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Why Go Nano Instead of Micro?

A Case for Well Designed Arrays

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What does this mean???

- **Nano scale technology is** *the* **new frontier.**
- **Centers for Nanotechnology are growing across the nation.**
- **The public is accepting this technology with a** *positive* **and** *enthusiastic* **attitude.**

Dec 15, 2006, Nano Science and Technology Institute: ***Survey Shows U.S. Public is Ready To Embrace Nanoproducts***

"Rice University's Center for Biological and Environmental Nanotechnology (CBEN), University College London (UCL) and the London Business School recently released the findings of their comprehensive survey on the public's openness to using nanotechnology products. The researchers found that consumers in the U.S. are willing to use products containing nanotechnology, and when factoring in health and safety risks, if the potential benefit is high, consumers are willing to take the risk. Study results also revealed that U.S. consumers think nanotechnology is less of a risk than several everyday chemicals including herbicides, chemical disinfectants, and food preservatives."

Maybe the title should read: *Why Not go Nano instead of Micro.*

- **Nano technology is the new *gold-rush* of the 21st century**
  - **This new technology is recognized in nearly every field of science.**
- *So what's the problem!*
- **In our rush to probe interesting phenomena's at the nano-scale, we maybe** *overlooking* **interesting phenomena's as a function of synergistic relationships between nano and micro scales.**

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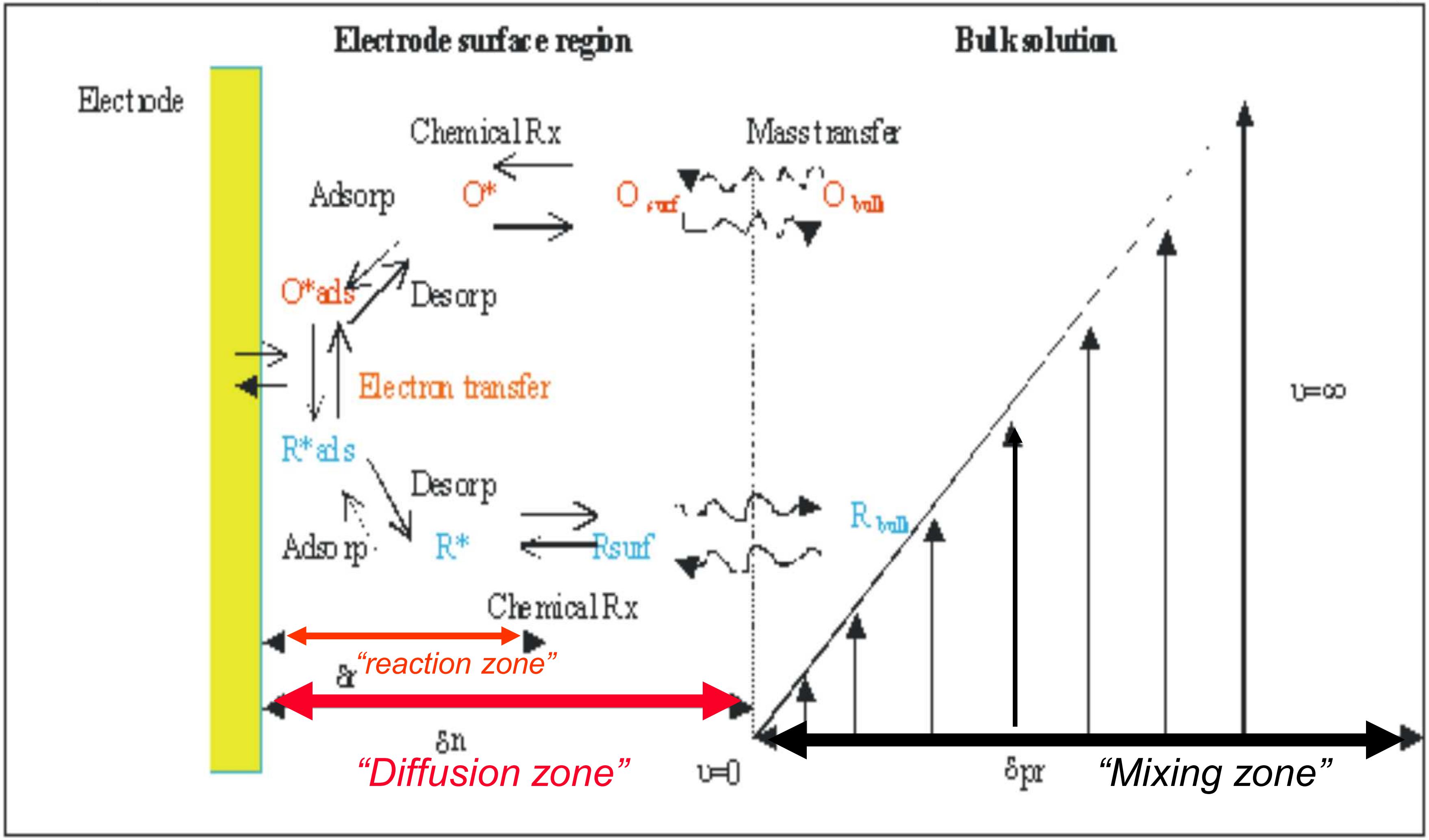
Migratory zones of ions in the *Interphase* for Faradaic Reactions



"reaction zone"

"Diffusion zone"

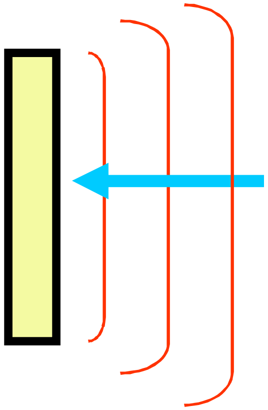
"Mixing zone"

For this talk: I would like to focus on **Electrochemical reactions in the *interphase***

