Electrochemical Deposition of Pt Metal Particles Using Nafion® Membrane as the Template

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Fuel Cells

www.fujitsu.com/img/ PR/2005/20050706-02.jpg

www.science.nasa.gov/.../ fuelcell/notebook_med.jpg

news.com.com/.../ 2009-1047_3-5647454.html

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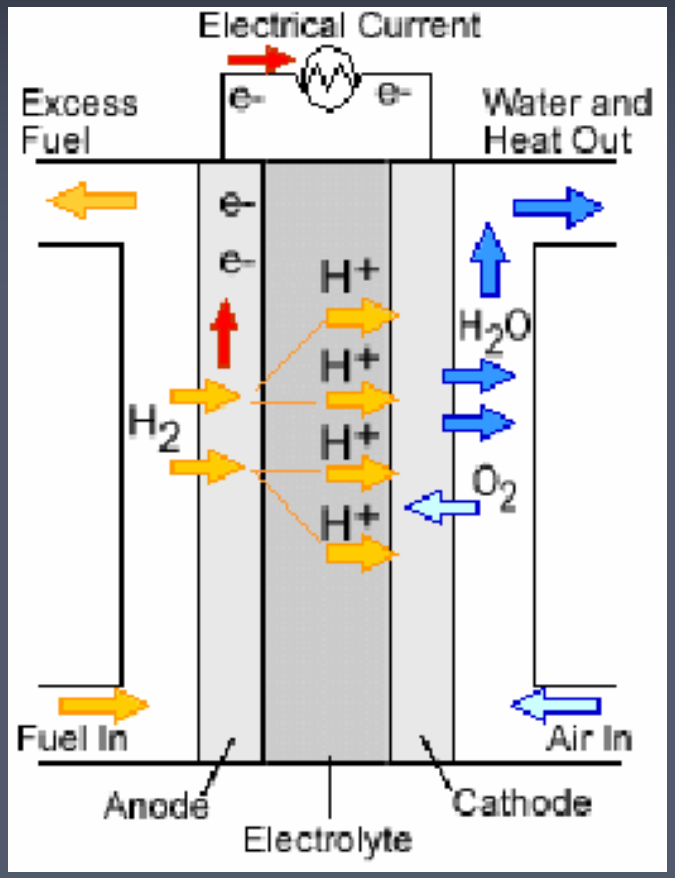
Proton Exchange Membrane (PEM) Fuel Cell



www.eere.energy.gov/.../ fuelcells/fc_types.html

$$2H_2 \longrightarrow 4H^+ + 2e \quad \text{Anode}$$

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O \quad \text{Cathode}$$

$$2H_2 + O_2 \longrightarrow 2H_2O \qquad E^{\circ} = 1.23\ V$$

Electrolyte;
=>Nafion®

Advantages;

- **Low weight and volume**
- **Quick start (less warm-up time)**
- **High power density**

Target: designing high performance, reliable, cheap, and light fuel cells

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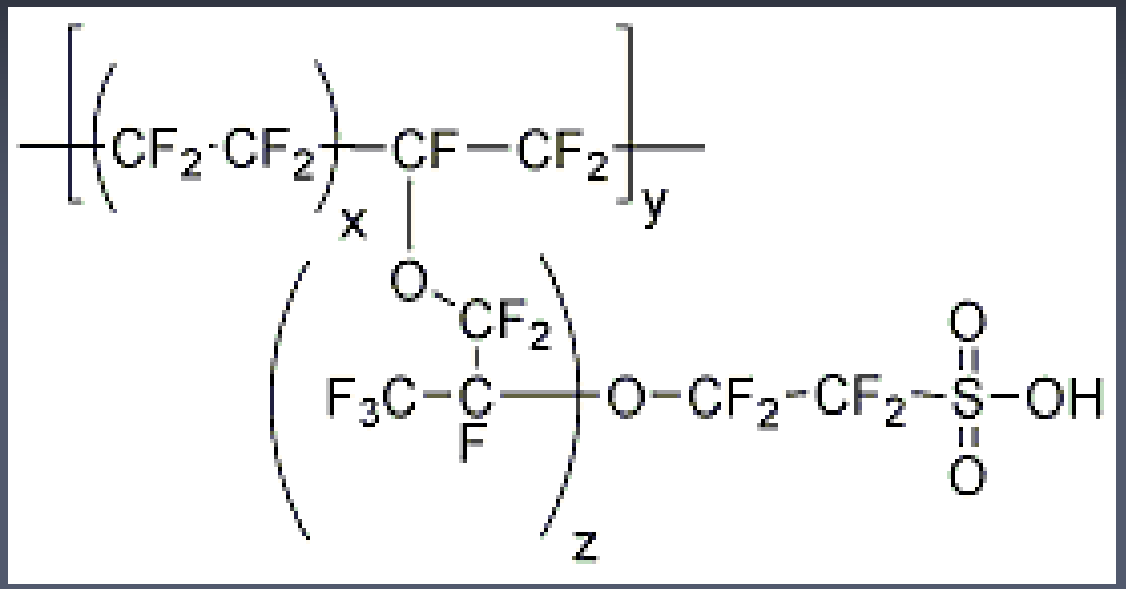
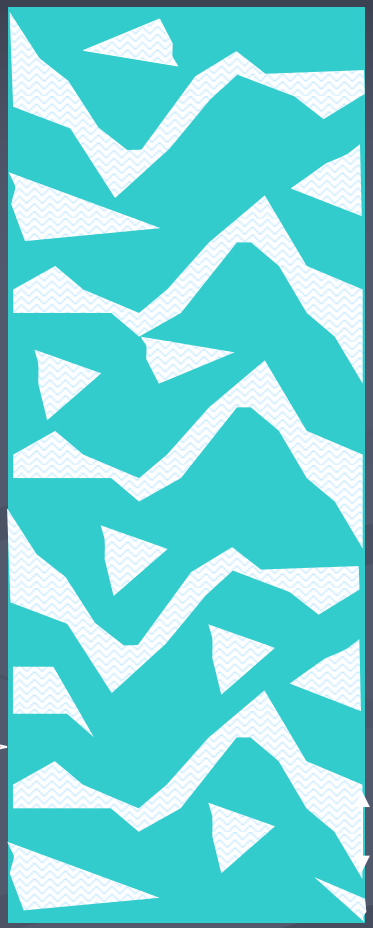
Nafion® - as a PEM

