Realizing Enzymatic Biofuel Cells Through Nano-Engineering

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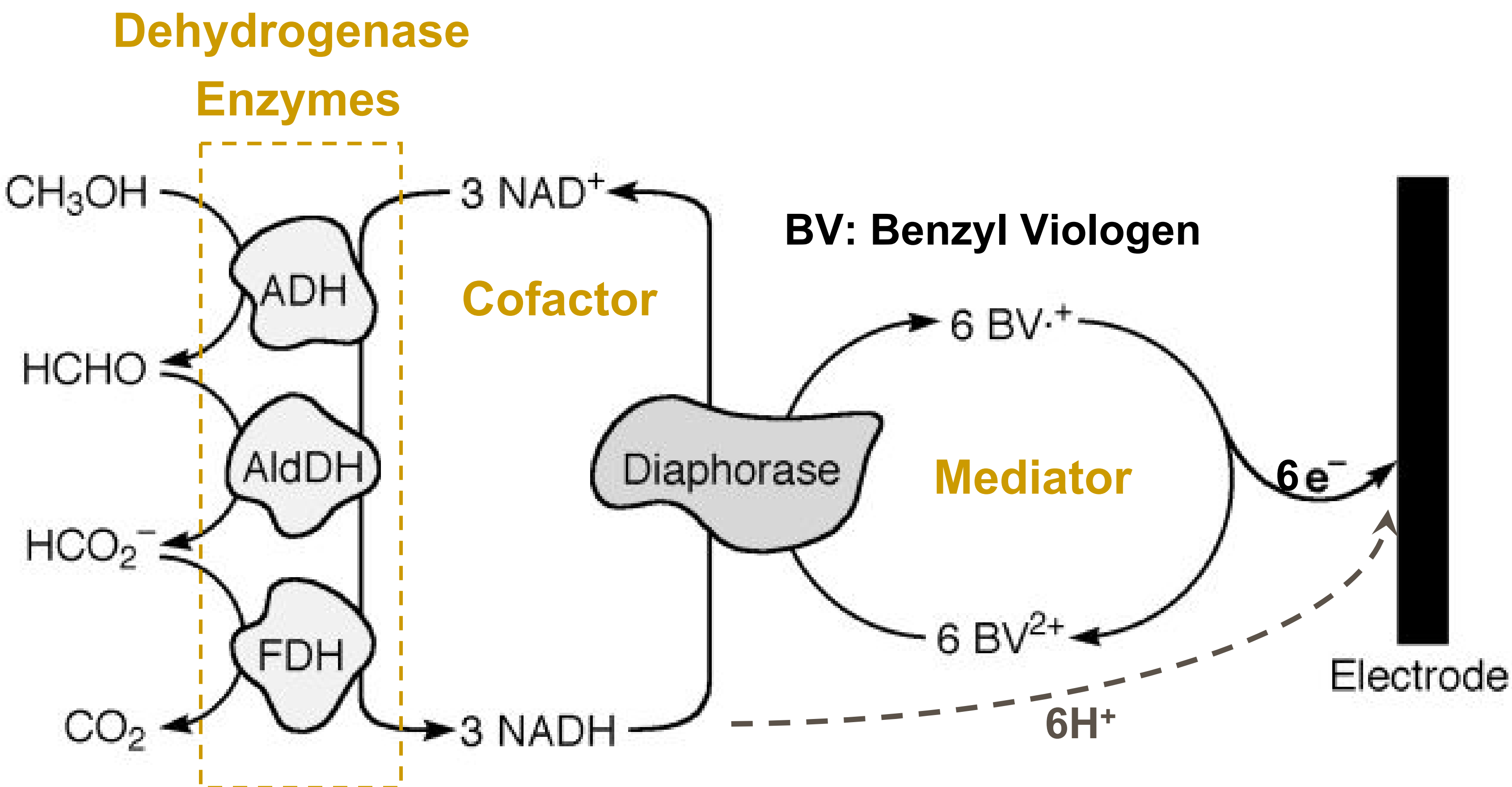
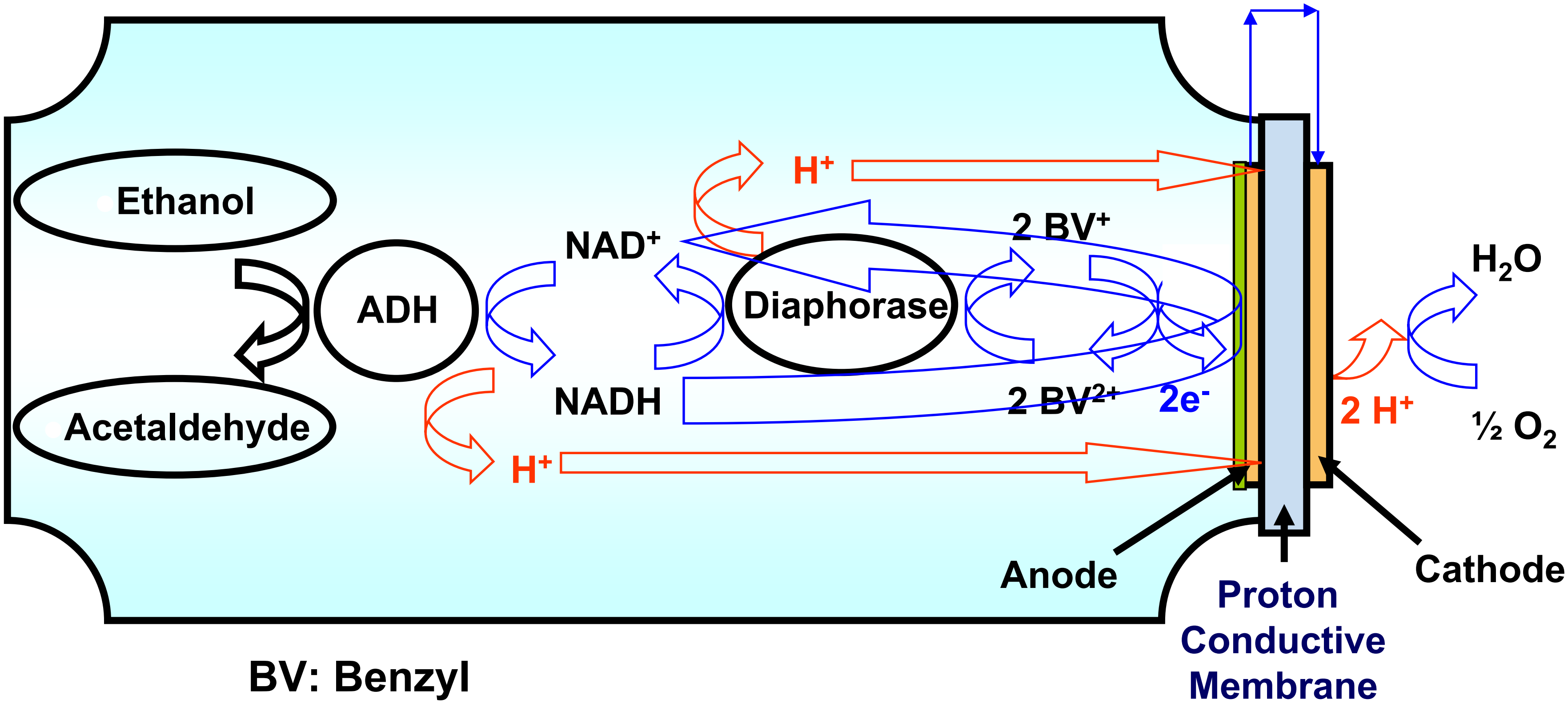
Enzymatic Bioelectrocatalysis



G.T.R. Palmore, et al. *J. Electroanal. Chem*. 443 (1998) 155.