Large electrodes

r >10um

Planar geometry



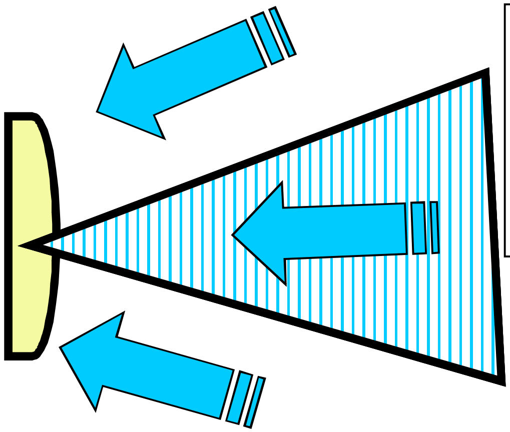
Semi-infinite linear diffusion

Electro-active material diffusing to the surface

Nano/micro-scale electrodes

r <<10 um

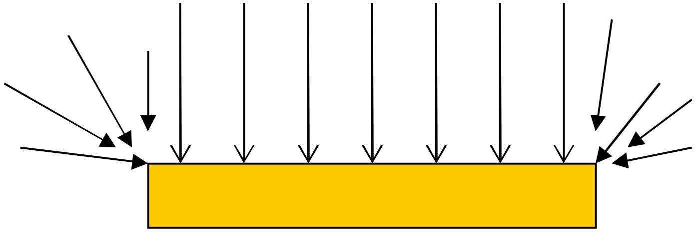
Spherical geometry



Hemispherical diffusion

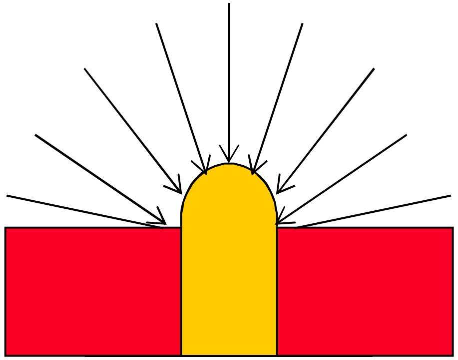
Resulting in larger cross-sectional influence in the interphase

Nanoelectrodes Have Advantages over Conventional Planar Electrodes



Macroplanar

$i_{t=\infty} \Rightarrow 0$



Hemispherical

$i_d = nFDC/r_0$

- **Limiting current**
  $i_d = n\,F\,D\,C\,(1/(\pi Dt)^{1/2} + 1/r_0)$
- **"Nanoelectrode" if size < $(\pi Dt)^{1/2}$ for timescale of measurement, typically < 50 μm.**
- **For $r_0 << (Dt)^{1/2}$, i.e., diffusion layer larger than electrode, current is time-independent, i.e., steady-state condition.**

Conditions for Spherical Diffusion at Nanoelectrodes

Nernst diffusion layer thickness $\delta = (\pi D t)^{1/2}$, r = electrode radius, L= electrode separation

Case 1 $\delta / r \leq 0.3$ (Semi-infinite linear diffusion)

$I_d = [nFDC° / (\pi D t)^{1/2}] (r/L)^2$ Time/size dependent

Case 2 $\delta / r \geq 3$ but $\delta / L \leq 0.3$ (No influence from nearby electrode)

$I_d = (nFDC° / r) (r/L)^2$ Independent of time, but dependent on size

Case 3 $\delta / r \geq 3$ (Complete diffusion overlap)

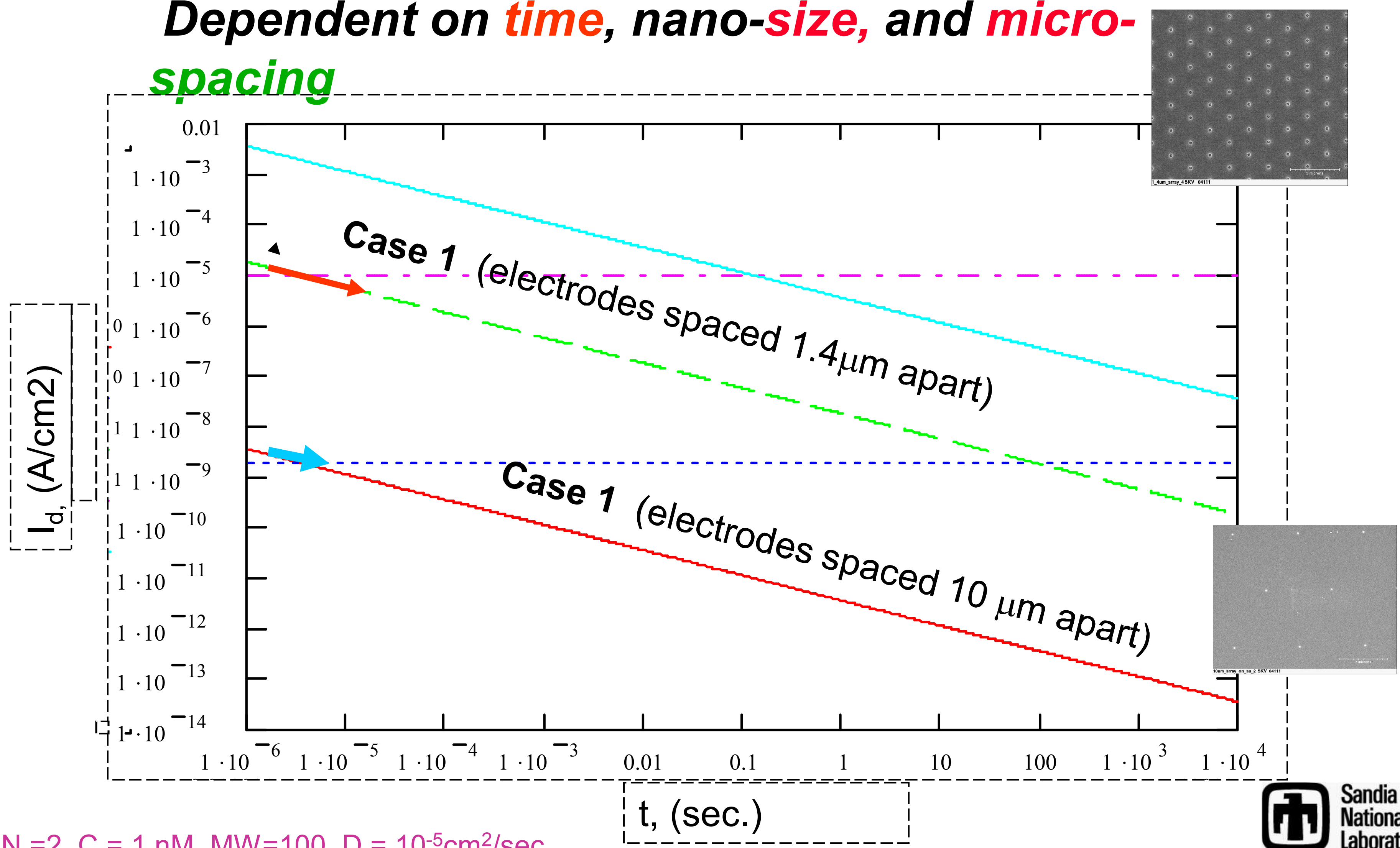
$I_d = (nFDC° / (\pi D t)^{1/2})$ Time dependent, but independent on size

For very fast sensing, Case 3 will yield the highest diffusion-limited current density.

