Highly Active and Durable Nano-electrocatalysts for PEMFC

Wenzhen Li

Department of Chemical Engineering
Michigan Technological University, Houghton, MI 49931

Proton Exchange Membrane Fuel Cell (PEMFC): a promising sustainable energy

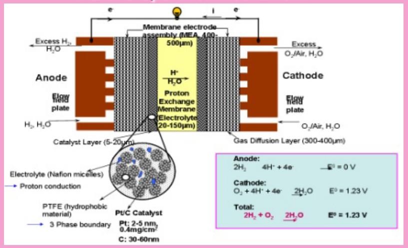
Portable electronics

Stationary

Automobile

GM Chevy PEMFC powered SUV run more than 300 miles without refuel!

PEMFC Operation Mechanism



Solid proton exchange membrane working as electrolyte, PEMFCs are electrochemical energy conversion devices, which directly change the chemical energy of fuel (H_2 or methanol) into electrical energy.

Advantages:
- Higher Power density (than other types of fuel cells)
- High energy conversion efficiency (cell: 50-70%)
- Environmental friendly (no noise, zero NO_x emissions)
- Low temperature operation (< 100°C)
- ………

Challenges in PEMFC Commercialization

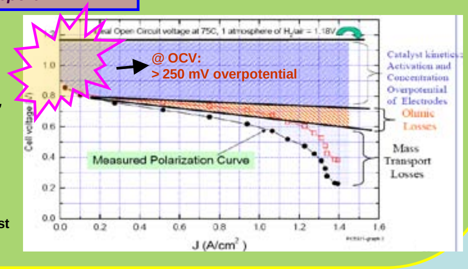
- Low Pt utilization in MEA (<30%)
  - *New efficient design and fabrication of ordered MEA with high Pt utilization and long life-time*
- Polymer membrane electrolyte
  - *High operation temperature (>120°C) and less water dependence*
- The stability & durability of fuel cell components
  - *Catalysts (Pt nanoparticle, carbon support), membrane, MEA, etc*
- Cost
  - *Pt or PtRu catalysts in the electrodes (0.5gPt/KW = $18/KW to $7/KW)*
  - *Nafion membrane electrolyte ($250/m² to $20/m²), Graphite bipolar plates*
- Slow kinetics of cathode oxygen reduction reaction (ORR)
  - *Pt-M alloy (M = Fe, Co, Ni, etc) catalysts*
  - *Novel carbon nanomaterials as catalyst support*

Catalyst Issues

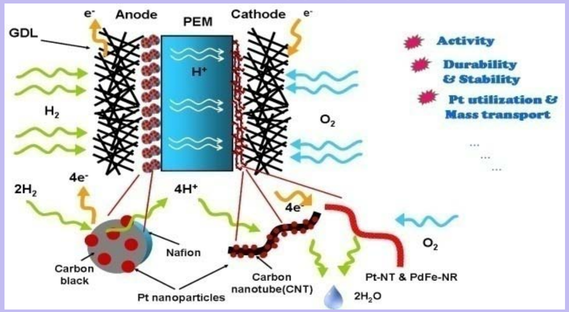
1) The significant over-potential for ORR:
@ OCV: more than 250 mV (on the most active Pt surface), $i_{exchange}=10^{-9}$ mA/cm² (six magnitude lower than hydrogen oxidation reaction HOR)

2) An approximate 5-fold reduction of the amount of Pt
(platinum loading: from 0.5 mgPt/cm² to 0.1 mgPt/cm² $7/kW, 2015 DOE target)

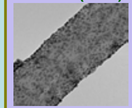
3) The dissolution / loss of Pt surface area in the cathode must be greatly reduced.



