Combinatorial Discovery of Fuel Cell Electrocatalysts

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University of Puerto Rico @ Rio Piedras

Non-Platinum Electrocatalysts Workshop
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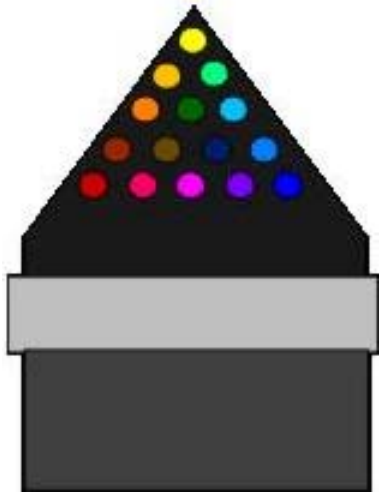
Marriot courtyard – Convention Center
New Orleans, Louisiana

Overview

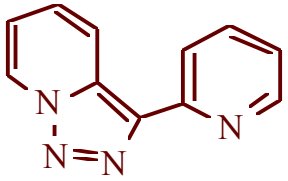
- Parallel Screening methods
  - Optical Screening method
  - Array fuel cell
- Array synthetic methods
- Partial review of non-Pt cathode work

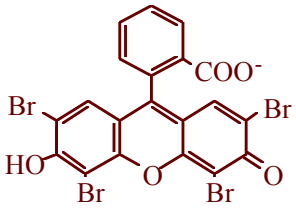
Optical Screening of Electrocatalyst Libraries

Tom Mallouk, Penn. State Univ.
Gene Smotkin, IIT



- Catalyst spots deposited on Toray carbon paper
- All array spots are shorted together
- Highest current density at any potential yields highest local ΔpH

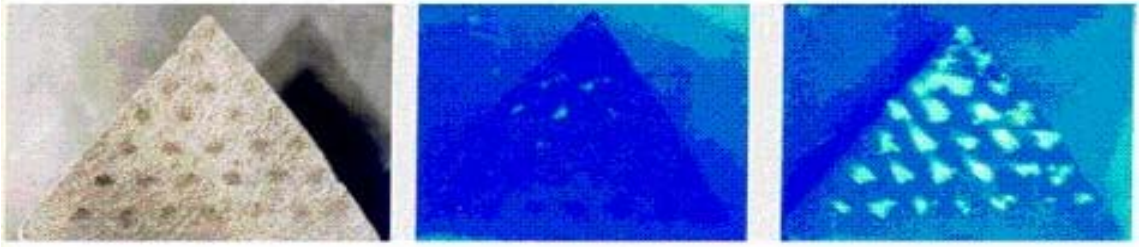


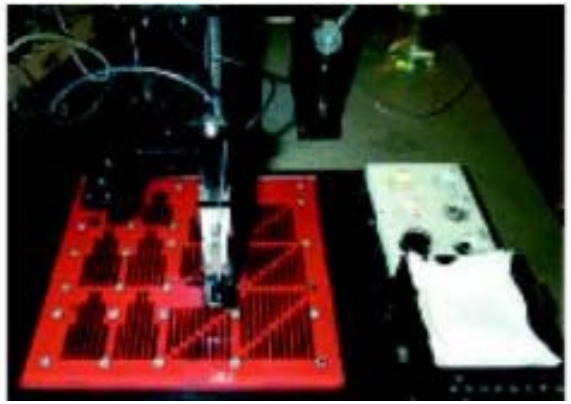


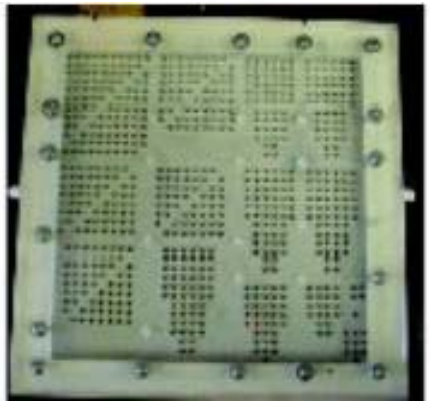
$$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$$

