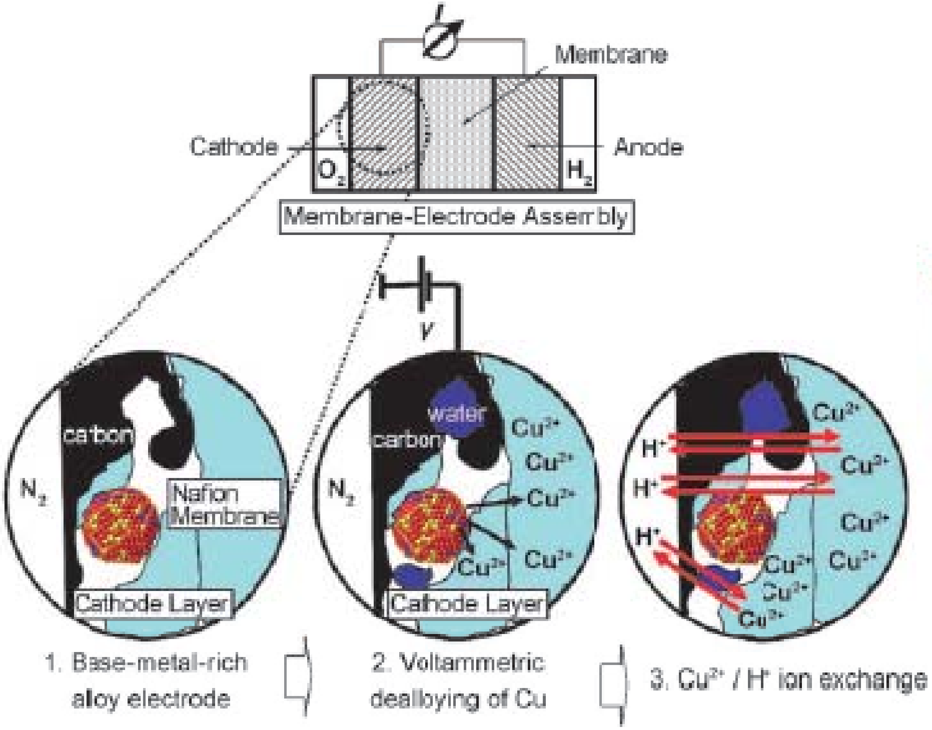
Increasing Activity #1: Morphology

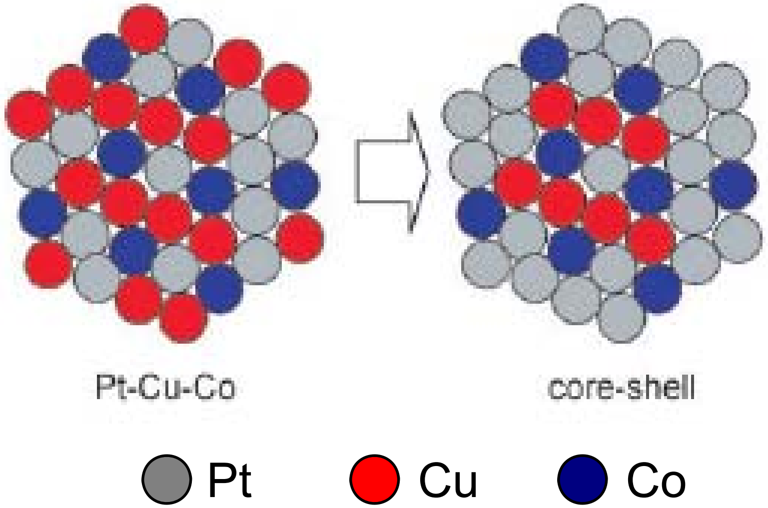


N. Tian, et al. *Science* **316** (2007) 732–735.

Optimizing the size and shape of Pt nanoparticles increases their ethanol oxidation activity 4-5x.