Alcohol Bio-Fuel Cells

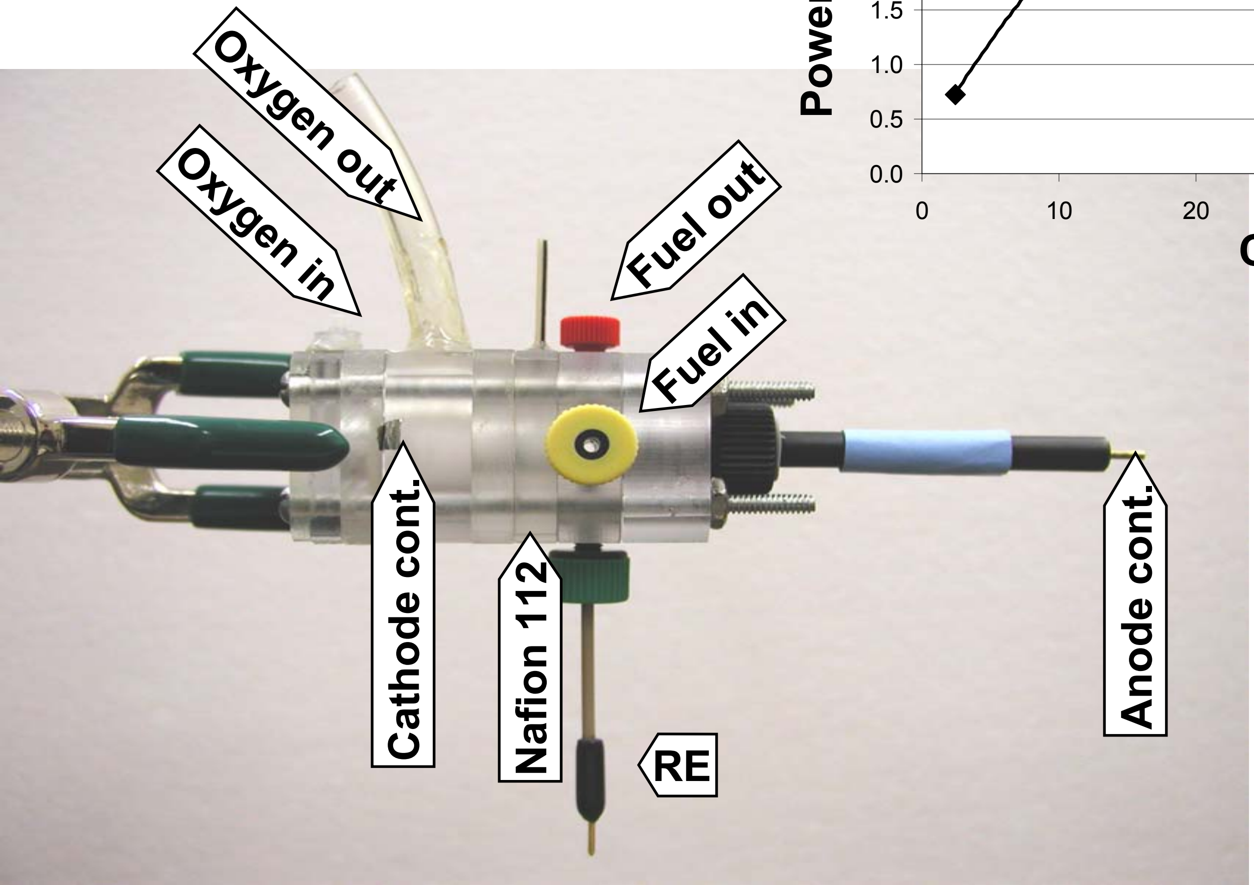


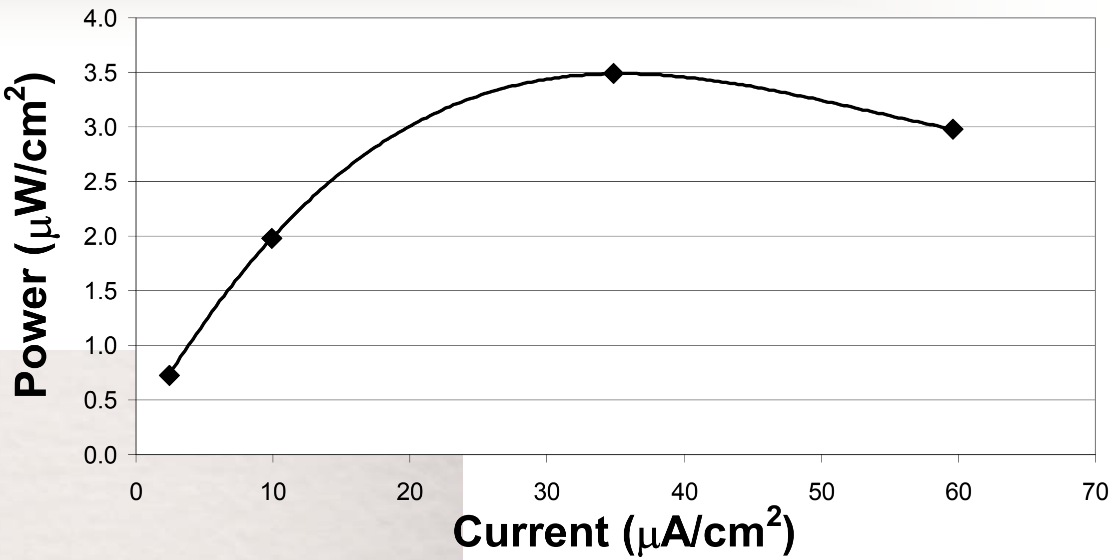
BV: Benzyl Viologen

N.L. Akers et al. *Electrochim Acta* 50 (2005) 2521

G.T.R. Palmore, et al. *J. Electroanal. Chem.* 443 (1998) 155.

A Working Ethanol Bio-FC (EBFC)





V. Svoboda et al. (2006)

Issues Critical to EBFC

- Power Density: Achievable power density is still far below theoretical value
  - Enhance enzyme loading
  - Minimize conductive loss
    - Electronic conductive network
    - Proton pathway
  - Improve charge transfer efficiency
    - Minimize transfer steps
    - Promote direct transfer
  - Facilitate fluid transport
    - Pore structure engineering: surface area vs. porosity • dimensionality • directionality • interconnectivity of pores
- Life (Stability)
  - Micro chemical environment engineering

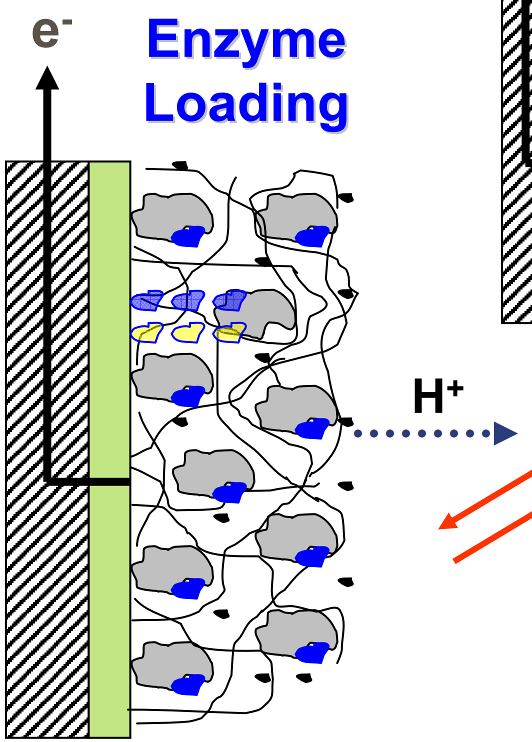
In Situ Characterizations

- Enzyme loading: spatial distribution and local (meso-scale) chemical environment
  - Fluorescence imaging
    - Tagged enzymes
  - Fluorescence polarization
- Reaction kinetics: temporal resolution
  - Electrochemical imaging ellipsometry + QCM
- Mass transport
  - In situ characterization of permeability relative to direction of flow
  - Porosity, pore/channel size, accessible surface area

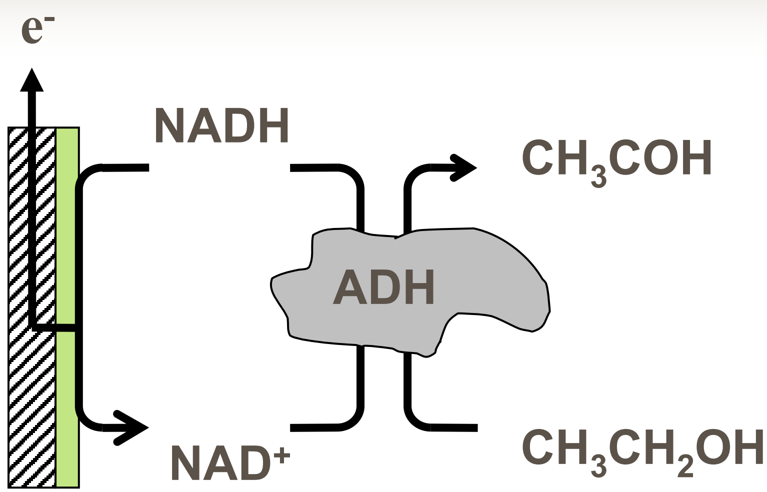
Need for In Situ Characterizations

- In today's nano-material and bioengineering research, control of materials synthesis and process require fast, non-intrusive, in-situ characterization over a large sample area.
- For enzymatic biofuel cell applications, such in situ, non-intrusive observations are highly desirable.
- Example:
  - Imaging ellipsometry + quartz crystal microbalance (QCM) + electrochemical techniques (e.g., CV, EIS), to study nano-materials and their properties:
    - Microstructure & surface morphology
    - Reaction kinetics