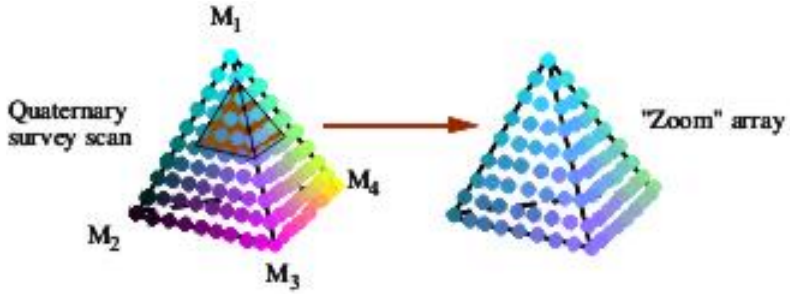
$$O_2 + 4H^+ + 4e^- = 2H_2O$$

Optical Screening Method

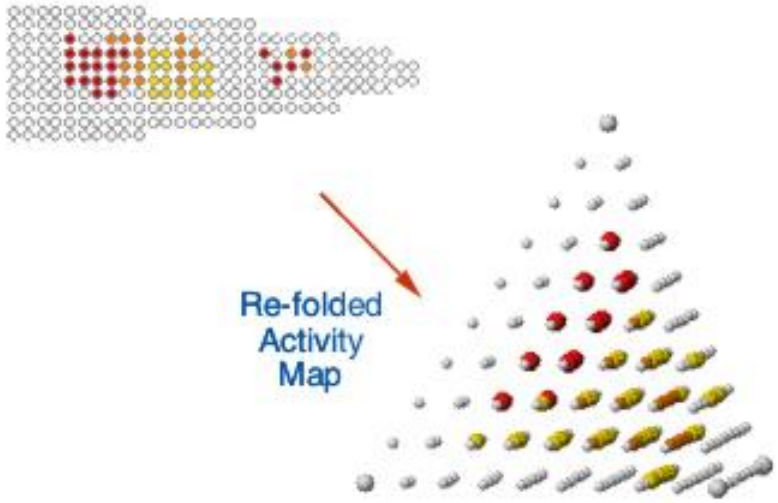








Active regions of survey maps are
expanded to pinpoint active catalysts



"Zoom" scans are followed by RDE and
fuel cell testing of best catalysts

Discoveries by Optical Screening (DMFCs)