Although, for Case 3 to hold $r \ll \delta \ll L$, and the kinetics must be fast

Case 1: $\delta/r \leq 0.3$, $I_d = [nFDC°/(\pi Dt)^{1/2}]\,(r/L)^2$

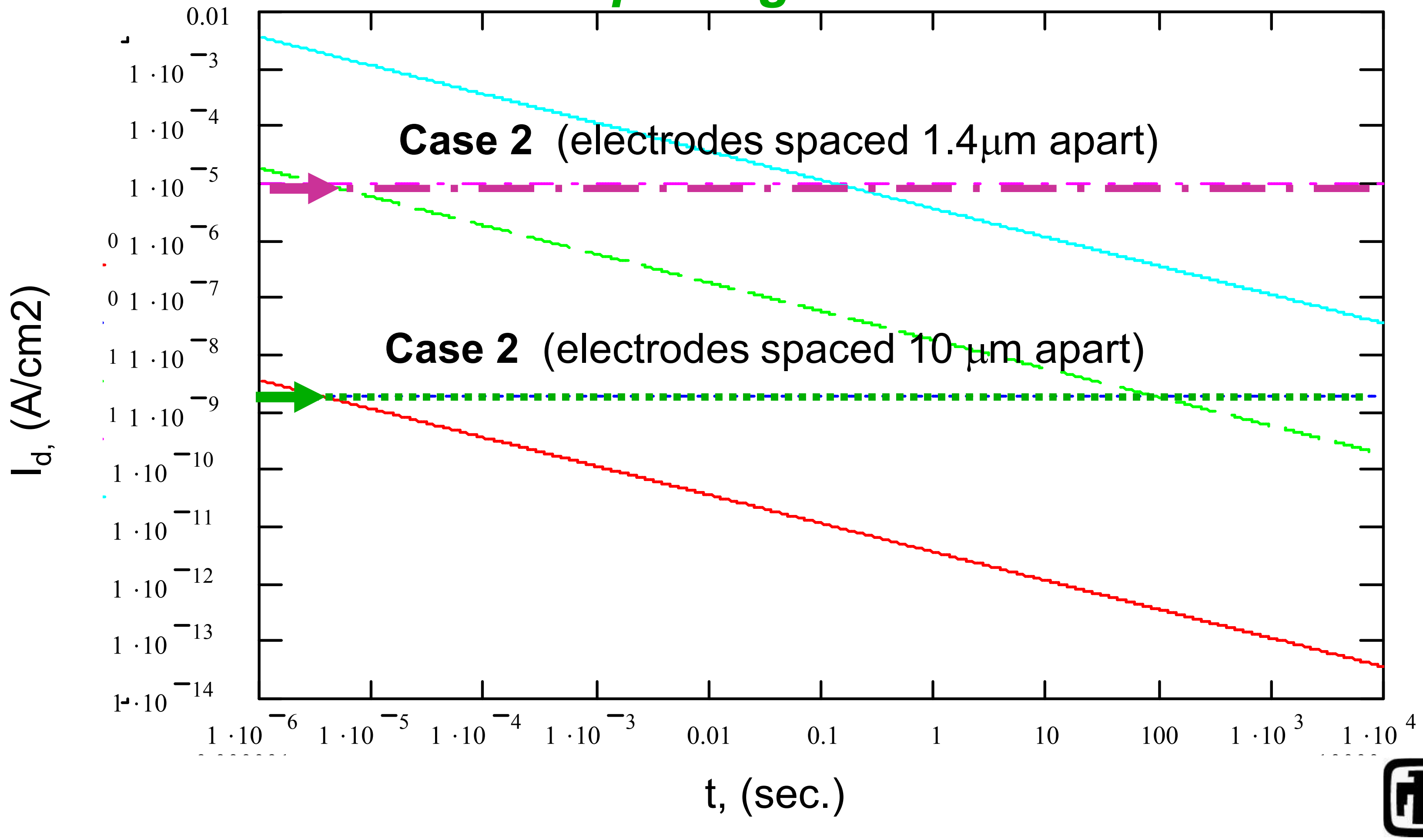
Dependent on *time*, *nano-size,* and *micro-spacing*



N =2, C = 1 nM, MW=100, D = 10^{-5}cm²/sec

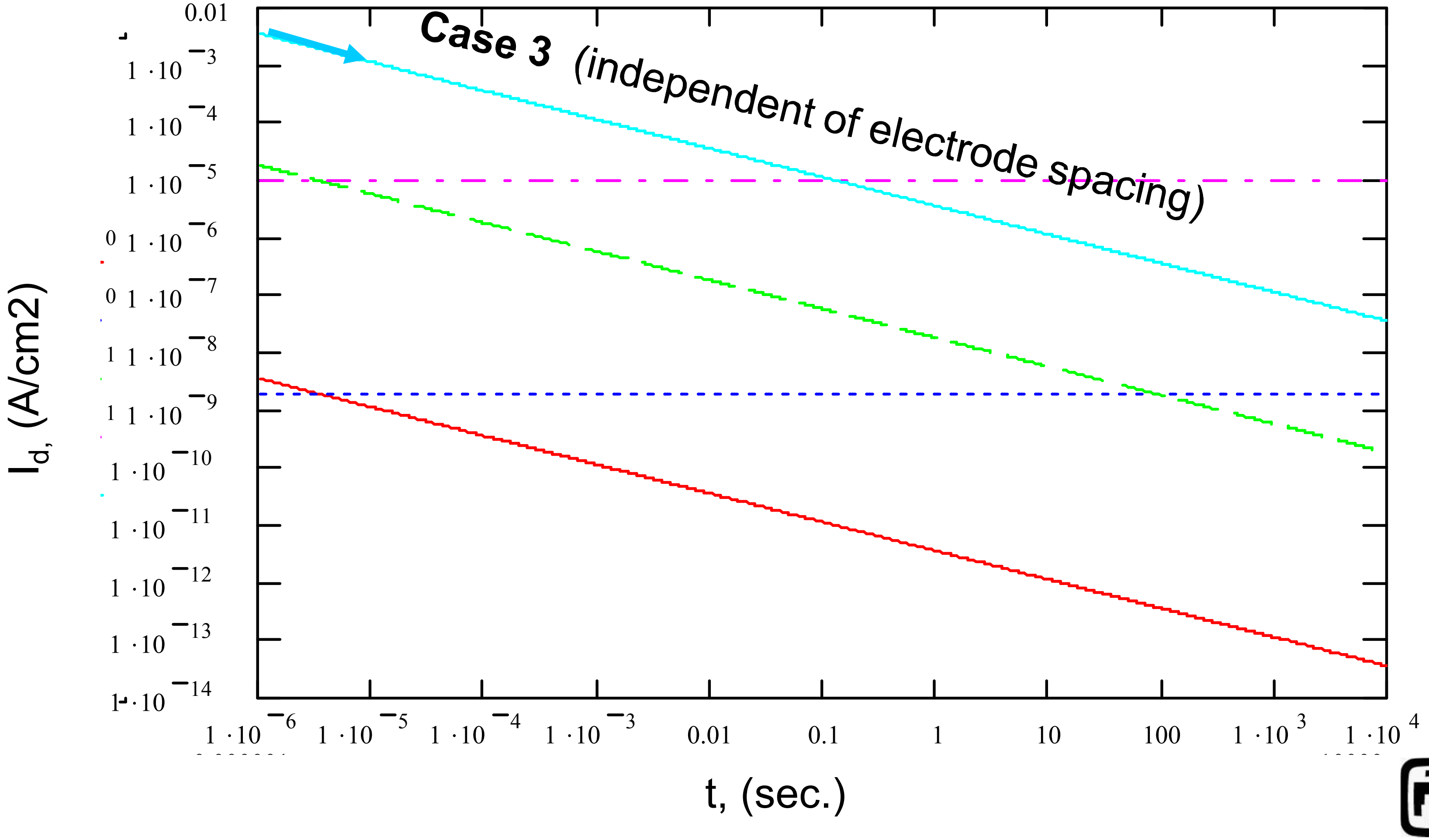
Case 2: $\delta/r \geq 3$ but $\delta/L \leq 0.3$, $I_d = (nFDC°/r)(r/L)^2$