Electrode Kinetics

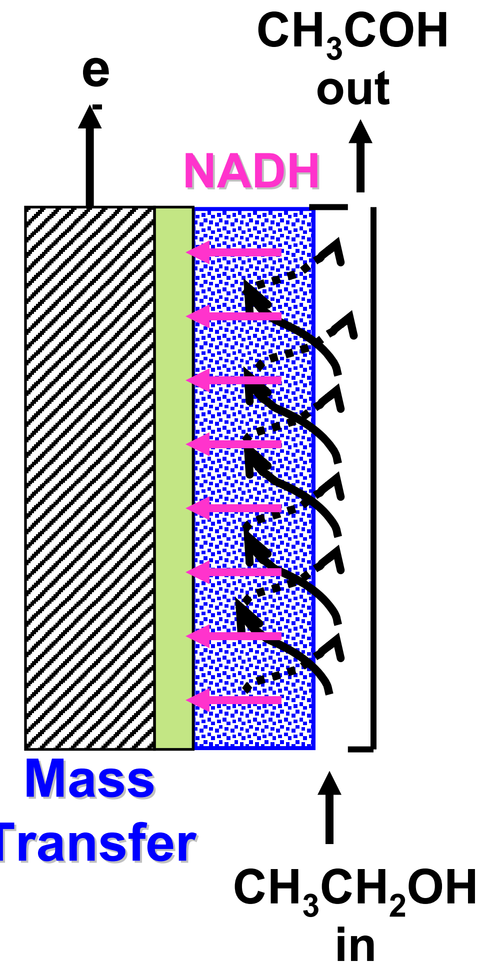


Charge Transfer



$$\frac{dS}{dt} = \frac{V_{\max} \bullet S}{K_M + S}$$

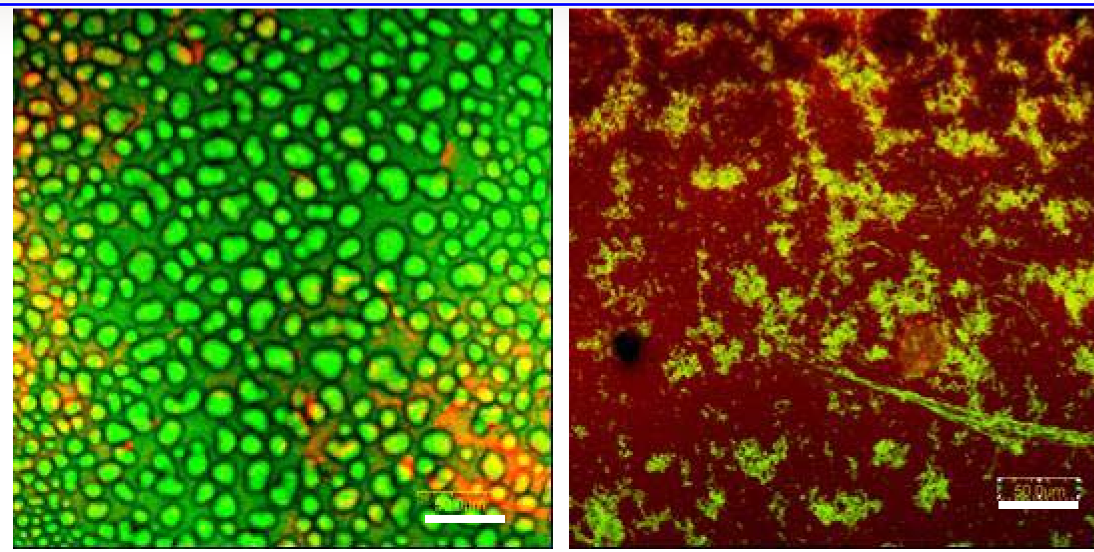
They must be calculated independently



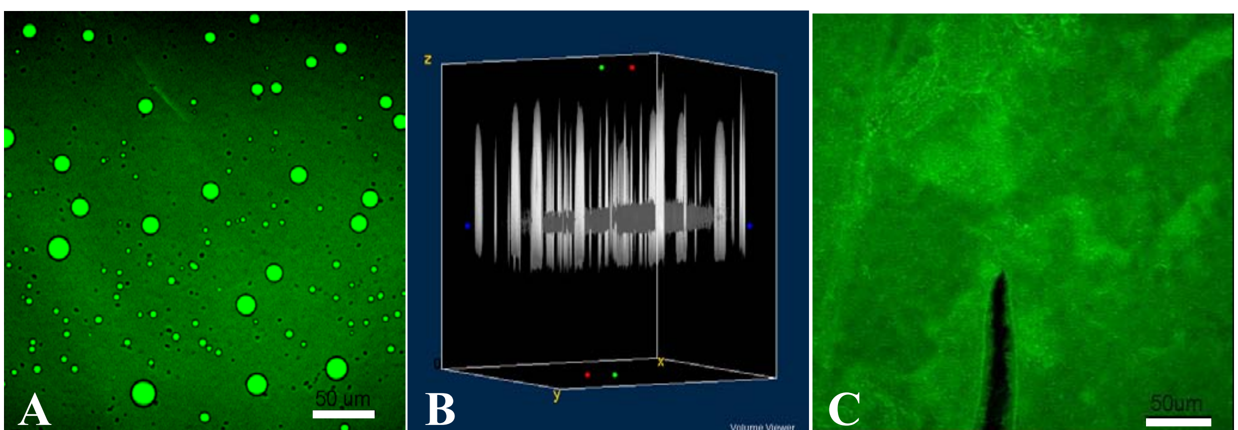
Mass Transfer

Probing Micro Environments

Fluorescent laser scanning confocal microscope (LSCM) images of co-immobilized Alexa-labeled dehydrogenase (green) and TAMRA-labeled lysozyme (red) in (A) Eastman AQ 55 (B) chitosan. (Scale bars: 50 µm.)



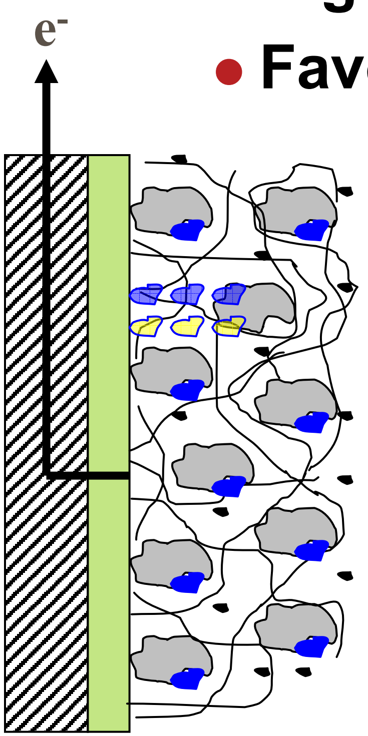
A. Konash et al. *J Mat. Chem.* 16 (2006) 4107.

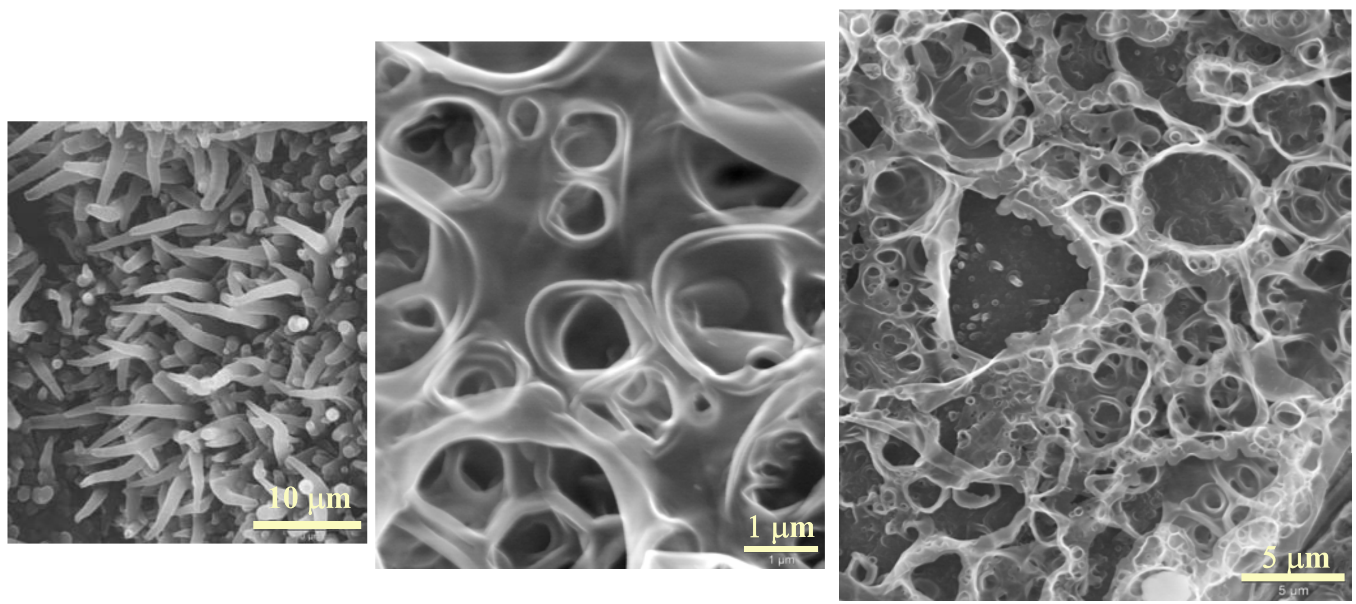


LSCM images of ADH tagged with Alexa-488 entrapped in (A) Eastman AQ 55 polymer matrix: 2-D slice; (B): 3-D reconstruction from 2-D slices; (C): Nafion: 2-D slice. (Scale bars: 50 µm.)