Structure



Hydrophilic domains

Hydrophobic domains



1-several 100 nm

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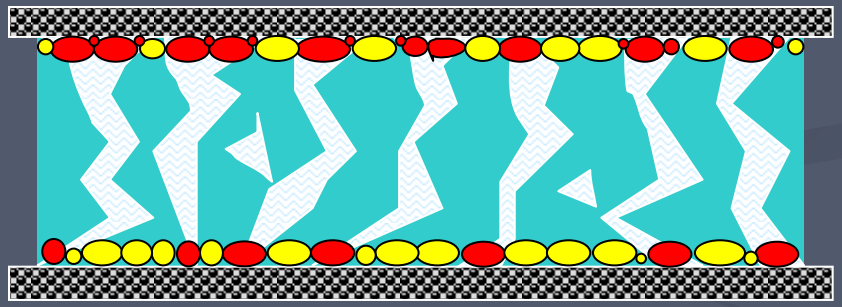
Utilization of the catalyst in a fuel cell

- Use expensive noble metals/metal oxides as catalyst (e.g. Pt, Ru, WO_3 etc)
- Not all of these metal catalysts particles are effectively being used (you don't achieve 100% utilization of the catalyst)

General cross section of a membrane electrode assembly (MEA) manufactured in industry

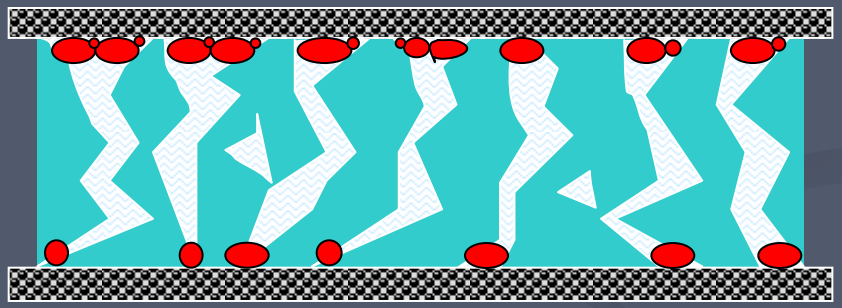


- Catalysts particles that only lie on hydrophilic channels participate in the fuel cell reactions (red)

- Particles placed in hydrophobic domains are not used efficiently (yellow)

How can we reduce the catalyst loading without changing catalytic activity?