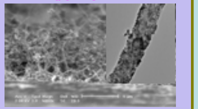
My Solution: One Dimensional (1-D) PEMFC Electrocatalyst



Pt/carbon nanotube(CNTs)



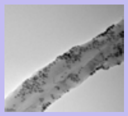
Pt/CNTs film

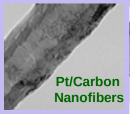


Self-developed 1-D PEMFC Electrocatalysts (nanotube, nanowire, nanorods, etc)

PtRu/CNTs

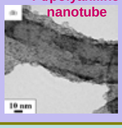
PtCo/CNTs



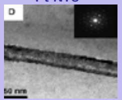


Pt/Carbon Nanofibers

Pt/polyaniline nanotube

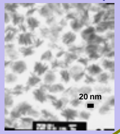


Pt-NTs



PtFe-Nanowires(NW)

PdFe-Nanorods(NR)



Future Research Plans

Nanomaterials Based System for Sustainable Energy Applications

1. Design and Synthesis of Highly Performing and Stable Catalytic Active Phase (1-D & core shell)
2. Exploring Durable Catalyst Support
3. Development of Support-less Catalyst System
4. Nanomanufacture of membrane electrode assembly (MEA) device

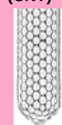
Nanotechnology | **Catalysis Engineering** | **Surface/Colloidal Chemistry**

High Performance Carbon Nanotube (CNTs) Supported Catalysts for Fuel Cell Application

Wenzhen Li

Department of Chemical Engineering
Michigan Technological University, Houghton, MI 49931

Advantages for CNT as fuel cell electrocatalysts support

	Carbon black (CB) (Vulcan XC-72)	Graphite	Carbon nanotubes (CNT)
			
Electrical conductivity (s/cm)	4.0-7.4	5.0 (vertical) 200-2500 (horizontal)	1250
Surface area (m^2/g)	250		50-1000
Micro-pores (%)	> 50%		0 %
Specific corrosion current (mA/g) (@0.9V, 60°C)	0.5		0.3

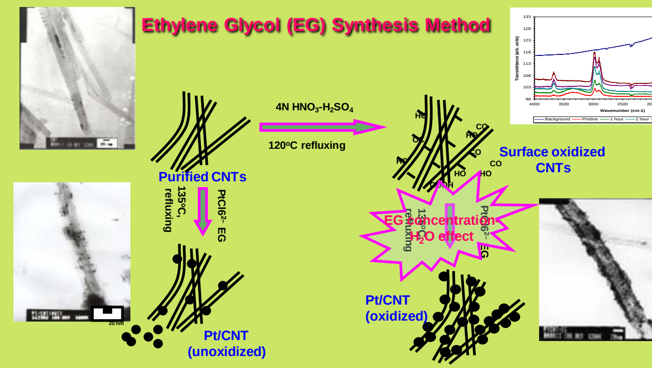
☆ High electrical conductivity and high aspect ratio (giving long range conduction paths)

☆ Superior morphology & pore structure – better mass transport

☆ High corrosion resistant ability in electrochemical environment

* Xin Wang, *Wenzhen Li*, et al , **Journal of Power Sources**, 2006, 158, 154

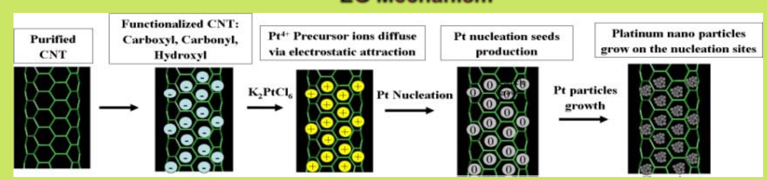
Ethylene Glycol (EG) Synthesis Method



Pros:
- Simple
- Low temperature
- Easy to scale up
- … … …

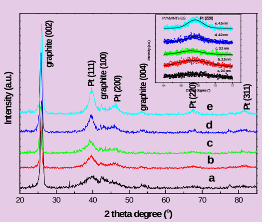
Wenzhen Li, et al. **Carbon**, 2002, 40, 791-794. *Wenzhen Li*, et al. ***Journal of Physical Chemistry. B***, 2003, 107, 6292-6299.