Micro and Nano Materials Synthesis

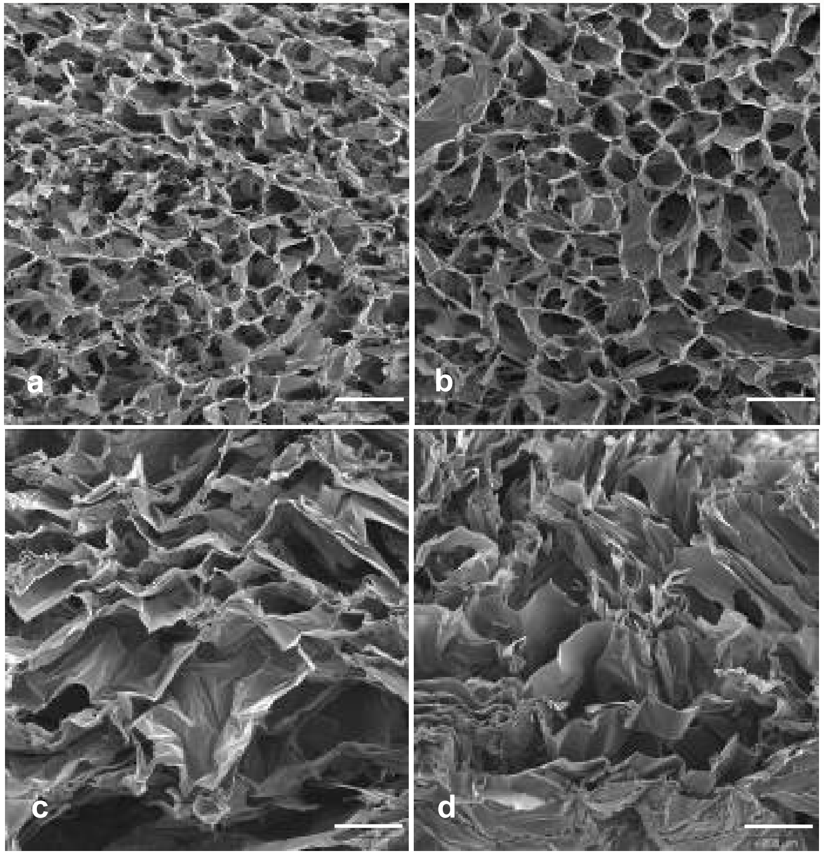
- Develop highly porous conductive polymer matrices:
  - High enzyme loading
  - Effective mass transport
  - Highly conductive network
  - Favorable micro environments for immobilization



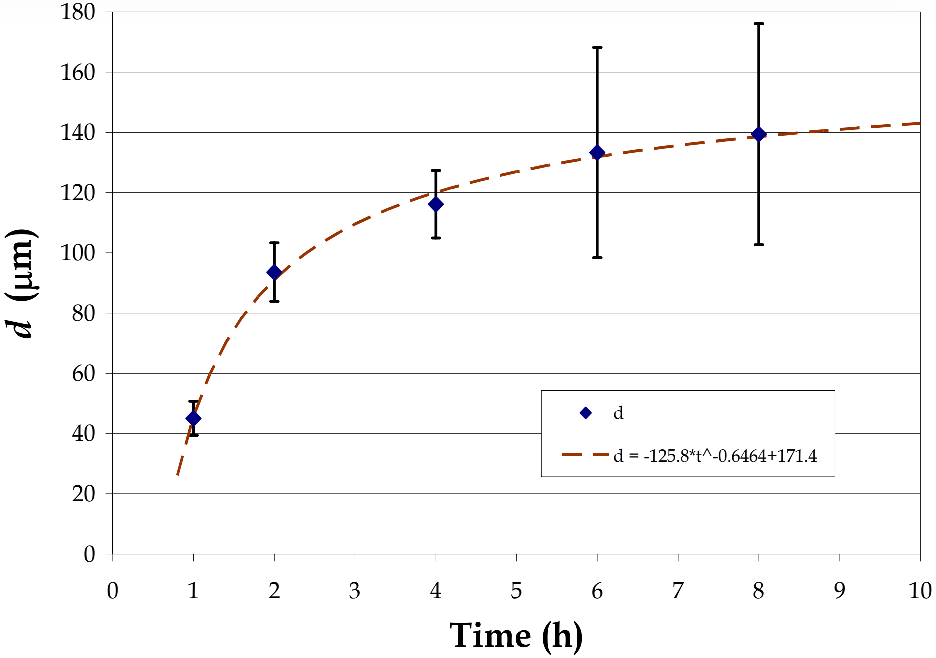


Polypyrrole (PPy) porous nano-fabrics, V. Svoboda et al. (2006)

Macro & Meso Pore Structure Engineering



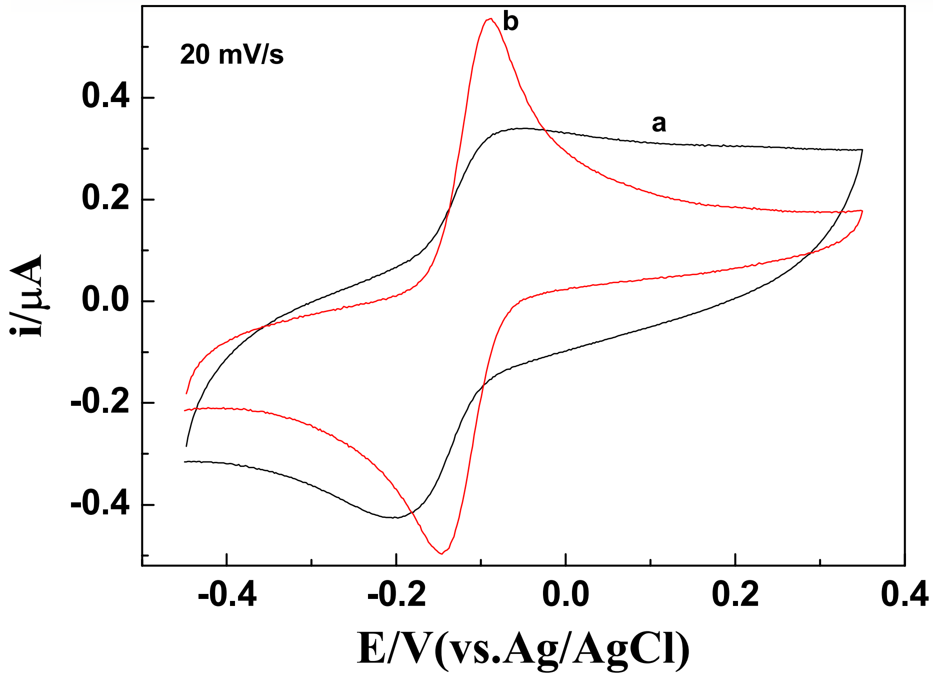
Scaffolds made from 1 wt% chitosan in 0.4 M acetic acid solution frozen under different durations: (a) 2 h, (b) 4 h, (c) 6 h, and (d) 8 h; scale bars = 200 µm.



Correlation of mean pore size *d* versus freezing duration

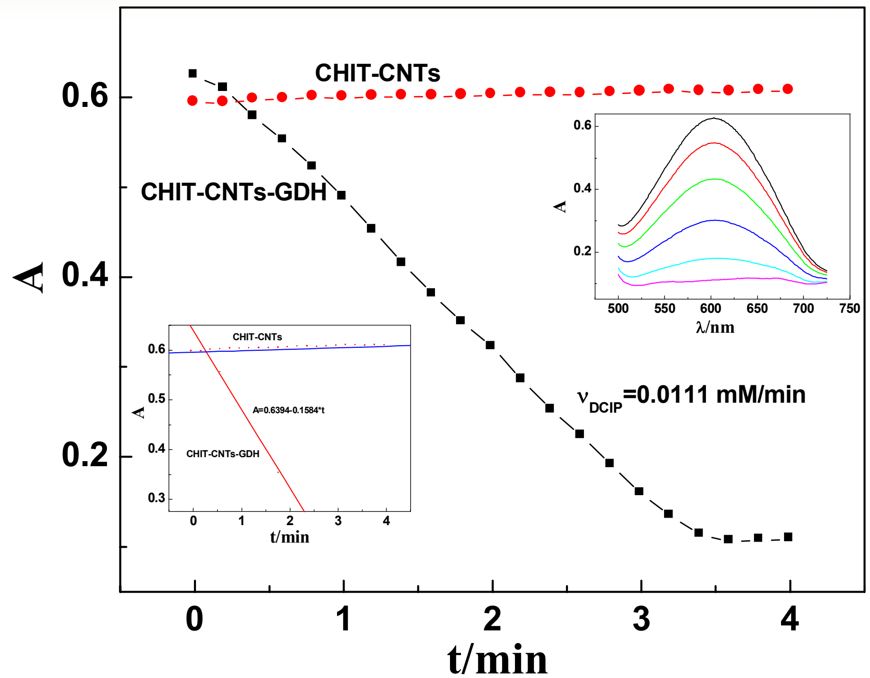
M. Windmeisser et al. (2006)

DET in PQQ-GDH-Chitosan-CNT



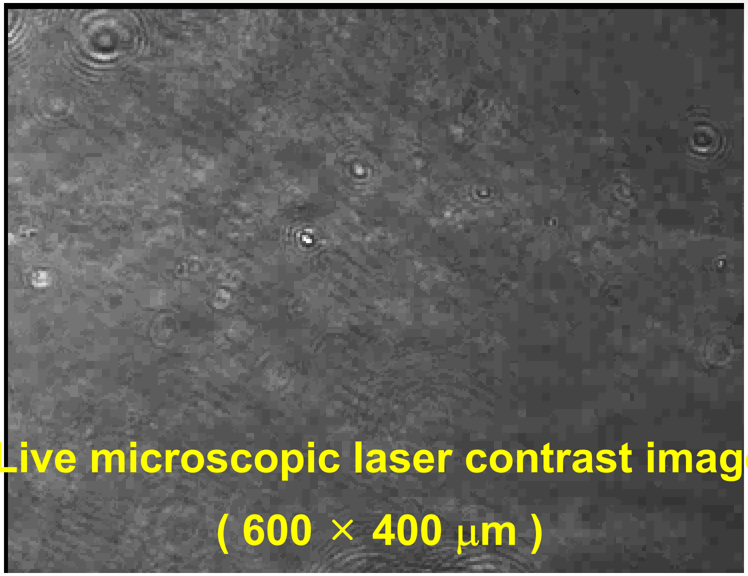
CV of (a) PQQ-bound CHIT/GCE and (b) PQQ-bound CHIT-CNT/GCE in 0.1 M PBS at 20 mV/s