Independent of time, but dependent on nano-size and micro-spacing

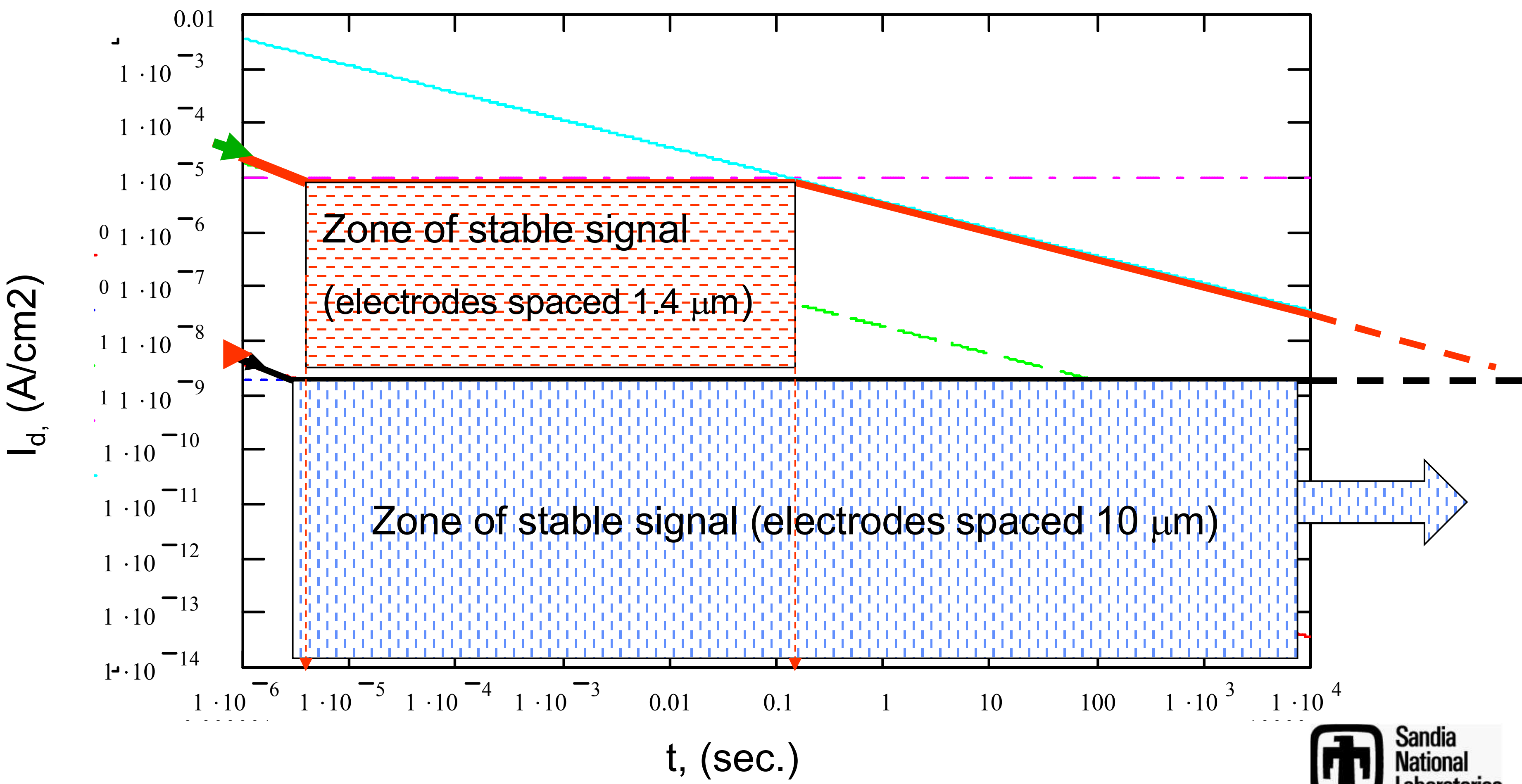


Case 3: $\delta/r \geq 3$, $I_d = (nFDC° / (\pi Dt)^{½})$

Time dependent, but independent on nano-size and micro-spacing

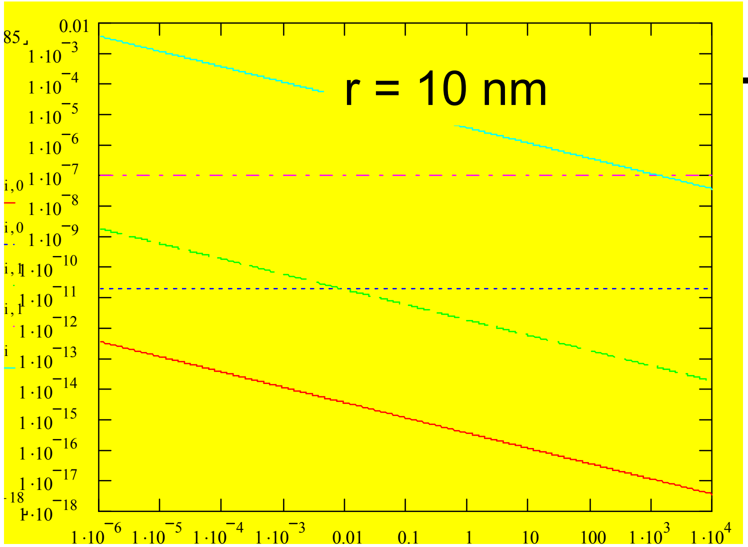


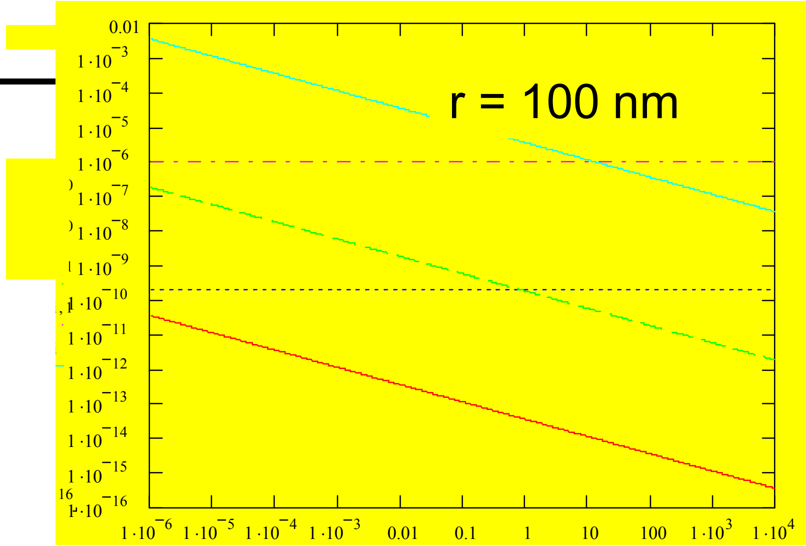
The compromise between a nice *big* signal or a *long* stable signal



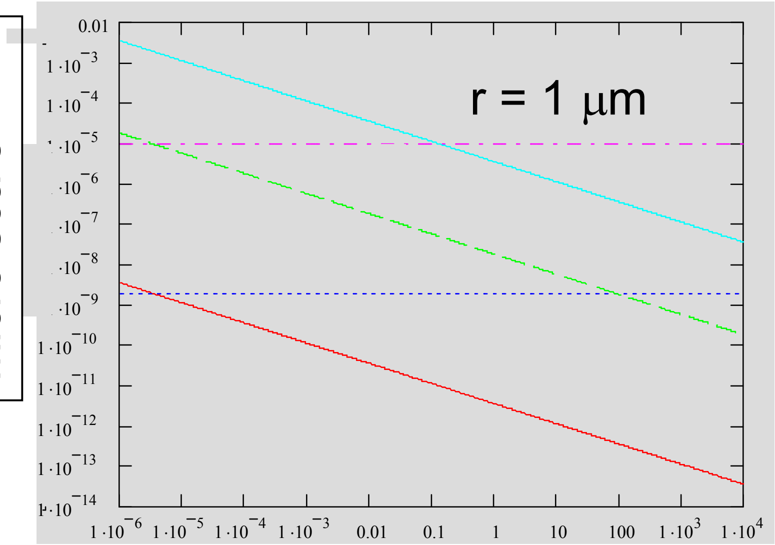
There is a trade off between signal ***stability*** and signal ***strength*** as a function of electrode size.