- Electrochemically deposit catalyst through hydrophilic channels of Nafion®

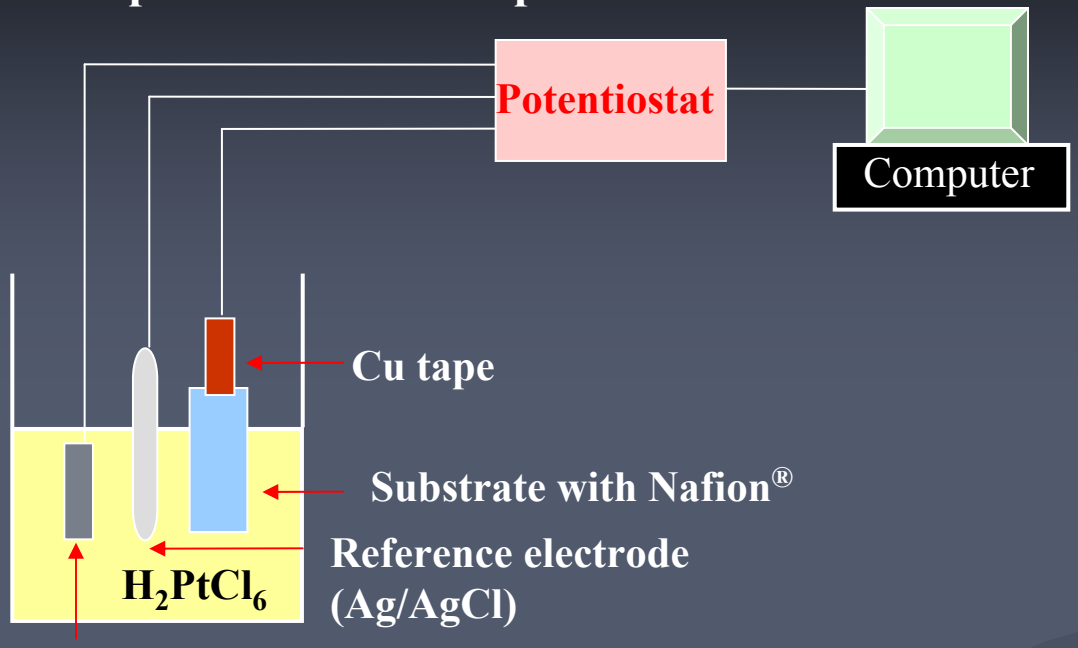


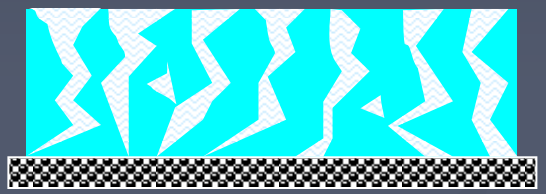
Expect to see….

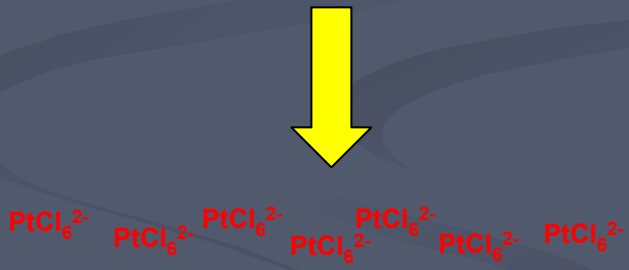
With a minimal loading, same or higher efficiency than a conventional fuel cell