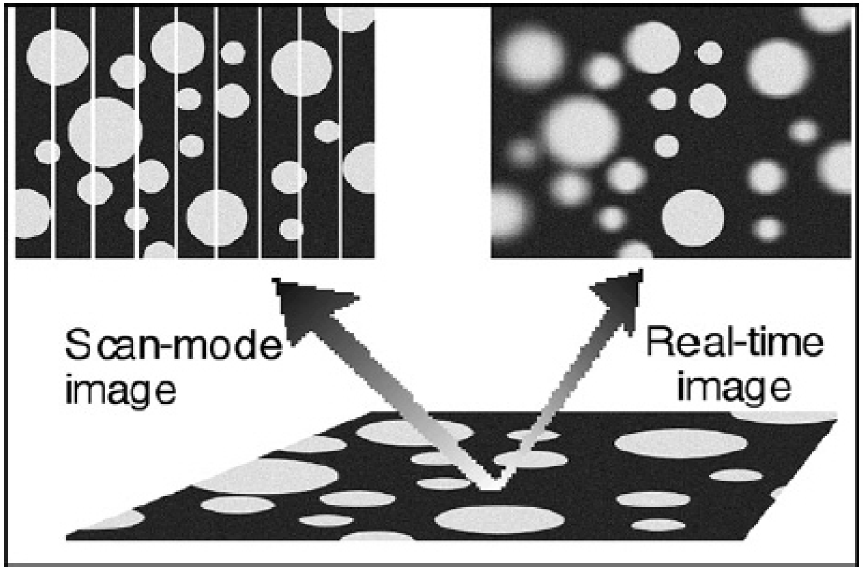
D.M. Sun et al. (2007)



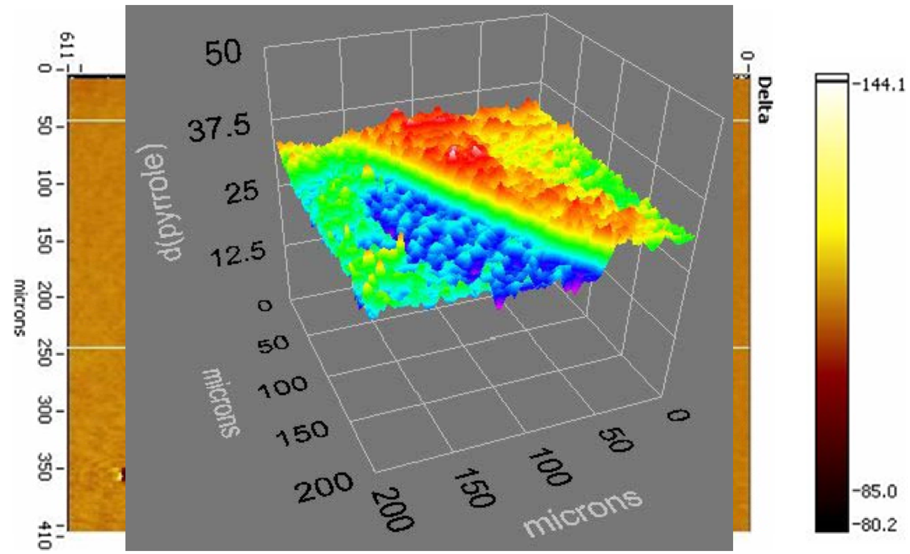
Kinetic curves of CHIT-CNT and PQQ-GDH-bound CHIT-CNT films in 0.1 M PBS with 0.1 M glucose, 0.8 mM PMS and 0.02 mM DCPIP. Insets: (left) linear fit plot and (right) the absorbance spectra of DCPIP at 600 nm with PQQ-GDH-bound CHIT-CNT film with time

Imaging Ellipsometry (IE)





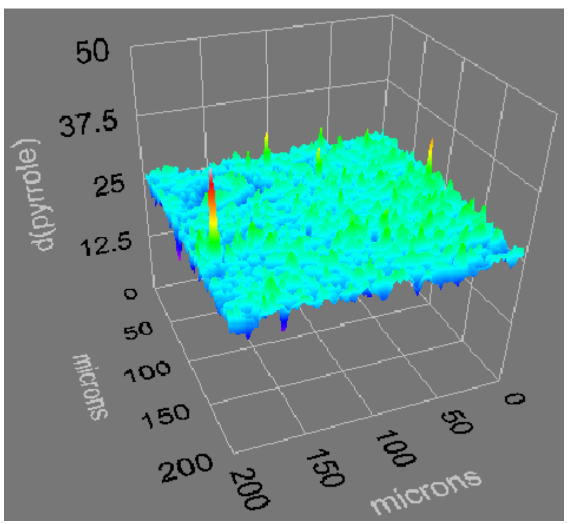
1) Locate region-of-interest
2) Real-time laser image observation via CCD camera
3) Measurement of Δ and Ψ in spatial distribution (600×400 μm)



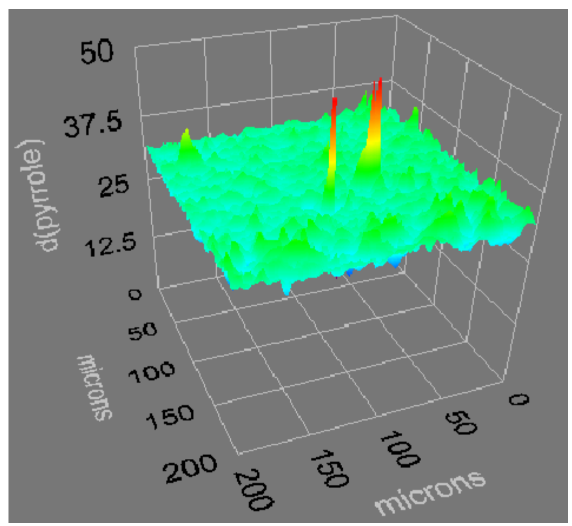
Polypyrrole Deposition

- Electrochemical Deposition & Control
  - Fabrication conditions
- Imaging Ellipsometry
  - Film thickness
  - Surface morphology

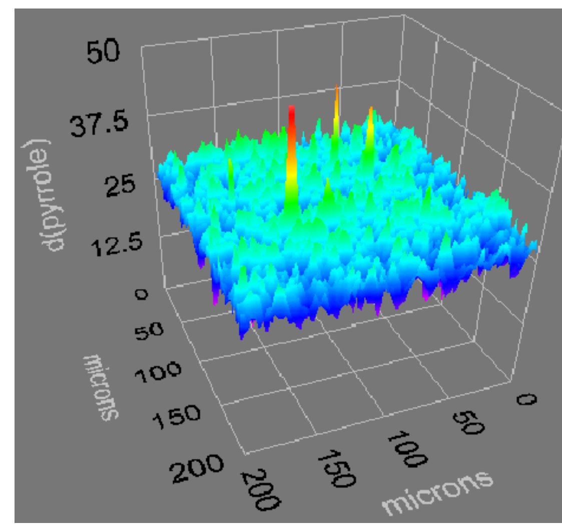
V. Svoboda et al. (2005)