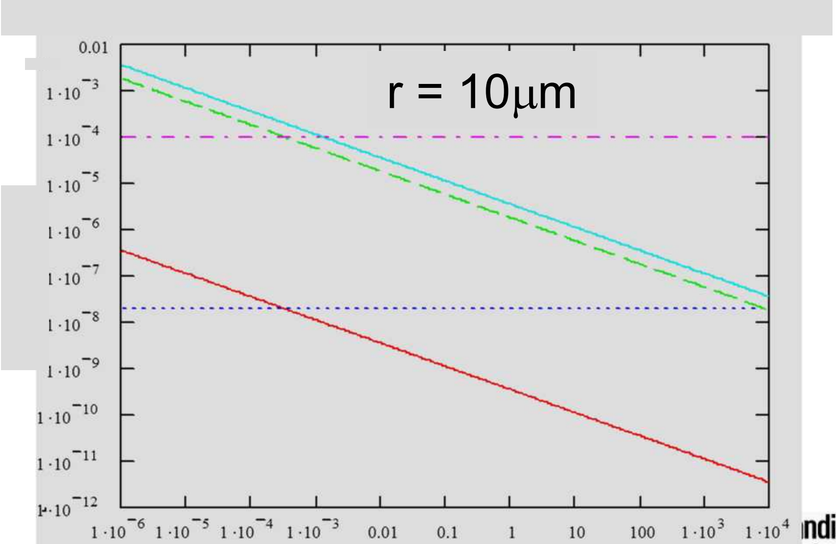
Nano scale



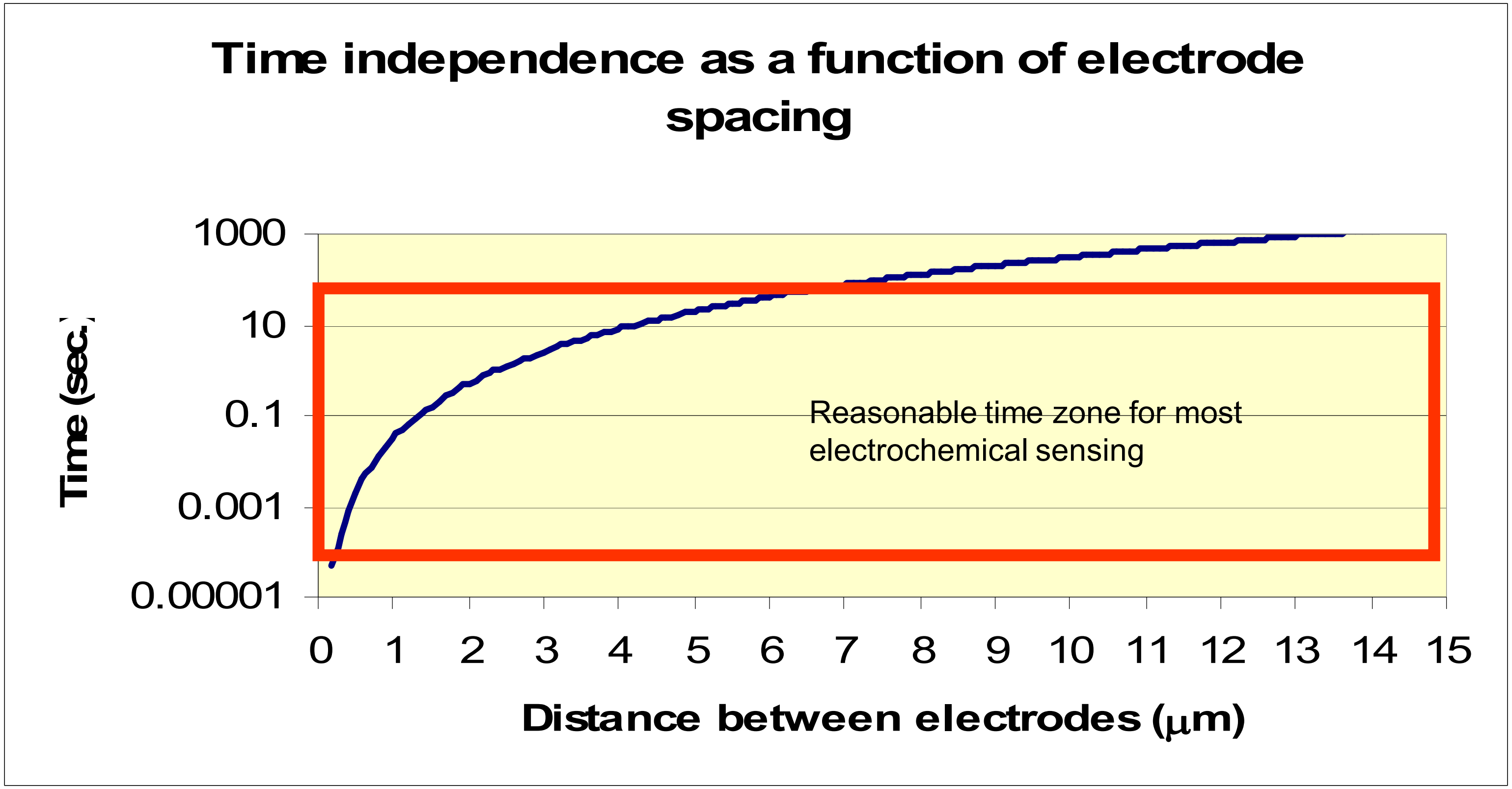


Micro scale





Micro-spacing consideration for nano-electrode for reasonable signal stability within nature convection*



* Normally nature convection taken place within 50 um to 200 um from the surface

But there are *disadvantages*…

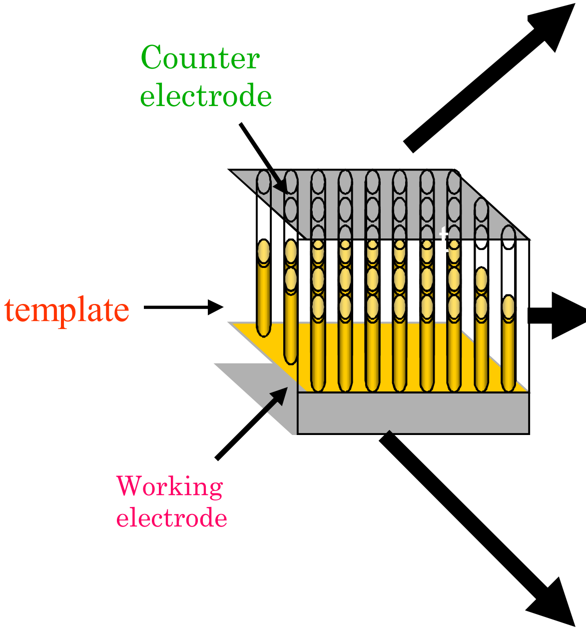
1) Although the current density at a nano-electrode is high, the surface area of the electrode small, resulting in a *small* total current difficult to measure in the field.

2) Also, since the surface area of these electrode are small relative to solution volume, they have a *greater* probability of fouling.