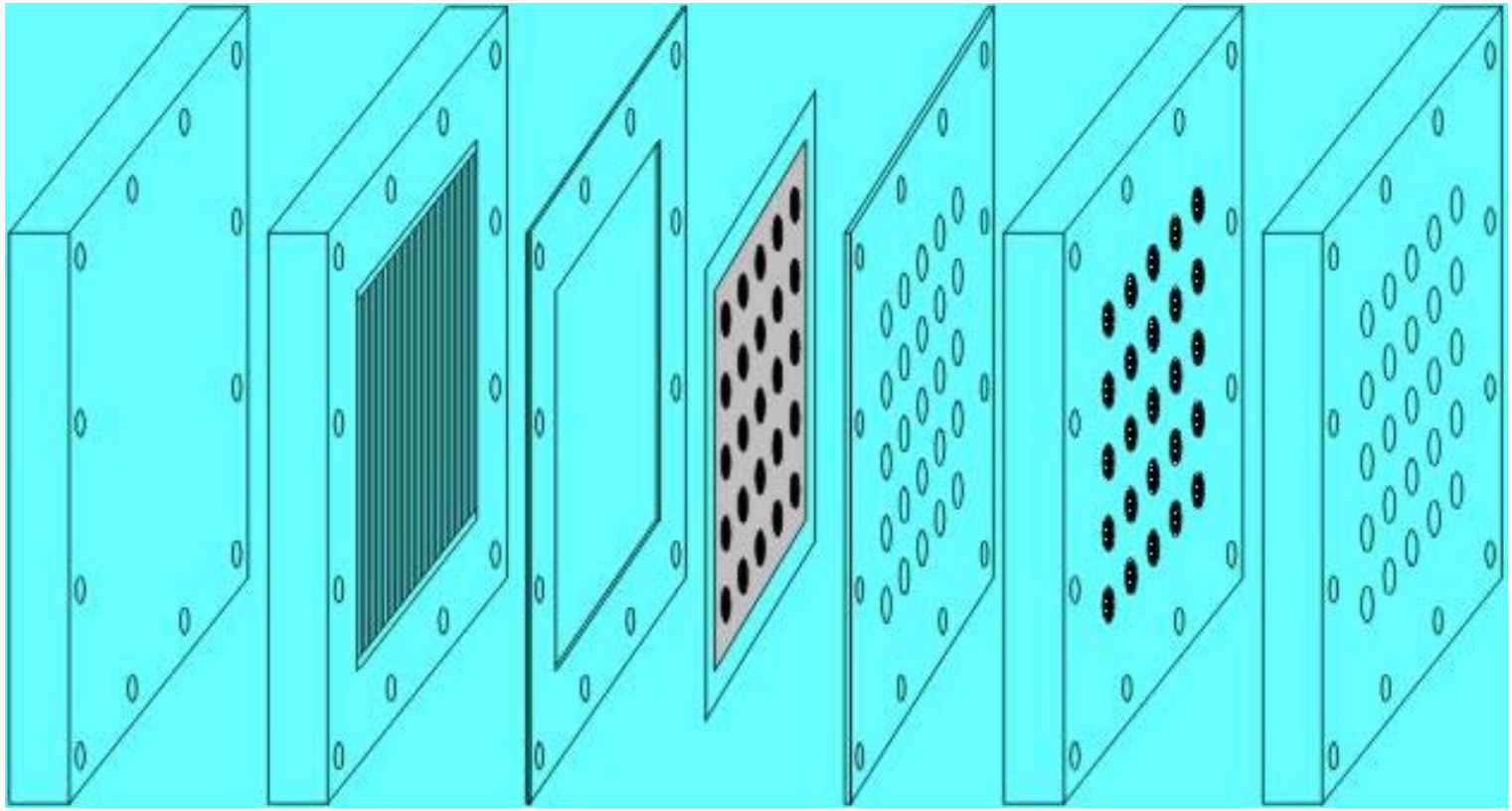
- Within borohydride synthetic regime:
  - PtRuOsIr > PtRuOs > PtRu
  - Typical surface area attained was 20 m^2/gram
- In the open field of ranking
  - Single cell testing of commercial ETEK or JM PtRu was superior to borohydride prepared binaries or ternaries.
    - JM PtRu ≈ 85 m^2/gram
- Optical screening method is reliable.
- Broad array synthetic methods (borohydride reduction) are not.
- Optical method must be decoupled from synthetic methods.