0.5 mA/cm²



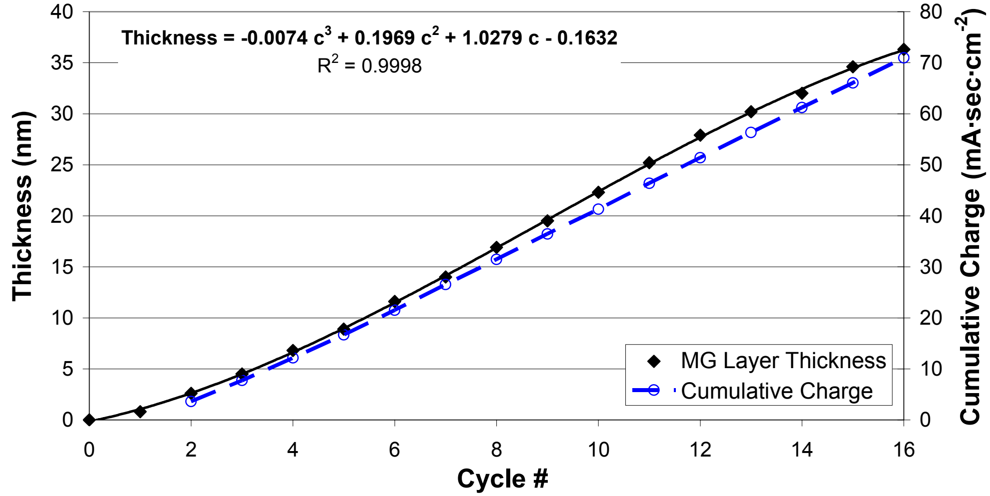
1 mA/cm²

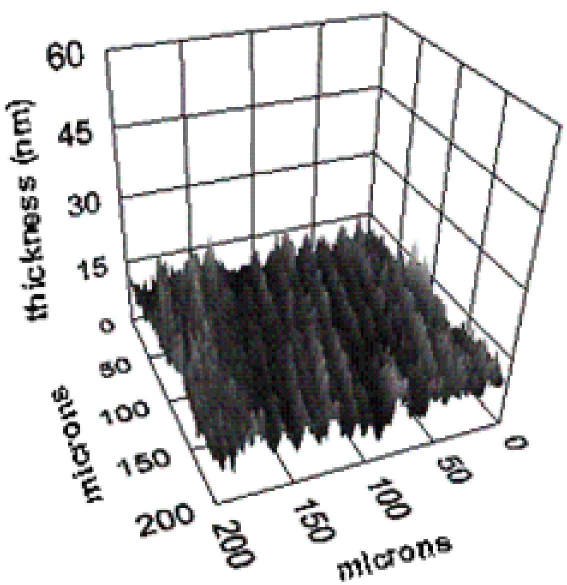


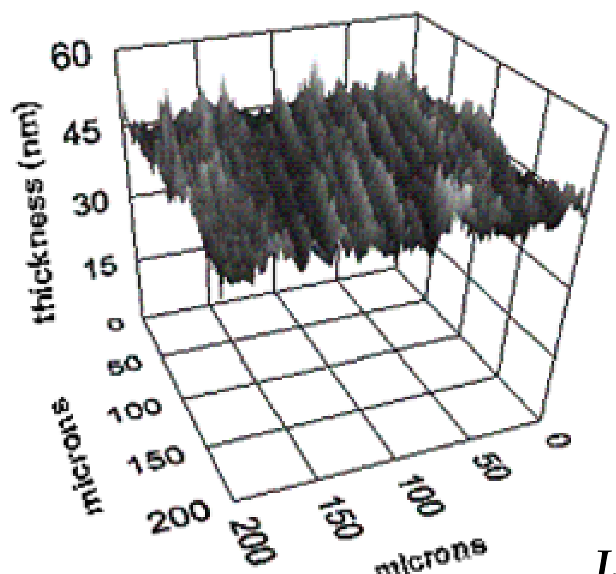
2 mA/cm²

Poly-MG Modified Surface

- Electrochemical Deposition & Control
  - Fabrication conditions
- Imaging Ellipsometry
  - Film thickness
  - Surface morphology







CV deposition of MG on Pt

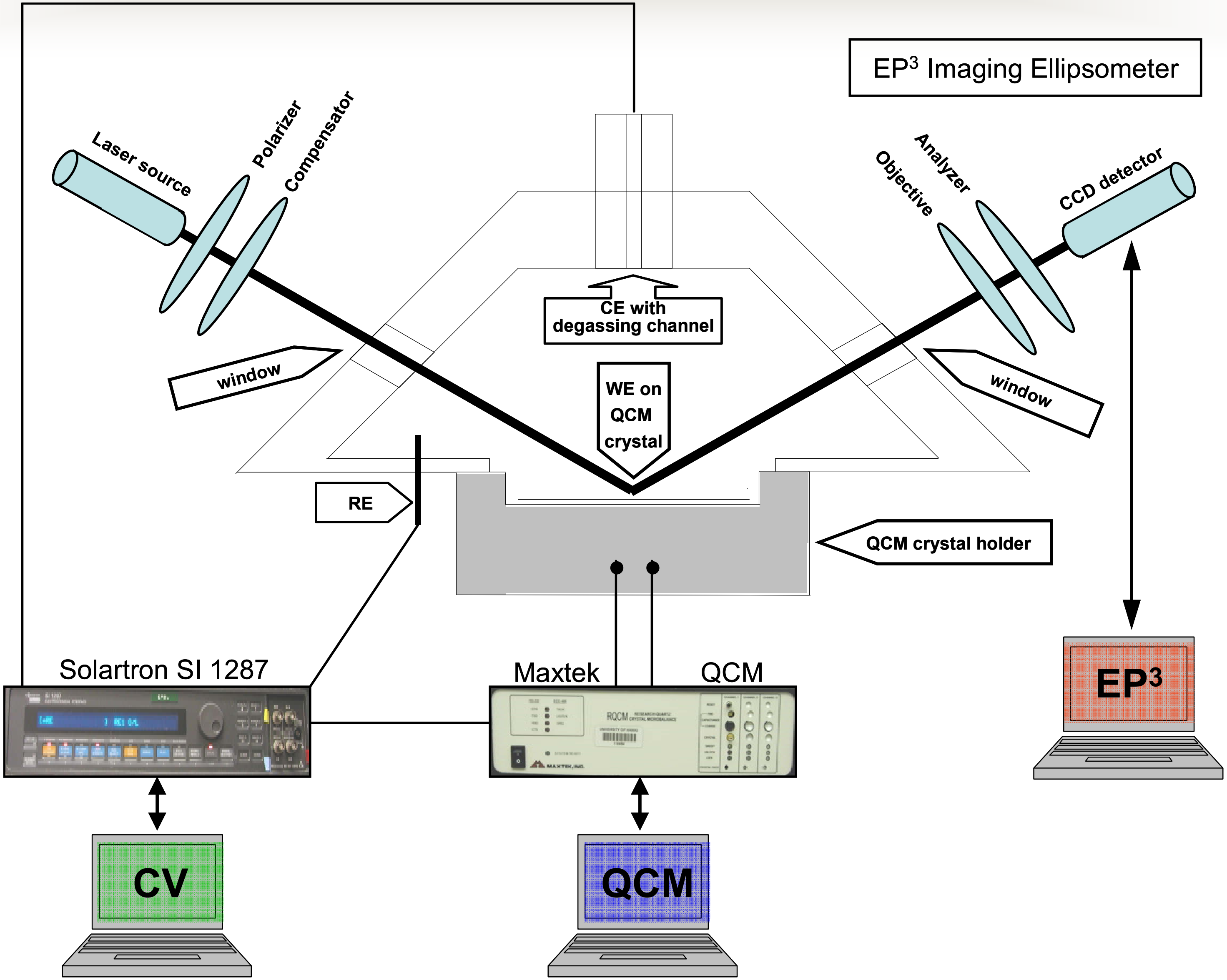
–0.5 V ←→ 1.2 V

(vs. Ag/AgCl)