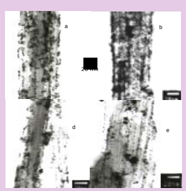
EG Mechanism

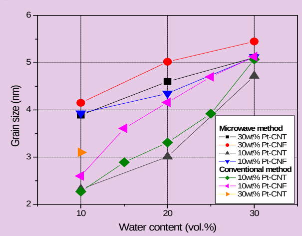


Seth Knupp, *Wenzhen Li*, et al, ***Carbon***, 2008, 46, 1276-1264

Water Effects on Pt Average Particle Size







Debye-Scherrer formula:

$$L = \frac{0.9\lambda_{K\alpha 1}}{B_{(2\theta)} \cos \theta_{max}}$$

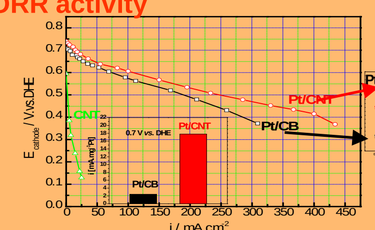
sample	H_2O (vol. %)	Particle size (nm)
a	0	2.0
b	5	2.5
c	15	3.2
d	40	4.0
e	70	4.5

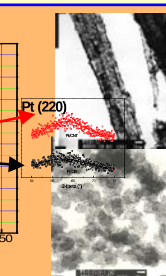
Water in synthesis system ↑

Pt particle size ↑

Wenzhen Li, et al.**Carbon**, 2004, 42, 436-439. Seth Knupp, *Wenzhen Li*, et al, ***Carbon***, 2008, 46, 1276-1264

ORR activity

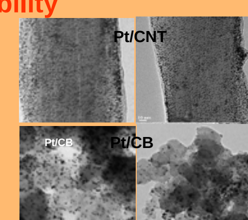


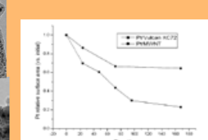


CNTs: unique electrical property, tubular structure, Pt-CNTs interaction

Wenzhen Li, et al. ***Journal of Physical Chemistry. B***, 2003, 107, 6292-6299.

Durability





The ECSA is improved 3 times for Pt/CNT catalyst than Pt/C

* Xin Wang, *Wenzhen Li*, et al , ***Journal of Power Sources***, 2006, 158, 154

Design and Synthesis of Special Nano-Structured Electrocatalysts with High Activity and Durability for Fuel Cells

Wenzhen Li

Department of Chemical Engineering

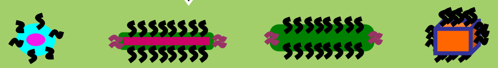
Michigan Technological University, Houghton, MI 49931

Large Scale Solution phase synthesis method

$M_1(acac)_x + M_2(acac)_y + ROH + RCOOH + RNH_2 + Ph_2O$ / $M_2(CO)_z$

↓ Nucleation T_1

↓ Growth & aging T_2



Core-shell Nanotube Nanorod Nanocube

↓ Deposition & 'activation'

Nano-Catalysts

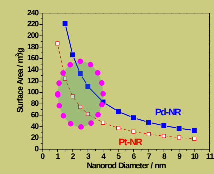
Advantages:

* Accurate control of shape, composition, morphology, etc
* Solution phase synthesis– simple & easy to scale up
* Multi-components catalyst system

… … …

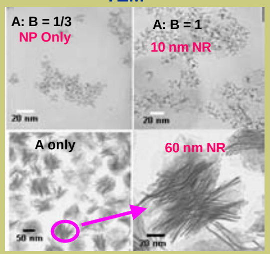
Support-less PdFe nanorod electrocatalyst