    - -typical electrode V/A ratio ~10 cm.
    - -thin film, high surface area electrode V/A ~low as 10^{-3} cm.
    - -nano electrode, V/A ratio on order 10^{8} cm.

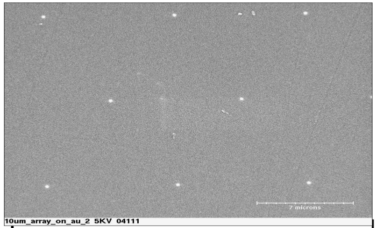
Solution: large arrays of well spaced nano-electrodes

Anatomy of the Nano-Array

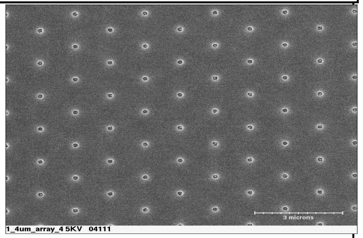
“Sandwich” Nanoelectrode array system for a two electrode cell.



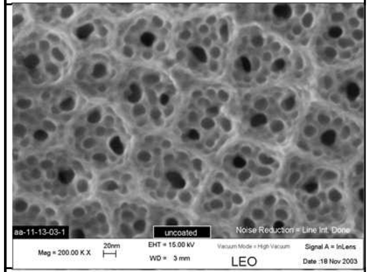
A “standard” nanoelectrode array is based on the same design framework as the “Sandwich” but without a counter electrode.



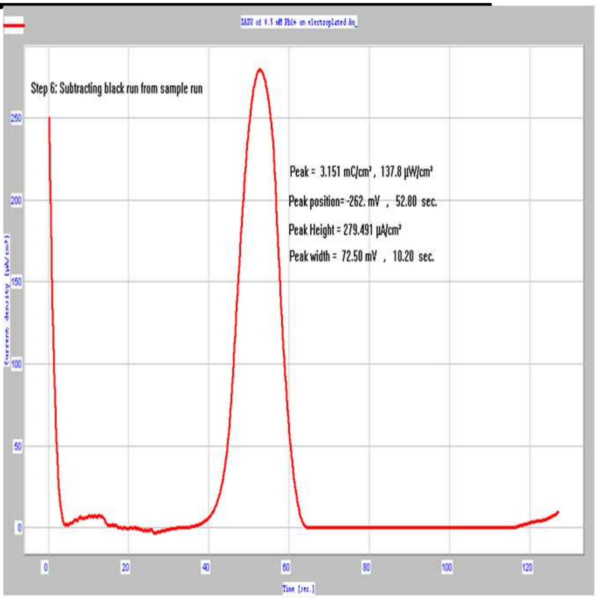
200 nm pores, 10 µm period with 9x10^6 electrodes cm^{-2}.



200nm pores, 1.4 µm period with 9x10^7 electrodes cm^{-2}.