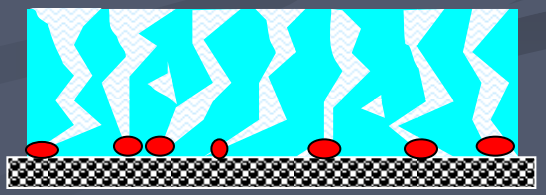
Experimental Setup

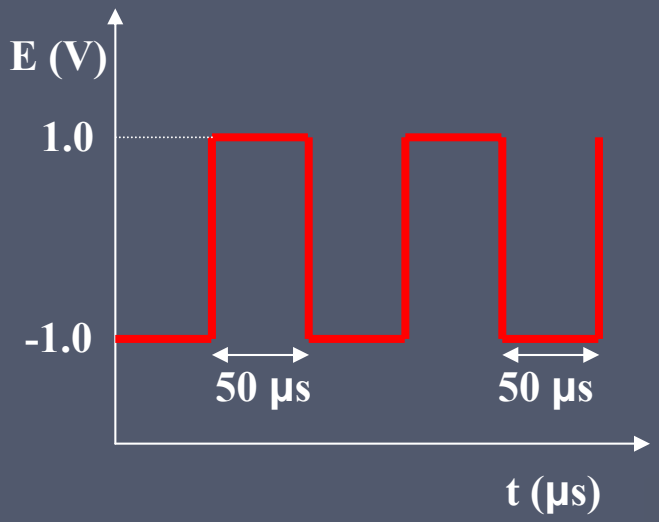
- Pulse deposition of Pt nanoparticles





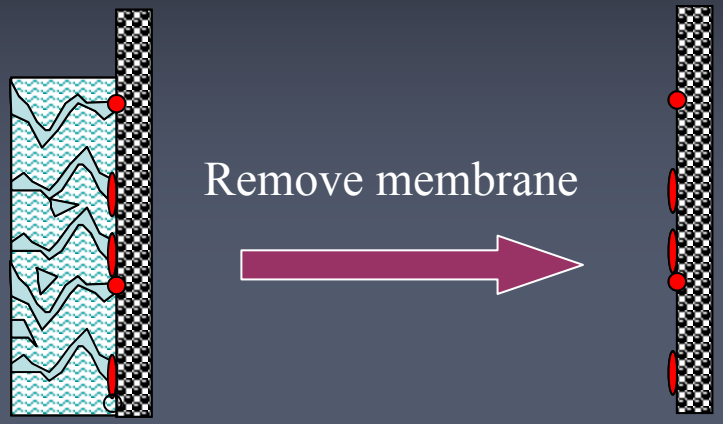




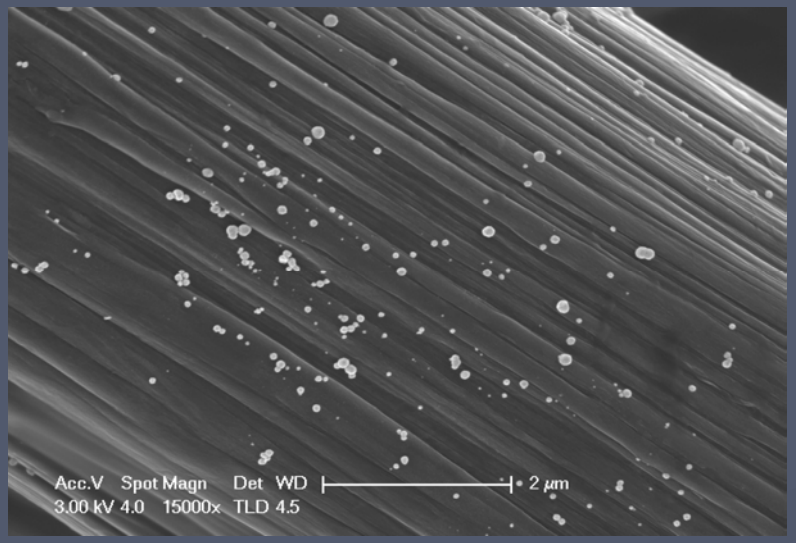


Initial results

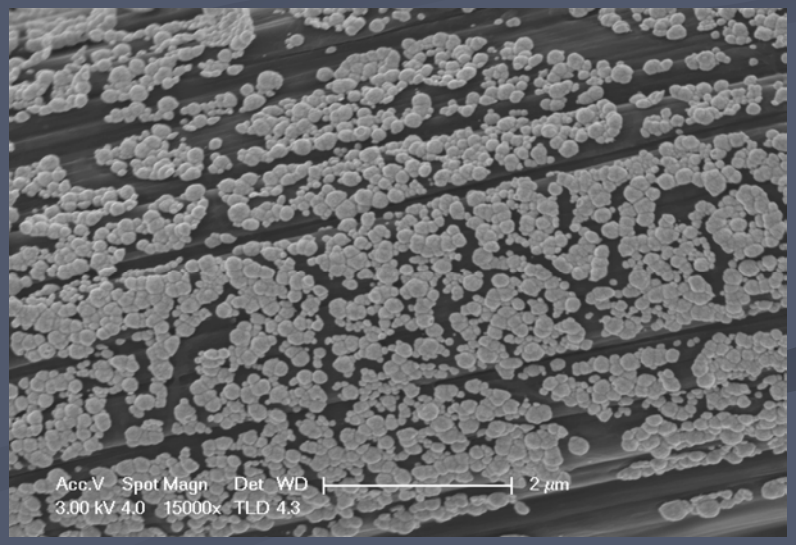
- Deposit Pt through the ion channels of the membrane, then peel off/remove the membrane, imaged in the surface of the substrate (carbon cloth) using the SEM