Theoretical calculation



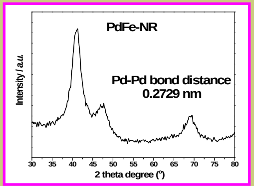
Measured ECSA of PdFe-NR : 55-60 m^2/g

TEM



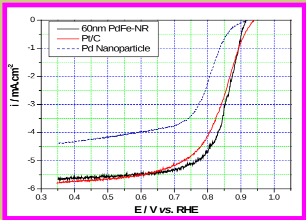
** A & B : two surfactants*

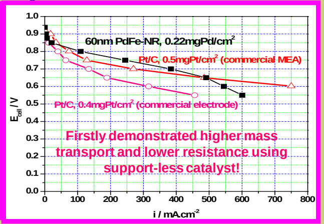
XRD



** Pd-Pd distance of Pd nanoparticles: 0.2753 nm*

ORR activity Test

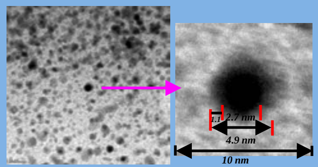




Advantageous Pd-Pd bond distance
-- higher ORR activity

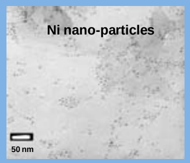
Super thin catalyst layer
-- lower resistance & better mass transport

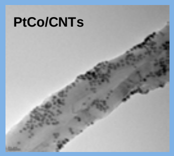
Other nanostrcutured materials



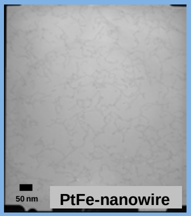
Pt core-Co_3O_4 shell nanoparticles

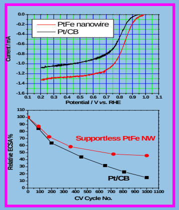
Core-shell



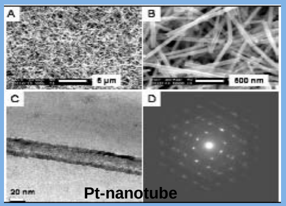


Nanoparticle





Nanowires



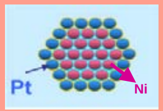
Nanotube

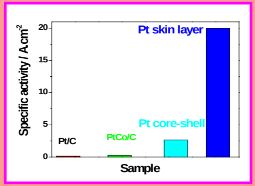
Zhongwei Chen, Mahesh Waje, ***Wenzhen Li***, Yushan Yan, Angewandte Chemie International Edition, 2007, 46, 4060.

Future work

* Experiment: de-alloying & post-treatment (annealing)
* Theoretical calculation / model: structure *vs*. activity
* Surface fuctionalization: bonding with nanostructures
* Multiple simulation on nanostructured catalysts: Pt dissolution / aggregation mechanism

Research Target





Ideal core-shell structure with ultra-high electrochemical activity and long life-time in real world !

Novel membrane electrode assembly (MEA) fabrication method: Filtration

Wenzhen Li

Department of Chemical Engineering
Michigan Technological University, Houghton, MI 49931

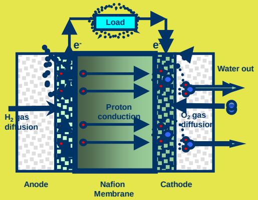
Schematic illustration of fuel cell operation principle

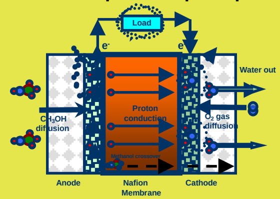
PEMFC

Anode:
$2H_2 \blacktriangleright 4H^+ + 4e^-$

Cathode:
$O_2 + 4H^+ + 4e^- \blacktriangleright 2H_2O$

Total:
$2H_2 + O_2 \blacktriangleright 2H_2O$





DMFC

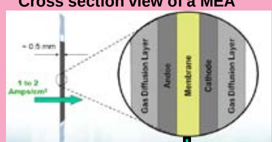
Anode:
$CH_3OH + H_2O \blacktriangleright CO_2 + 6H^+ + 6e^-$

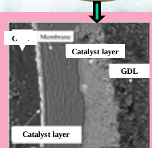
Cathode:
$\frac{3}{2}O_2 + 6H^+ + 6e^- \blacktriangleright 3H_2O$

