New Electrocatalysts For Fuel Cells

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Materials-by-Design Approach

Taylor made surfaces

synthesis of nanoparticles

Fuel cell catalyst

Characterization techniques

LEIS, XPS, AES, LEED

HRTEM, XRD

Kinetics

HOR, ORR, CO Tolerance

HOR, ORR, CO Tolerance
Collaborations

Industry

- GM, Rochester, NY, USA
- Honda, Japan
- E-Tek, New Jersey, NJ, USA
- 3M, Minneapolis, MN, USA

Universities and Institutes

- Max-Planck-Institut fuer Kohlenforschung, Muelheim/Ruhr, Germany
- University of Ulm, Germany
- Paul-Scherrer-Insitut, Villigen, Switzerland
- Universidad d’Alicante, Spain
- Texas Tech University, Lubbock, TX, USA
- University of Eindhoven, Holland
- University of Wales, UK
- University of Bonn, Germany
- University of Liverpool, UK
Future Research 2000

**Anode Side**

- Optimization of PdAu catalysts
  - Stoichiometry and particle size
- Electrocatalysis on Pd thin metal films
  - Electronic effects
  - Select the most promising substrate for the Pd thin film electrode concept
- Simulation of ‘Air-bleed’
  - on FC catalysts under FC conditions

**Cathode Side**

- Optimization of PtNi and PtCo catalysts
  - Stoichiometry
  - Minimization of Pt amount
  - Pt-skin effects (electronic modification of Pt)
  - Anion effects
- New class of ORR catalysts
Publications (Since 10/2000)

Refereed Journals and Refereed Conference Proceedings:


Future Directions

- Unified concept for both anode and cathode catalysts utilizing PGM-based bimetallic nanoparticles with “grape” structure (PGM skin with base metal core) stability of high surface area Pt-bimetallic catalysts
  - Choice of skin and core metals different for anode and cathode

- New synthetic chemistry for nanoparticles with “grape” structure

- Investigation of Re as metal core in PGM “grape” structured nanoparticles
  - Pt and Pd monolayers on Re(0001) model system
  - Re colloidal chemistry

- Optimization of AuPd anode catalyst for HT membranes

- Computational screening of non-PGM catalyst concepts using newly developed (under BES funding) *ab initio* theory of the ORR
Segregation on Pt₃Ni and Pt₃Co alloys surfaces

Pt$_3$Co: AES, LEIS

Platinum ‘Skin’ on the surface

**AES:**
- Co depleted on the annealed surfaces
- Pt enrichment?

**LEIS:**
- Complete Pt enrichment on the annealed surface
- Bulk composition achieved during in situ sputtering
Kinetic Enhancement by Skin Effect

- The most active surface at 60°C: Pt₃Co skin

Factor: Pt₃Co (s) > Pt₃Co (b) > Pt₃Ni (b) > Pt > Pt₃Ni (s)

4.2  2.8  1.9  1  0.15

Skin structure is either more or less active than sputtered structure

Electronic effects
Characterization of Pt/Vulcan Catalyst

- **Transmission electron microscopy**

- **The particle size effects:**
  Correlation between the ORR on Pt(hkl) and exposed facets on Pt/C catalysts at fuel cells relevant conditions

- **Mainly cubo-octahedral particles**
  with (111) and (100) facets

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- **d~3.5 nm**

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- **Frequency [%]**

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- **Particle Size [nm]**

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- **Low magnification**

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- **High magnification**
Particle size effect

- Catalysts: 10, 20, 30, 40% Pt/C
- d = 3.1 ± 1 nm, 3.3 ± 0.7 nm, 3.8 ± 1.7 nm, 4.7 ± 2.7 nm

SA increases with SAD(111)

SA increases with SAD(100, e+c)
Characterization of PtCo/Ni Vulcan Catalysts

H\text{upd} coverage decreases with increase of Ni or Co wt%.

(a) Graph showing the current density (I) as a function of potential (E) for different catalysts: Pt/Vulcan, PtNi/Vulcan, Pt$_3$Ni/Vulcan.

(b) TEM image of PtCo/Ni Vulcan catalysts with a cubo-octahedral shape.

(c) Histogram showing the particle size distribution with a peak at 4.4 ± 1.6 nm.

(d) HRTEM image showing the cubo-octahedral shape with (111) and (100) facets.

HR Transmission electron microscopy

Complete alloying
Some Pt-M alloys have better performance than Pt

- Pt-Co has the highest activity

Benefits:
- Higher activity (!?)
- Substitution of Pt

![Graph showing ORR kinetics on Pt-bimetallic surfaces](image-url)
### Pd thin metal films on Pt(111)

#### a) E/V [RHE]

- n < 1
- n = 1
- n ~ 2
- n > 2

- 0.25 mA/cm²
- 0.15 mA/cm²

#### Pt(111) - nML Pd

- E/V [RHE]
- E₁/E₀

- Intensity / a.u.

- n < 1
- n = 1
- n ~ 2
- n > 1

#### b) 0.05M H₂SO₄ 293K

- Pt(111) - nML Pd

#### c) Pt(111) - nML Pd

#### d) Pt(111) - nML Pd

#### e) Pt(111) - nML Pd
HER/HOR on Pt(111)-Pd in $\text{H}_2\text{SO}_4$/KOH

- Maximum catalytic activity for 1 ML of Pd film
  - Adsorption vs Absorption of H
- Activation energy:
  - Reduced by 50% on 1ML Pd
ORR on Pt(111)-x Pd in KOH

0.1 M KOH
50 mV/s, 1600 rpm, 293 K

I [%A]

0 20 40

E [V/RHE]

0.1 M KOH
50 mV/s, 1600 rpm, 293 K

I [mA/cm²]

0 20 40

amount Pd / ML

0 0.5 1.0 1.5 2.0

@ 0.9V

“I /mA/cm²

0 1 2 3 4

Electronic Effect

“Vulcano Plot”
ORR on UHV Prepared Au(hkl)-Pd Alloy Surfaces

- **Vapor deposition of Pd**
  - 30% Pd
  - 50% Pd
  - 75% Pd

LEIS He⁺

- Au(hkl)-Pd

- **Structural Effect**
- **Electronic Effect**

**0.1M KOH @ 0.85V 333K**

- **ORR**
  - i[k] [mA/cm²]
  - Pd coverage [%]

- **Electronic Effect**
  - Au(111) + Pd
  - Au(100) + Pd

- **Structural Effect**
  - Au(111) + Pd

- **Vapor deposition of Pd**
  - 30% Pd
  - 50% Pd
  - 75% Pd