Through Nafion®



Direct



Deposition time = 10 minutes, concentration of H_2PtCl_6 = 1mM

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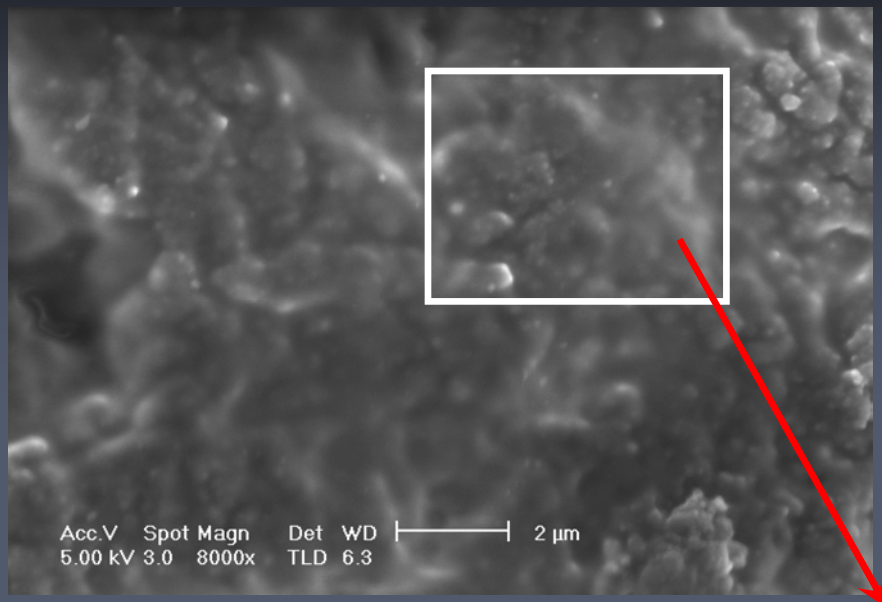
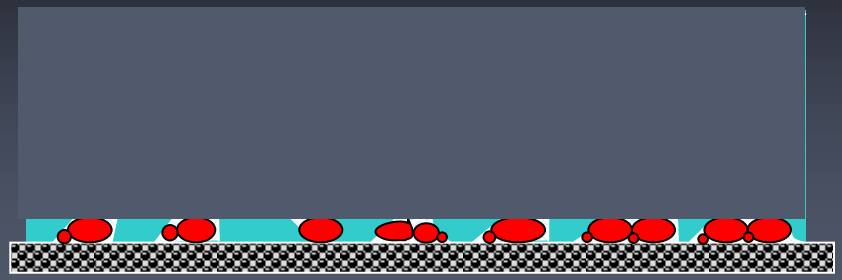
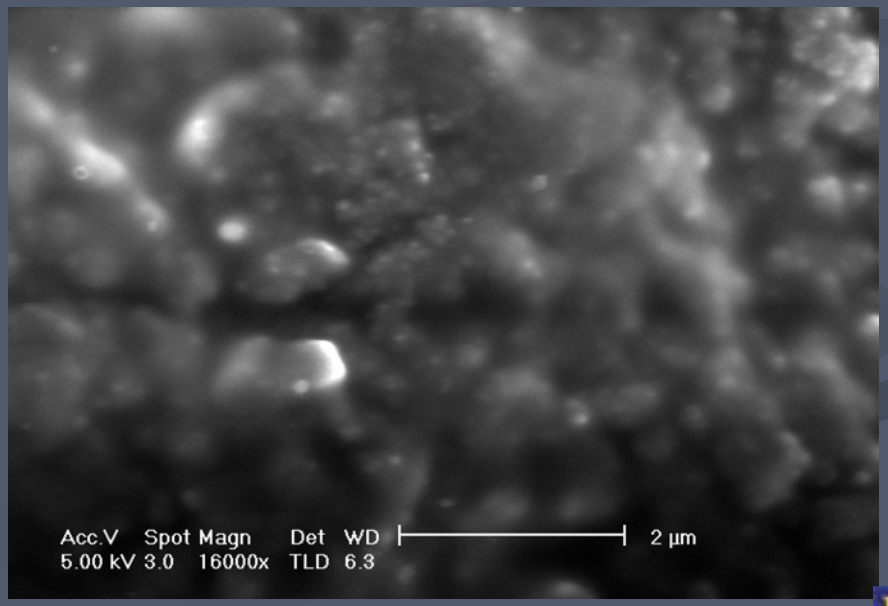
A View through the membrane







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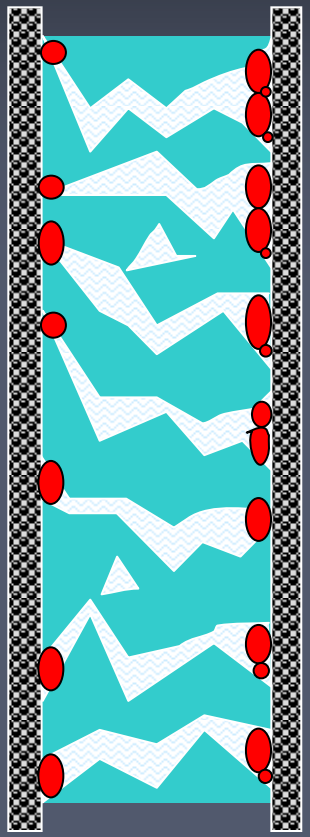
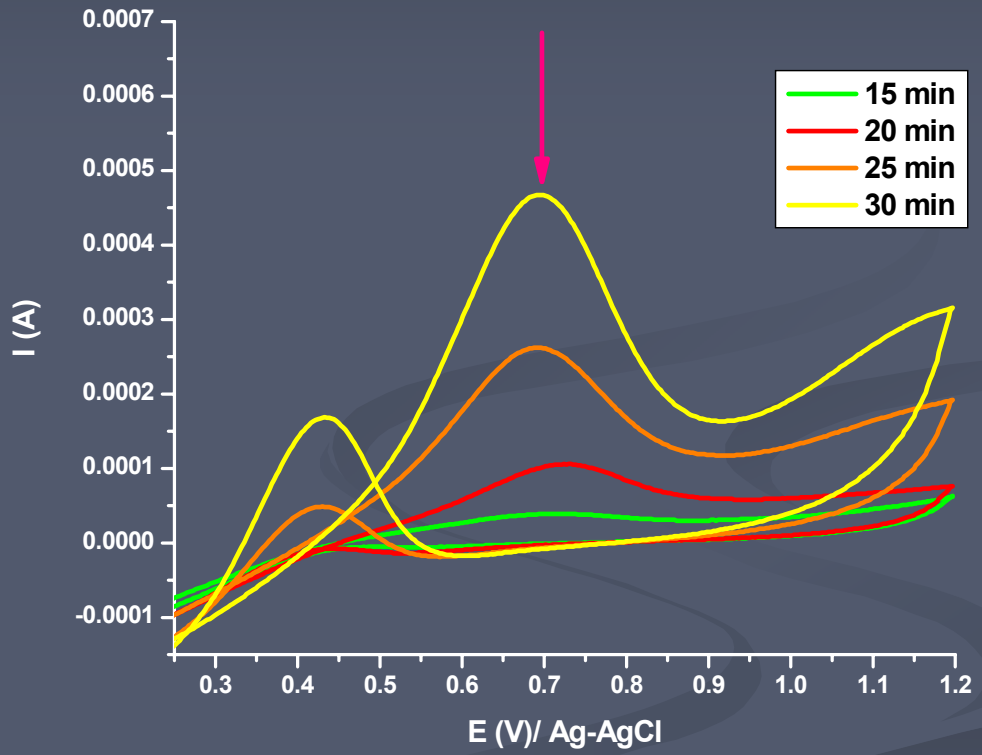
Construction of Fuel Cells