Increasing Activity #2: Composition

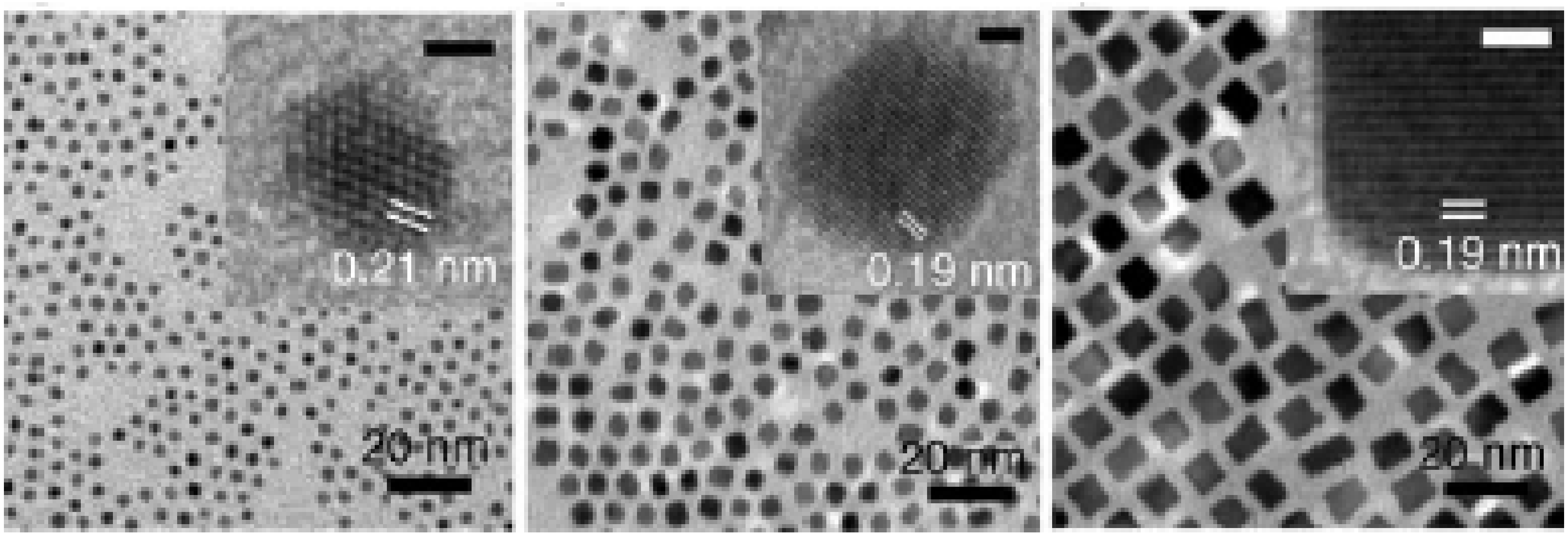




R. Srivastava, et al. *Angew. Chem. Int. Ed.* **46** (2007) 8988–8991.

Core-shell nanoparticles of Pt alloys increase their oxygen reduction activity 4x.

Reducing Poisoning #1: Morphology

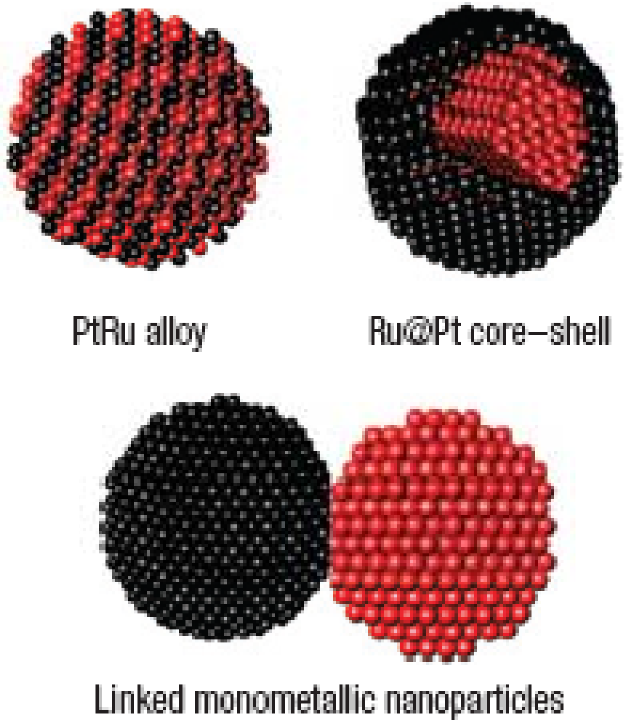


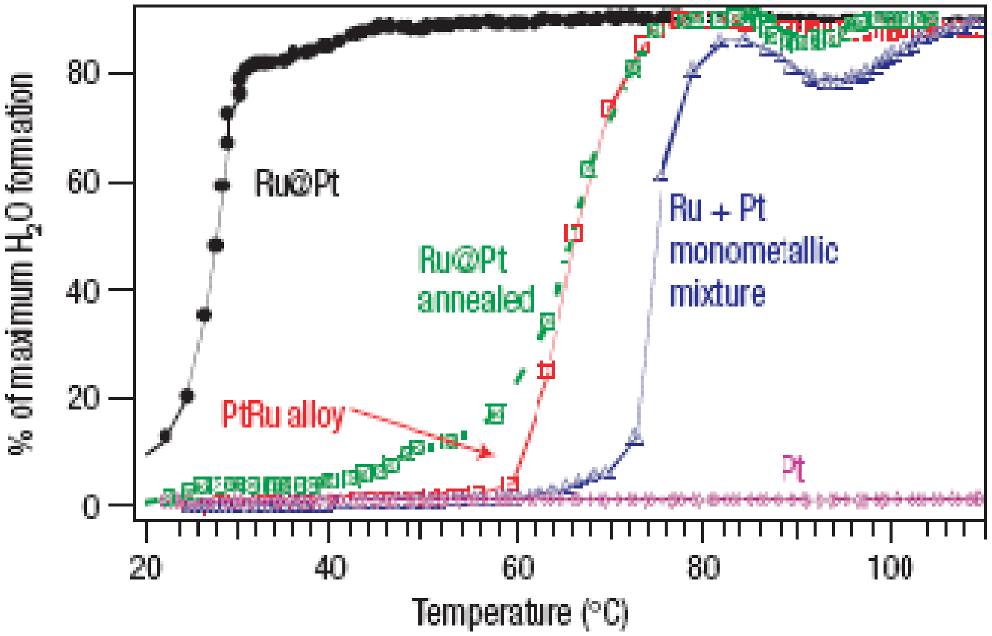
~3 nm polyhedra ~5 nm truncated cubes ~7 nm cubes

C. Wang, et al. *Angew. Chem. Int. Ed.* **47** (2008) 3588–3591.

The (100) facets of Pt nanocubes do not bond SO_4^{2-} as strongly, leaving more sites for O_2 oxidation.

Reducing Poisoning #2: Purification





S. Alayoglu, et al. *Nature Materials* **7** (2008) 333–338.

Ru-Pt core-shell nanoparticles effectively oxidize CO at suitable PEMFC operating temperatures.

Conclusions

Part I: Fundamentals of Catalysis in FCs

- Catalysts decrease activation E
- Essential for operating at high current densities

Part II: Current Research for PEMFCs

- Increase activity by:
  - Increasing surface density of reactive sites
  - Modifying electronic structure near surface
- Reduce poisoning by:
  - Modifying catalyst surface
  - Purifying fuel