Total:
$CH_3OH + 3/2O_2 \blacktriangleright CO_2 + 3H_2O$

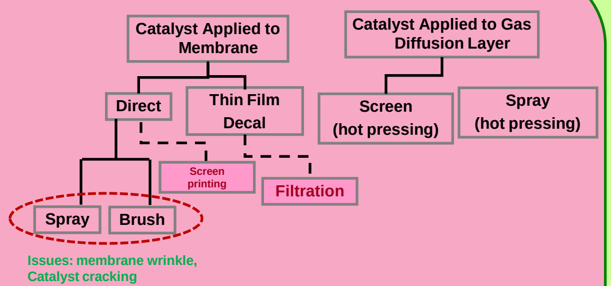
MEA

Cross section view of a MEA





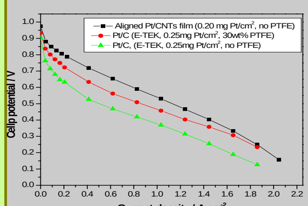
MEA Fabrication Methods



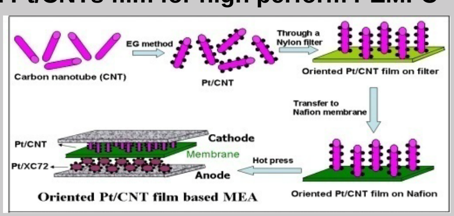
Pros for filtration method

Ordered CNTs film
Simple & cheap
Easy to scale up
… … …

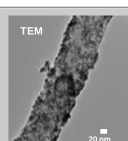
Oriented Pt/CNTs film for high perform PEMFC

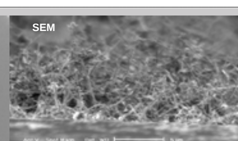


PEMFC single cell performance



Contact angle Superhydrophobic: 153°

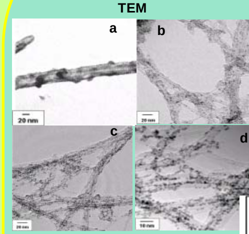




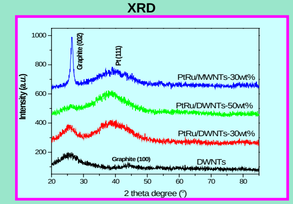
Wenzhen Li, Xin Wang, Zhognwei Chen, Mahesh Waje, Yushan Yan, ***Langmuir***, 2005, 21, 9386-9389.

PtRu/CNTs film for High perform DMFC

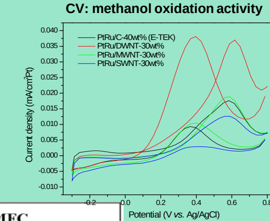
TEM

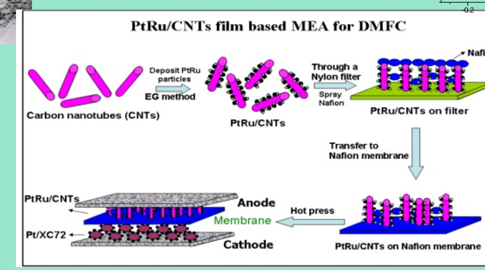


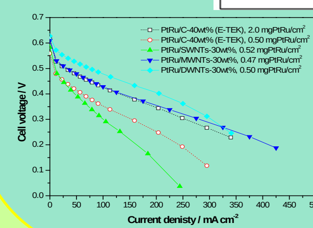
XRD



CV: methanol oxidation activity

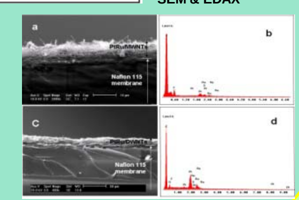






DMFC single cell performance

SEM & EDAX



Wenzhen Li, Xin Wang, Zhognwei Chen, Mahesh Waje, Yushan Yan., Journal of Physical Chemistry-B, 2006,110, 15353.

Conclusions

- Polyol catalyst synthesis method: small particle size (2-3 nm) and uniform size distribution.
- MEA for PEMFC: oriented super-hydrophobic Pt/MWNTs film of 20 um and super-hydrophobicity (153°); MEA for DMFC: uniform thin catalyst layer of 5-20 um, 75% noble metal loading reduction & 68% peak power density improvement.

Acknowledgements

* Profs. Qin Xin (DICP, CAS), Yushan Yan (University of California-Riverside), Masahiro Watanabe (University of Yamanashi, Japan) & former colleagues
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* GM China Natural Science Foundation
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