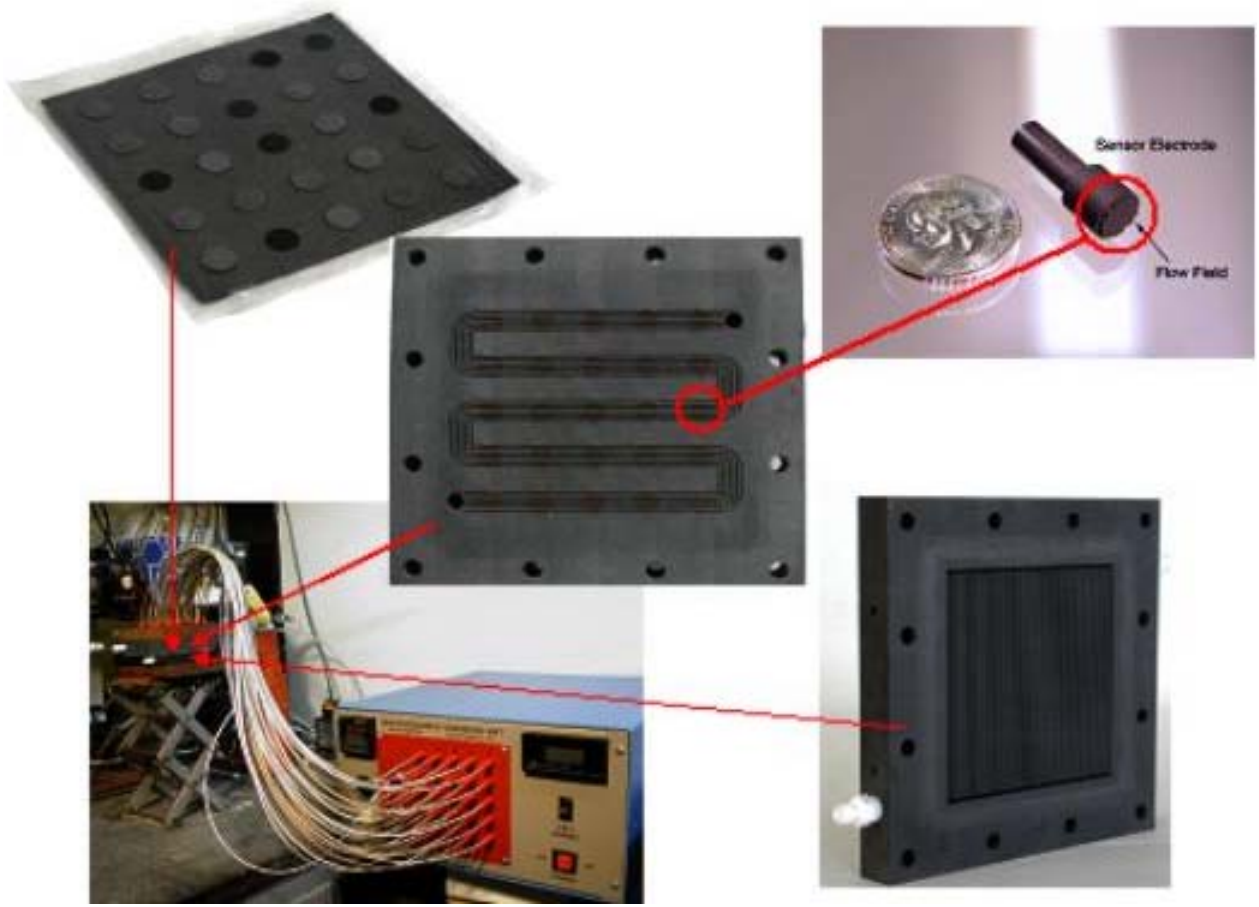
Array fuel cells

Renxuan Liu, NuVant Systems Inc.
Gene Smotkin, UPR at Rio Piedras

- GDL catalyzed MEA (ink or vapor deposition) fabrication methods.
- Discovery or focus level screening.
- Conventional single cell temperature control and reactant delivery.
- Realistic fuel cell conditioning.

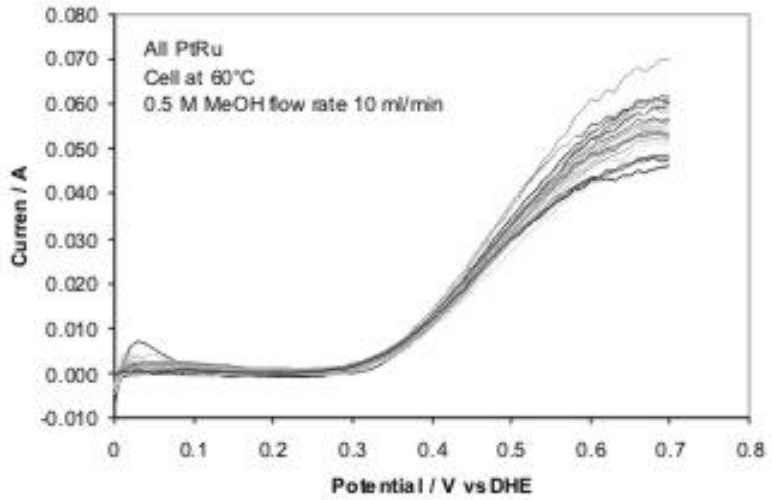
UPR/NuVant Systems Inc. Array Fuel Cell System