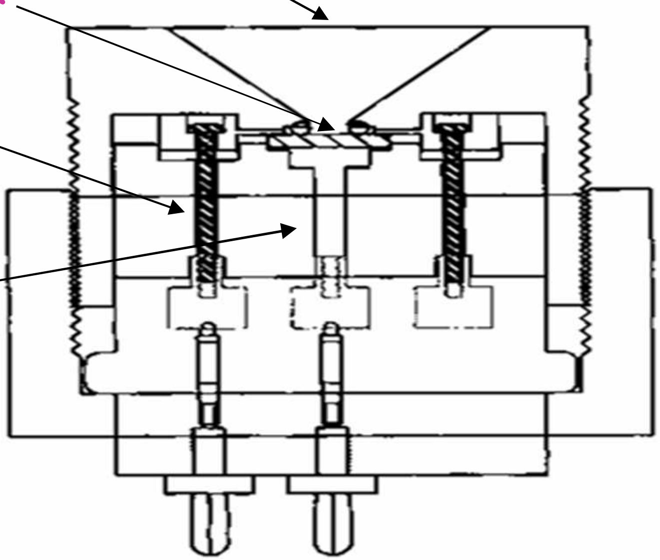


AAO template with~30 nm pores, 80 nm period with 9x10^{10} electrodes cm^{-2}



SASV result gives a well-defined baseline and signal. The signal is easy analyzed to determine analyte concentration against a standard.

Sampling Head



Small Volume Sample Stage

Electrochemical Sensor*

Counter/quasi-reference electrode contact

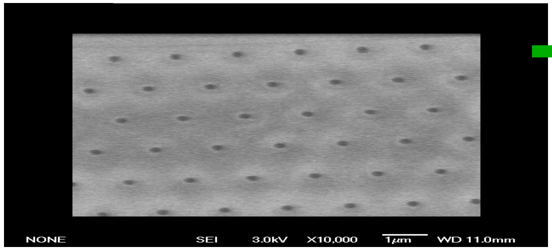
Working electrode contact

Connection Pins to Handheld Potentiostat

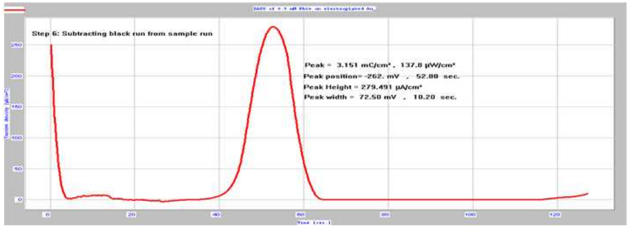
*Electrochemical sensor consist of nanoelectrode arrays of various counter/working electrode materials which are interchangeable or placed in a series of sample heads.

The big picture: *how the the array was used*

Design and Engineering of Nanoelectrode Arrays



Analytical protocol in Low-Conductivity solutions



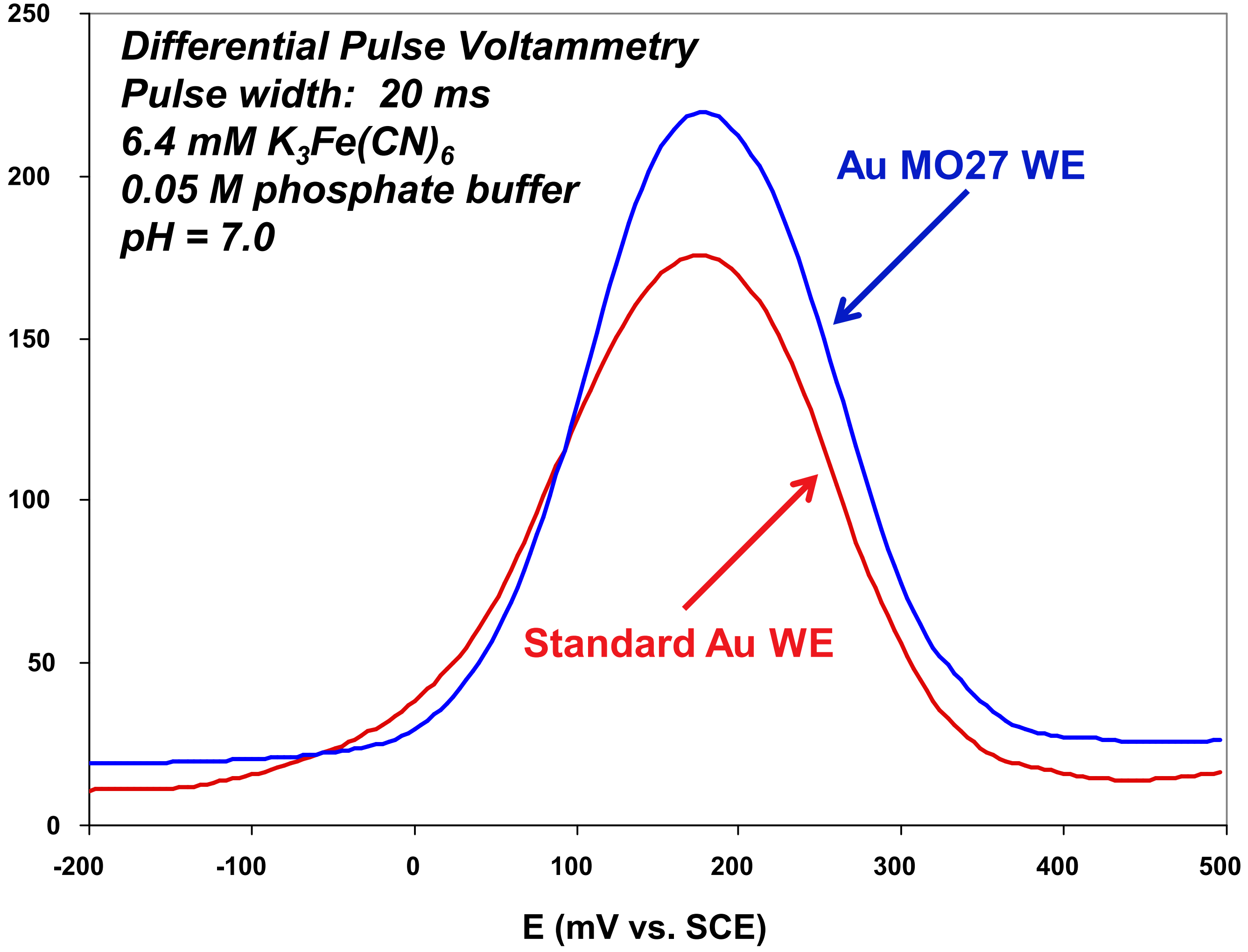
High-Speed Potentiostat

System integration

But according to the models…

- The maximum signal should be limited to conditions under Case 3.
- If analysis is possible under short transients, at best, maximum signal is independent of (r/L), limited by Case 3.
- But in the lab, this was not the case!
- The additive effect of Spherical Diffusion appears greater than expected.