CV for oxidation of Methanol in H_2SO_4 shows the progress of pulse deposition of Pt at different deposition times



We are trying to optimize deposition conditions to construct fuel cells to get the best I-V characteristics

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Conclusions

- This method can be utilized to deposit metal catalysts in fuel cell fabrication

- Is not limited to Nafion® but for any porous membranes that can be used in fuel cells

- Varying deposition parameters (i.e. pulse potentials, width and frequency of the pulses, solution concentration) produces metal clusters with increased surface area

- <u>This method significantly reduces the cost of fuel cells</u>
  - mg/cm^2 industrial Vs. $\mu g/cm^2$ to ng/cm^2 using this technique (million times less loading)

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Work in progress….

- Construction and testing fuel cell devices constructed using this technique

- Testing the fuel cells by changing various parameters such as change in relative humidity, temperature etc

- To calculate the available surface area of Pt nanoparticles using electrochemical techiniques

Acknowledgements

- Asanga Ranasinghe
- Buratto & McFarland group
- Dr. Ju Chou
- Dr. Shrisudersan Jayaraman
- Alan Kleiman Shwarsctein
- James O'dea
- Wei Tang
- INSET Faculty
- Special thanks to my parents for all of their support

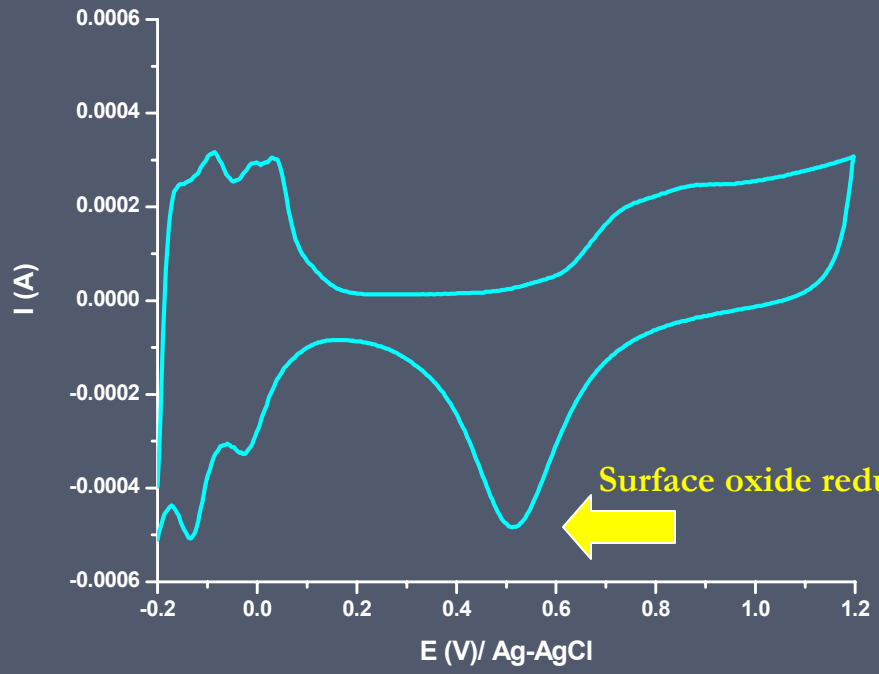
Progress of pulse deposition of Pt

Use cyclic voltammetry (CV)