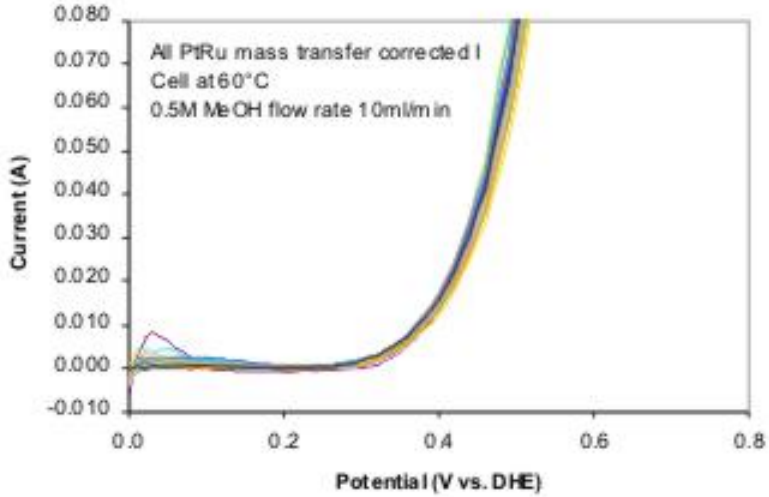



Sensor Electrode
Flow Field

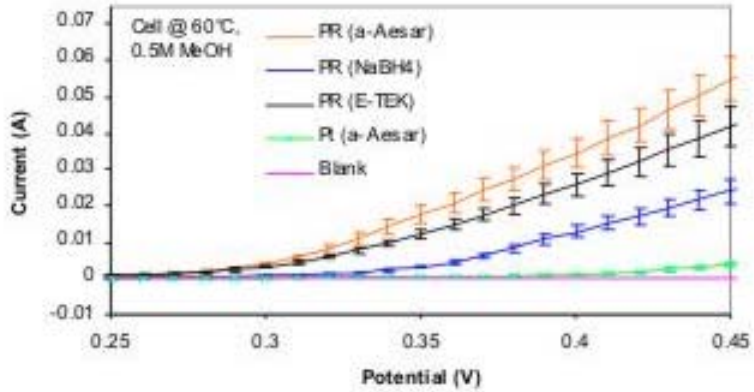
Array Flow field designs

- Segmented flow field.
- Segmented gas diffusion layer (GDL disks on array side)
- DMFC
  - Serpentine serial flow fields with high reactant stoichiometric ratios.
- Hydrogen air fuel cells
  - Gas fed parallel flow fields.
  - Pressure dropping inlet manifold ensures uniform flow across the array.