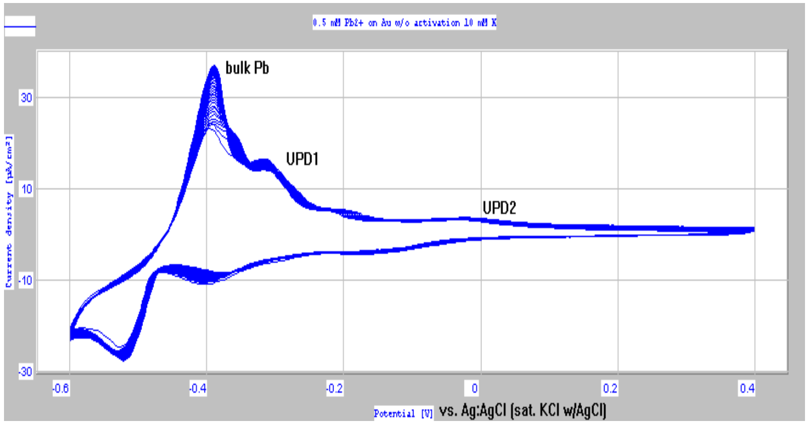
Au electrodeposition into pores of ion track membrane produces a functional working electrode for high sensitivity analysis

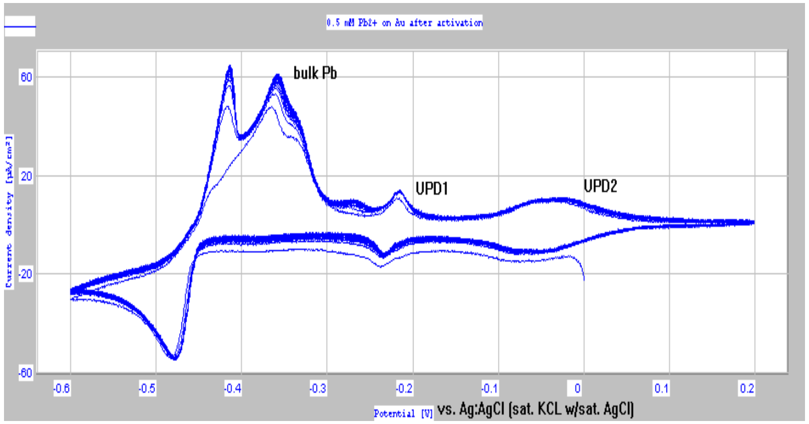


- Current focus:
- Characterization of membrane-based electrodes to determine if electrodeposition produces isolated electrodes or whether plating leads to coalescence of adjacent nanoelectrodes

Au (macro) Electrode ***Affinity*** *for Trace Lead*

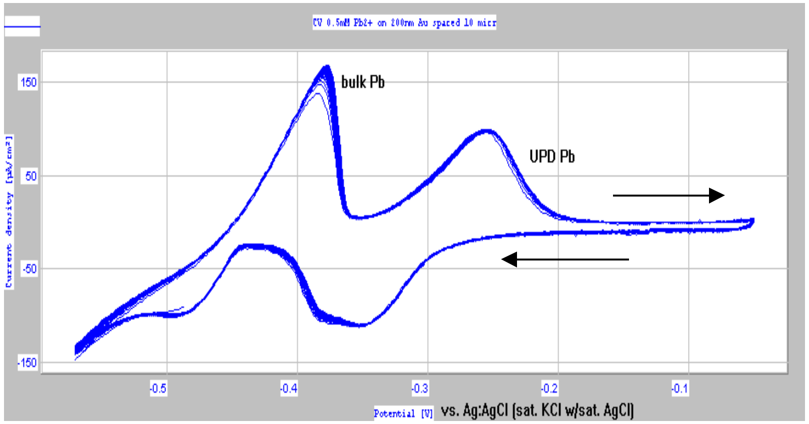
- **Fouled electrodes. On 5mm** (diameter) **gold electrodes two UPD peaks poorly visible.**
- **Sharp peaks clearly visible from polished and chemically activated electrodes.**
- **10 mV/sec, 100 cycles**
- **500 μ<u>M</u> Pb^{2+}. Reference vs. Ag:AgCl {sat. KCl/AgCl}.**

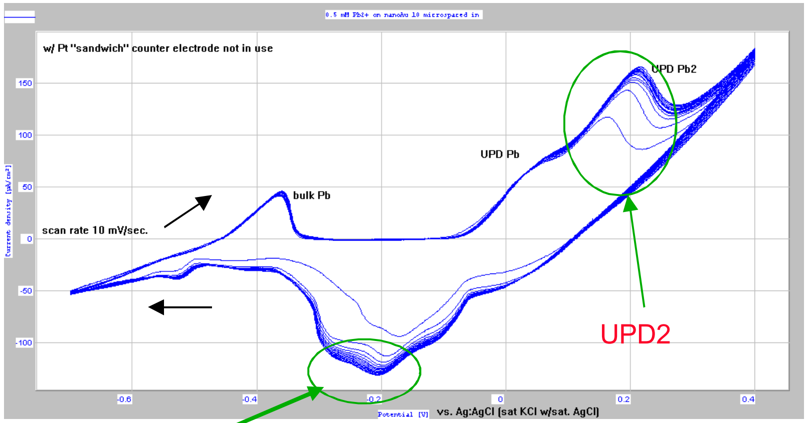




Au Nano **Electrode** Affinity for Trace Lead

- **CV scan of lead on Electrodeposited Au nanoelectrodes in *200 nm* pores with *10μ* spaced pores with same *5mm footprint*. ~3x signal increase.**
- **CV scan of lead on similar array with “sandwich” Pt counter electrode serving as a pre-concentration platform. Peaks are similar except for UPD2. Shift in peak locations for UPD.**
- **500 μM Pb^{2+}. Reference vs. Ag:AgCl {sat. KCl/AgCl}, 10 mV/sec.**





Larger reduction peak

Conclusions

- The diffusion limiting current due to edge effects dominates for electrodes with shapes below 10 um.
- For r<1 um, the diffusion limiting currents appear to have a "time independence" window.
- For nano-electrode arrays with micron spacing, the time-independent signals appear greater than the semi-infinite diffusion limiting current for macro electrodes with a similar foot print, but a fraction of the active electrode area.