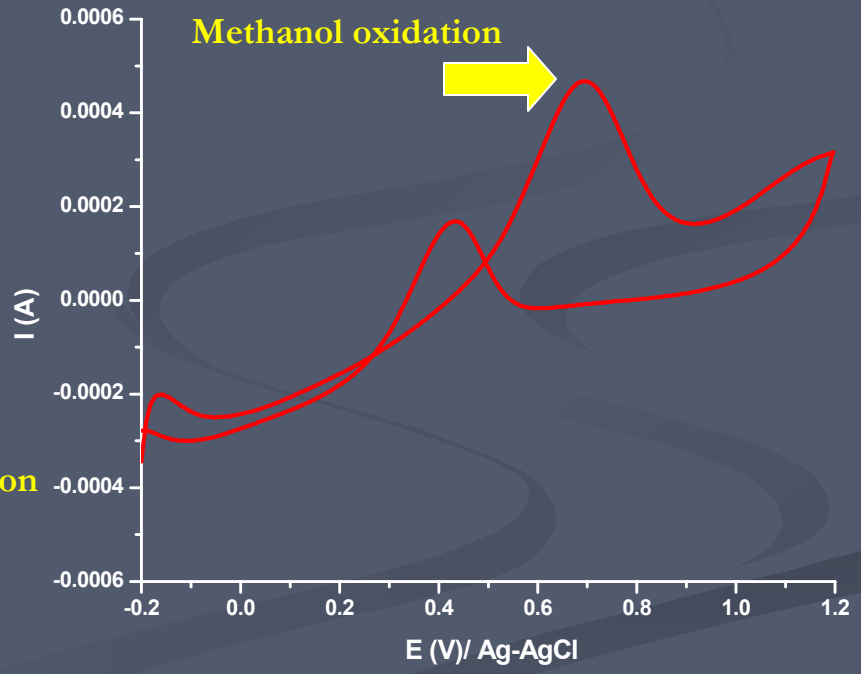
- To investigate the catalytic activity of Pt nanoparticles deposited

- Scan the potential -0.2 V to 1.2 V

H_2O oxidation on the Pt surface



CH_3OH oxidation on the Pt surface



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Calculation of the amount of Pt deposited

From Faraday's Laws

$$W = (M_w It)/nF$$

M_w- molecular wt./rel. atomic mass (195.09 for Pt)

I- current (amperes)

t- time (seconds)

n- no. of electrons ($Pt^{4+} + 4e \leftrightarrow Pt$)

F- Faraday's const (96500 C)

Open Circuit Voltage Comparison

Sample	Pt loading	Open Circuit Voltage (V)
Commercial components	0.5mg/cm^2	~0.95
Press MEA then pulse deposit THROUGH Nafion	~1.8 μg/cm^2	0.433
Pulse deposit ONTO electrode then press MEA	~4.0 μg/cm^2	0.017

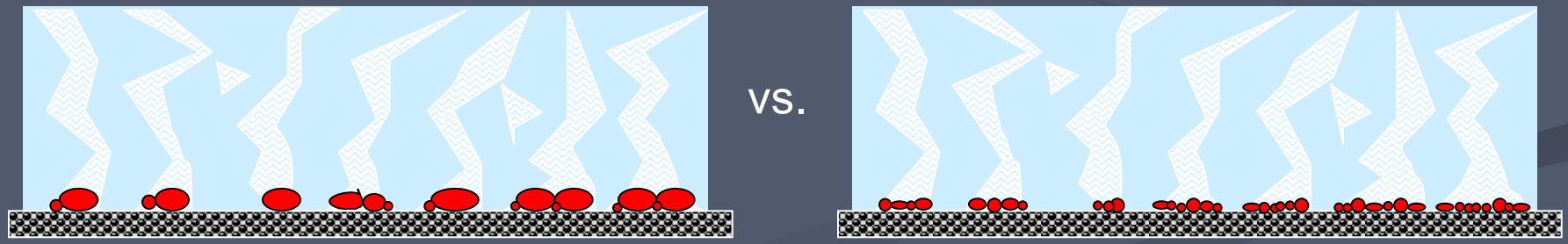
**25 min deposition time, $PtCl_6^{2-}$ solution: 1mM, pH ~ 2.8

** All MEAs using Nafion 117 as membrane

How to increase the catalytic activity ?