Ranking of catalysts in DMFC anode operating region



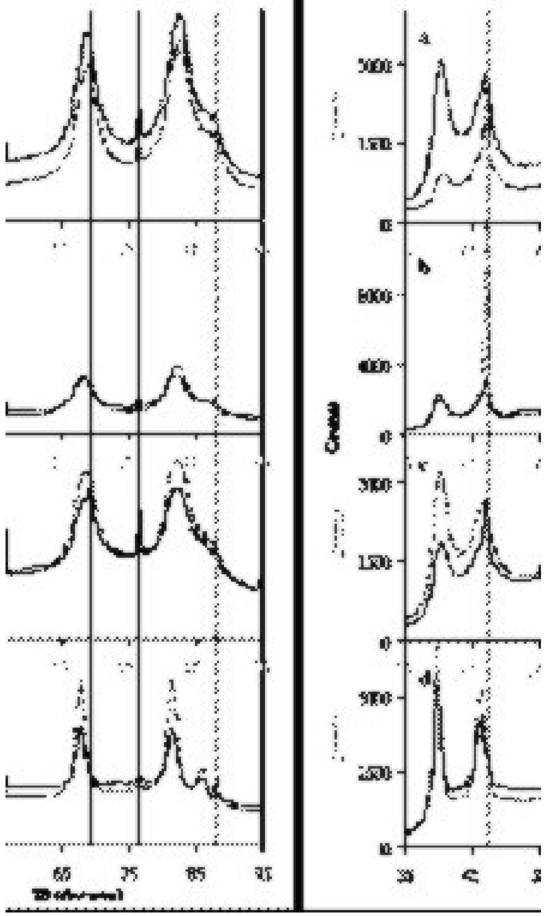


TABLE 1 XRD full pattern fitting results

Sample	a / Å	Displacement / deg	χ^2
Pt (calibrant)	3.9160(3)	0.009(5)	3.42313
Bona PtRu	3.8711(7)	0.253(6)	0.56462
Adams PtRu	3.8908(5)	0.352(1)	2.76403
JM PtRu	3.8830(3)	0.349(8)	0.61446