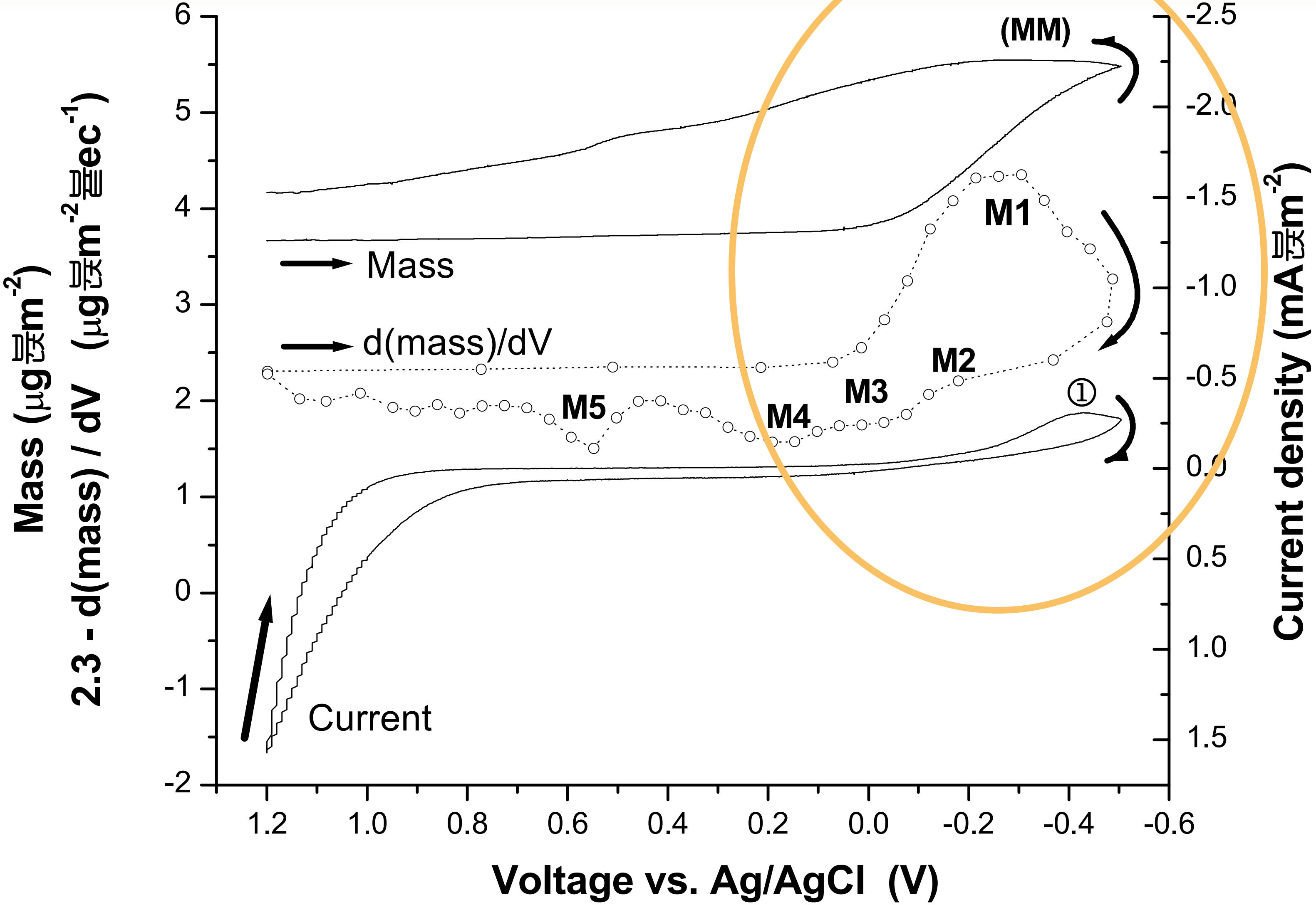
Scan rate: 50 mV/sec

V. Svoboda et al.
J. Electrochem. Soc. 154 (2007) D113.

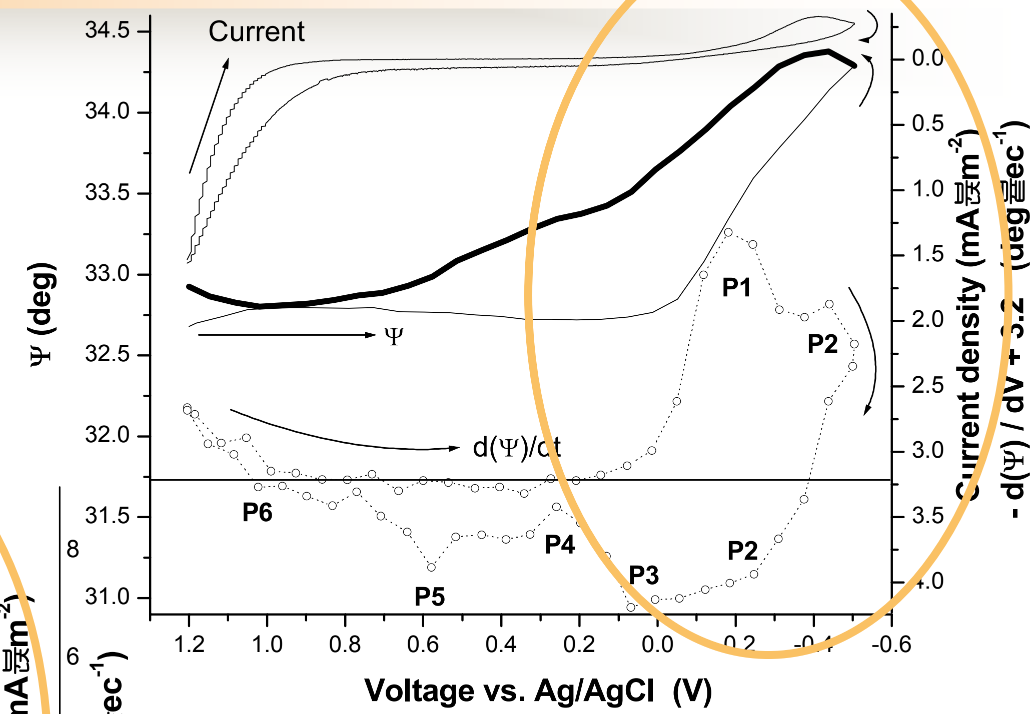
Electrochem. Microgravimetric IE

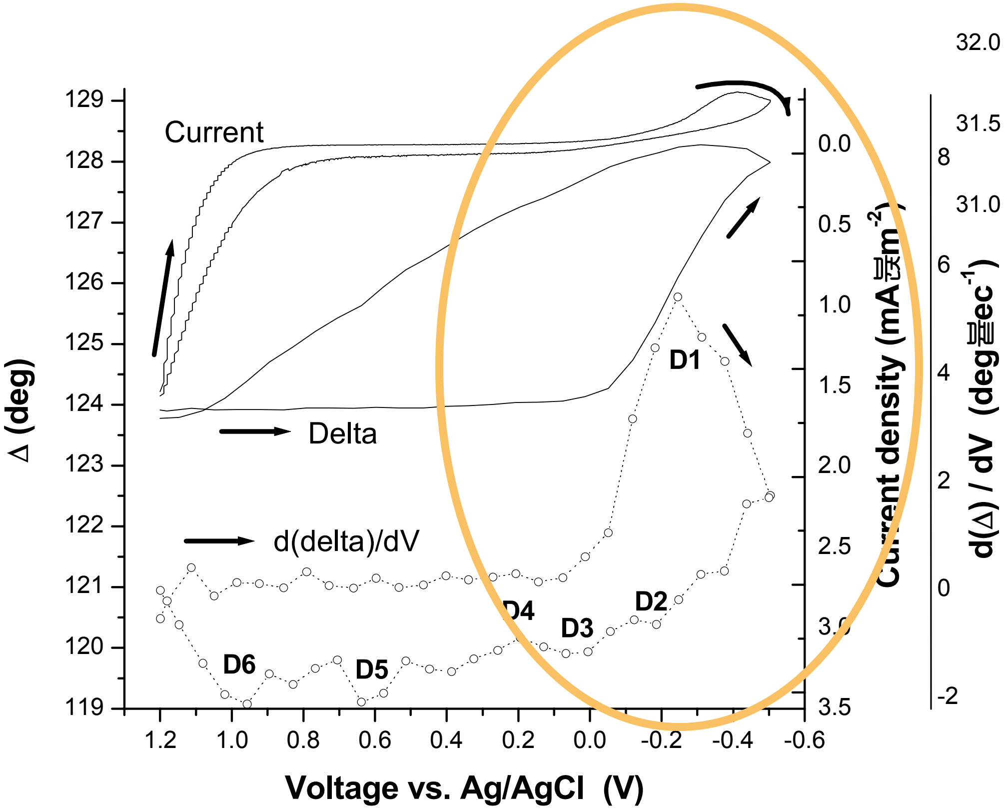


Current & Mass Changes

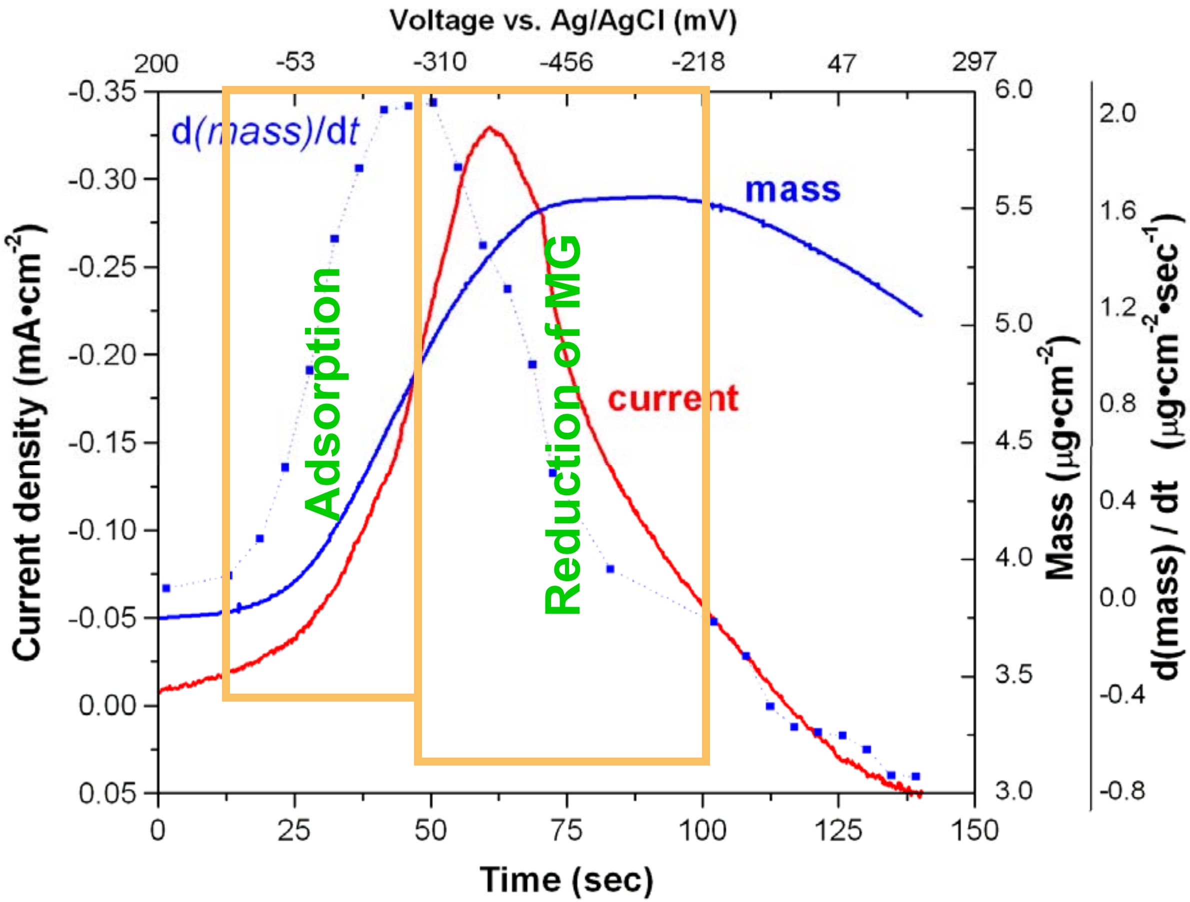


Current & Ellipsometric Angles





Reduction of MG to l-MG



Faraday's law

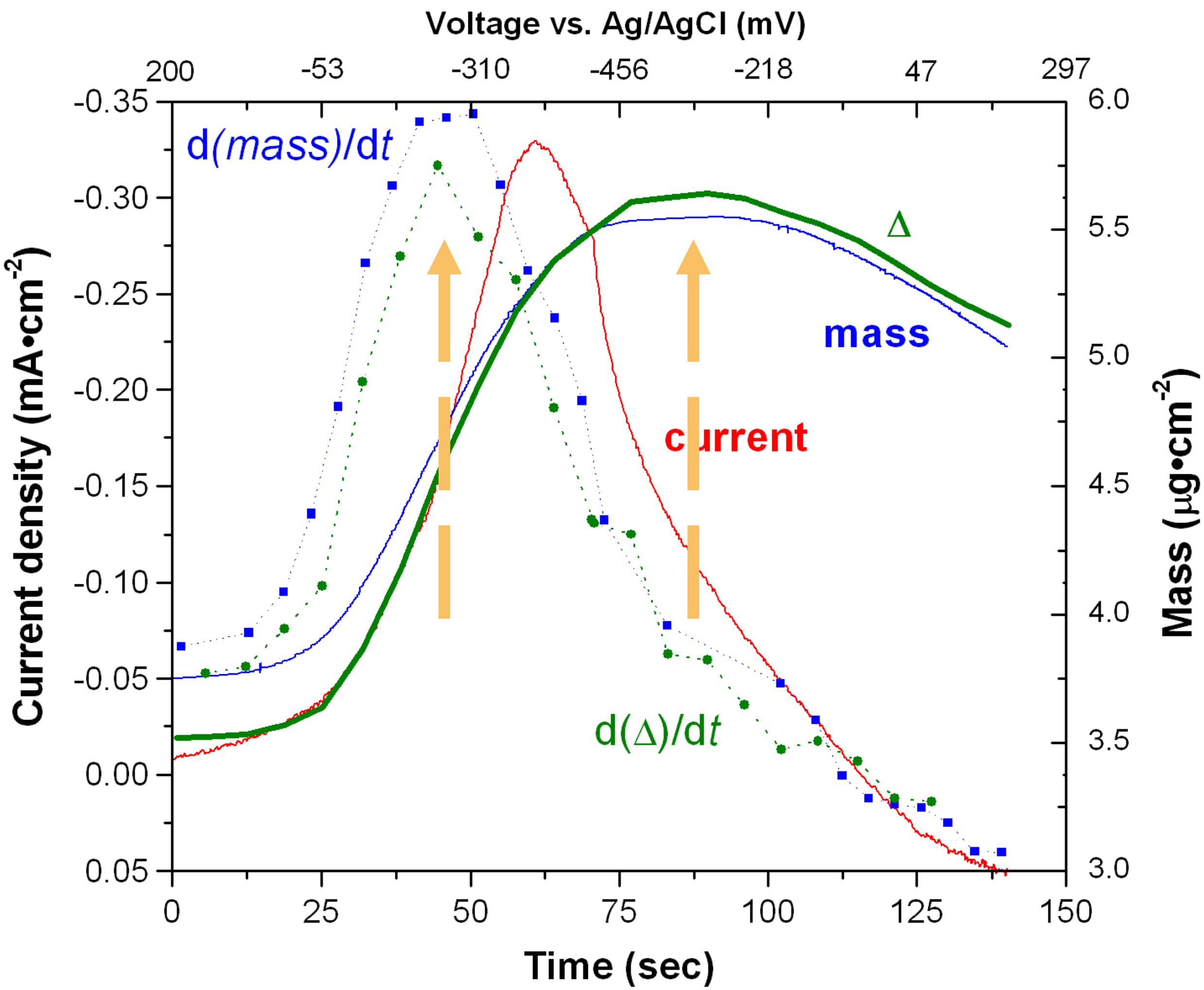
$$m = \frac{M}{F \bullet n} \bullet Q$$

$$m = \frac{M}{F \bullet n} \int_0^T i(t)dt$$

$$\boxed{\frac{dm(t)}{dt} = \frac{M}{F \bullet n} i(t)}$$

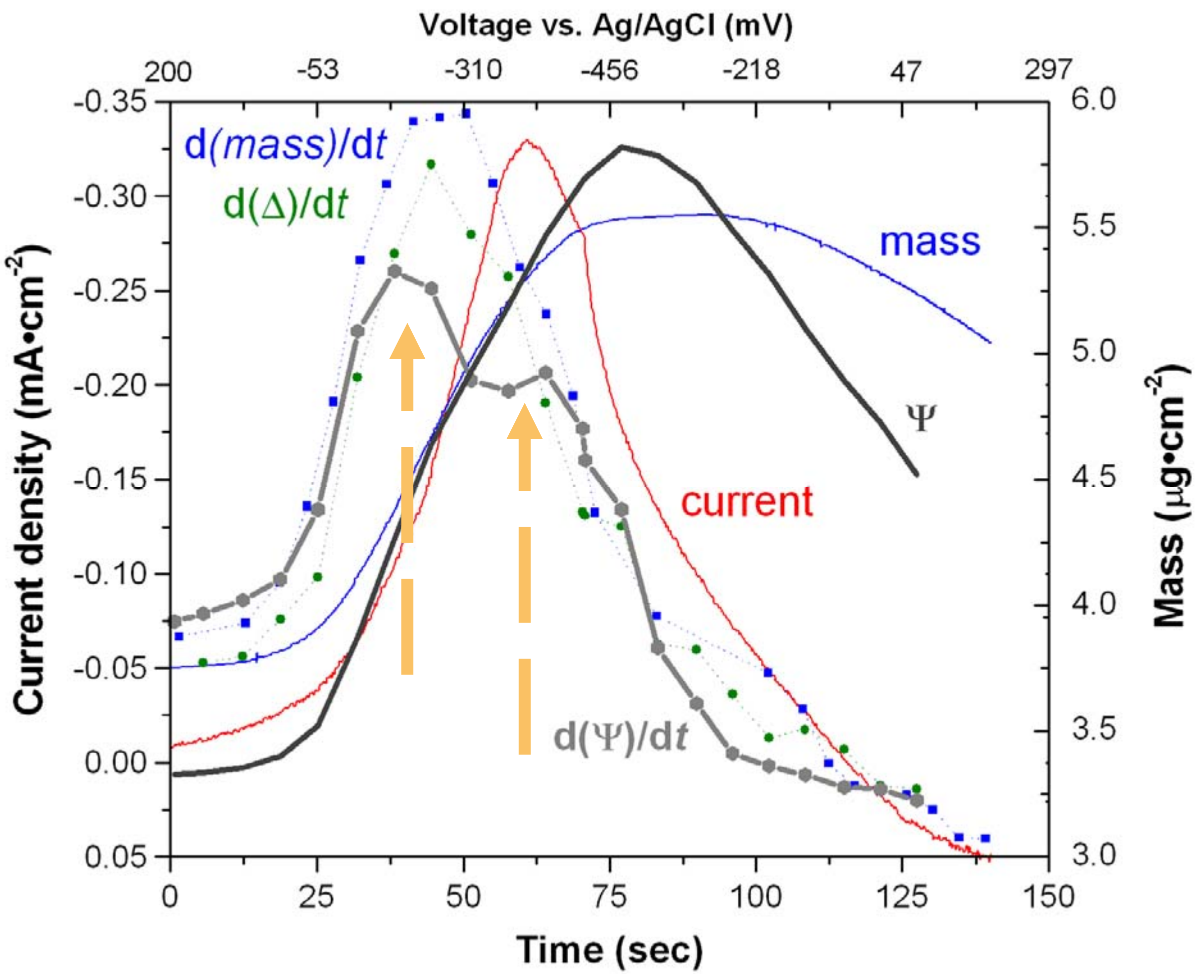
> ➢ **In the reduction phase: the mass deposition was driven by adsorption, followed by electrochemical reduction of MG to l-MG**

Mass & Δ



➢ **The progression of Δ and d(Δ)/d*t* follows mass changes.**

Mass, Current, & Ψ



- The progression of Ψ and d(Ψ)/d*t* reflect both mass and chemical changes in the film.

Conclusion

- Enzymatic bio-fuel cells need delicate optimization of electrode fabrication, which requires pore structure engineering, from macro- to meso-scale.
- Nano-material synthesis and electrode fabrication require in situ observations and non-intrusive characterizations of the process.
- Several intriguing in situ characterization techniques were demonstrated of their utility:
  - Fluorescence and polarization
  - Imaging ellipsometry + QCM + Electrochem. tech.
  - Microporometry
- Dynamic transient observations → mechanistic details

Acknowledgements

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  - Students: Chris Rippolz, Mona Windmeisser, Swati Nagpal, Ruey Hwu, Eric Brown

Thank you for your attention!