Increase the available surface area of Pt particles (smaller particles)

- **Nucleate Pt particles with large negative pulse (-1.0 V) through the Nafion® channels on the surface of the electrode**
- **Induce a competing reaction to hold the further growth of nucleated Pt particles**
  - **By adding an acid (e.g., H_2SO_4) in the deposition electrolyte, we induce vigorous reduction of protons on the nucleated Pt particles to restrict the growth during subsequent negative pulses**



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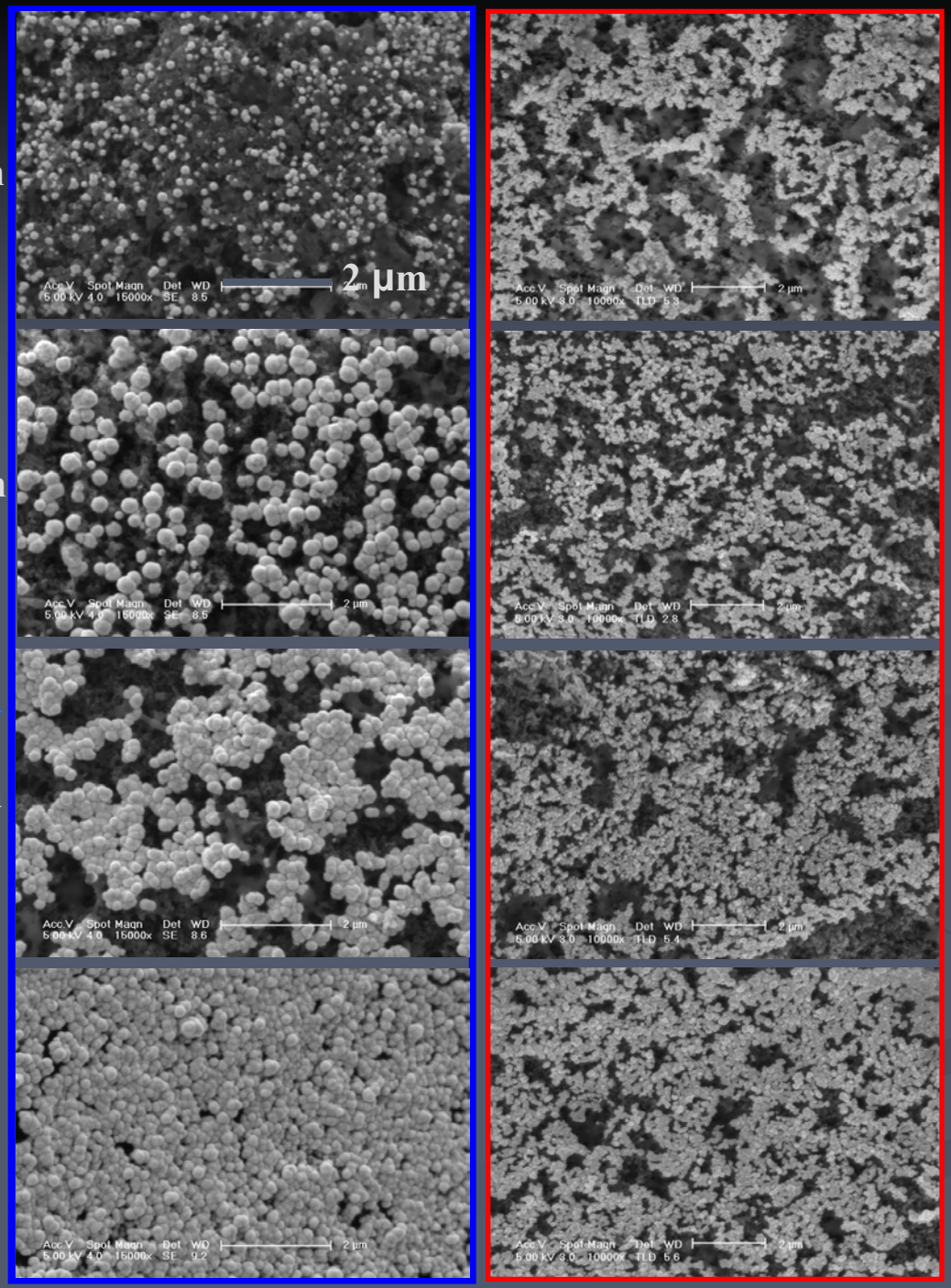
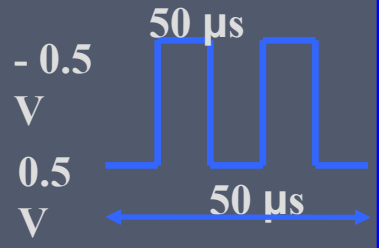
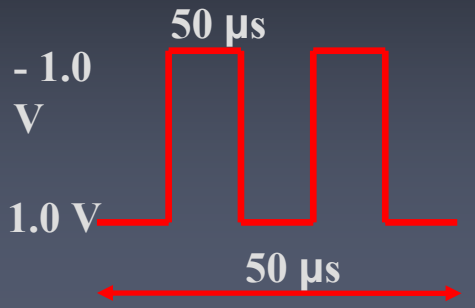

3 min
5 min
10 min
15 min
2 µm


50 µs
- 0.5 V
0.5 V
50 µs


50 µs
- 1.0 V
1.0 V
50 µs