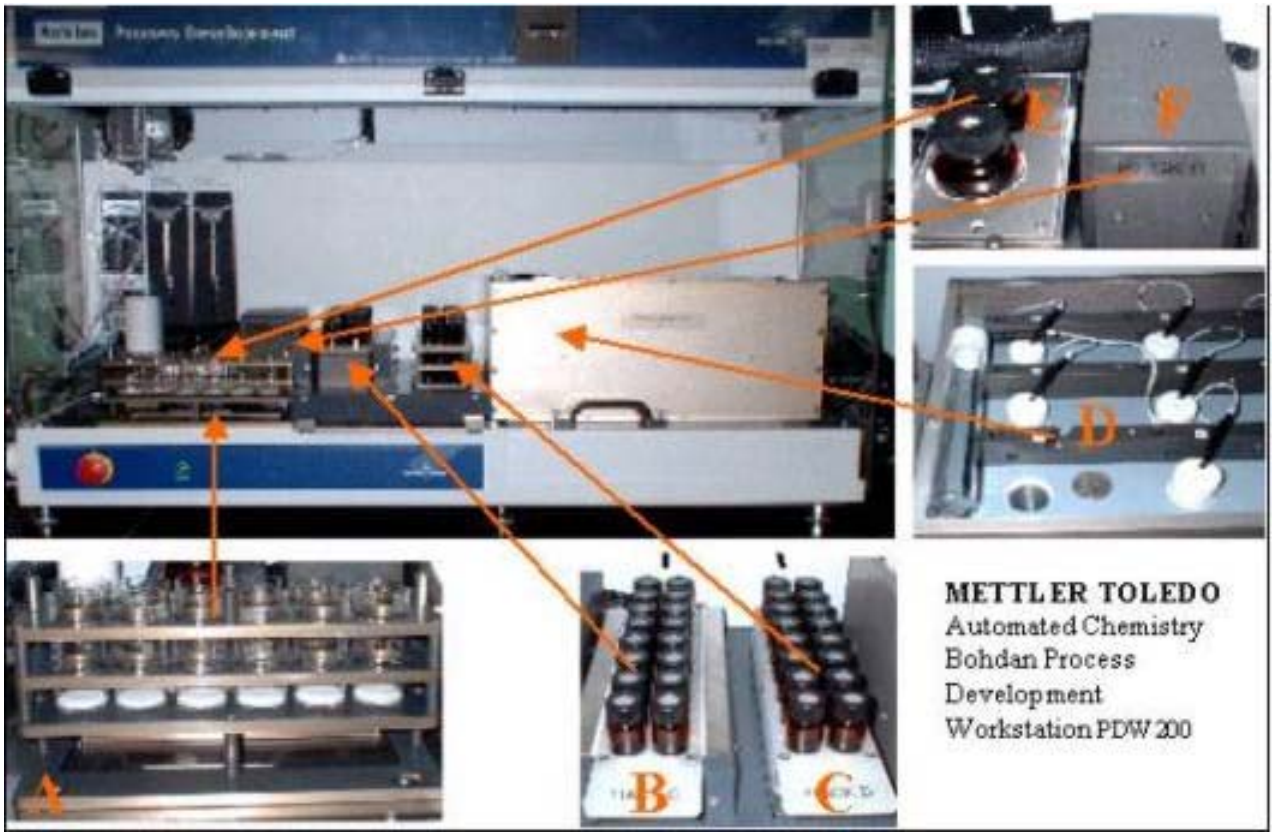
Array fuel cell summary

- Screening under fuel cell conditions.
- Any GDL deposition method can be used.
- Pre and Post screen XRD and XPS analysis demonstrated.*
- Liquid feed or gas fed array flow fields available.
- Screening rate (1 instrument): 100 week
  - Arrhenius plots*
  - Tafel plots*
  - Fuel or oxidant stoic ratio dependence (within the “safe” window”)*
- Can also screen ink formulation or catalyst deposition methods

* R. R. Diaz et al., manuscript in prep.

Array synthetic methods

- Vapor deposition upon the GDL
  - Sputtering upon blank & Pt catalyzed GDLS
  - Pulsed laser deposition
  - Chemical vapor deposition
- Robotics development and hybridization of “single beaker” methods followed by ink deposition upon GDLs.
  - Reetz, Watanabe, Bönnemann, Stonehart, Christensen, and H. Tributsch, Adams, others.



METTLER TOLEDO
Automated Chemistry
Bohdan Process
Development
Workstation PDW 200

Non-Pt chalcogenide cathode work (complete review in progress)

- DMFC (methanol tolerance)
  - Alonso Vante & Tributsch, Nature 323 (1986) 431
    - Transition metal sulfides; $Mo_{6-x}Ru_xX_8$ X = S, Se, Te (thought to be Chevrel phases)
  - Alonso Vante, Tributsch & Solorza-Feria, Electrochim. Acta 40 (1995) 567
    - Report that O_2 reduction on chalcogenides is a 4-electron process direct to H_2O.
  - M. Bron*,… Tributsch et al., JEAC, 517 (2001), 85 – 94
    - Showed that Mo not important for Ru based catalysts but Se is.
    - Active catalysts are mixed phase with two or more phases including a Ru metal core and amorphous shell. Catalysts are poorly characterized.
    - Carbon support improves mass specific activity
    - About an order of magnitude lower activity than Pt
  - RW Reeve, PA Christensen* et al., Electrochim. Acta 45 (2000) 4237
    - $RhRu_5S_5$/Ketjen EC600JD (Fig. 4 on page 4242!)
    - 4 M methanol; **overlaid Pt performance** at 150 mA/cm^2 at 300mV cell voltage
      - 0.5 bar oxygen versus 1 atm. at the Pt cathode

Acknowledgments

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  - Thomas E. Mallouk of Penn. State University
  - NuVant Systems Inc, Chicago Ill.
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  - ARO HUB Program (Optical Method)
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  - University of Puerto Rico at Rio Piedras (Robotics)
- Please see
  - T. E. Mallouk, E. S. Smotkin, Combinatorial Catalyst Development Methods. In Handbook of Fuel Cells – Fundamentals, Technology and Applications, Vol 2: Electrocatalysis, ed. W. Vielstich, H Gasteiger, A. Lamm, pp. in press, John Wiley & Sons, Ltd.
  - Eugene S. Smotkin and Robert R. Diaz-Morales, "New Electrocatalysts by Combinatorial Methods" in Annu. Rev. Mater. Res., 33, **(2003),** in press