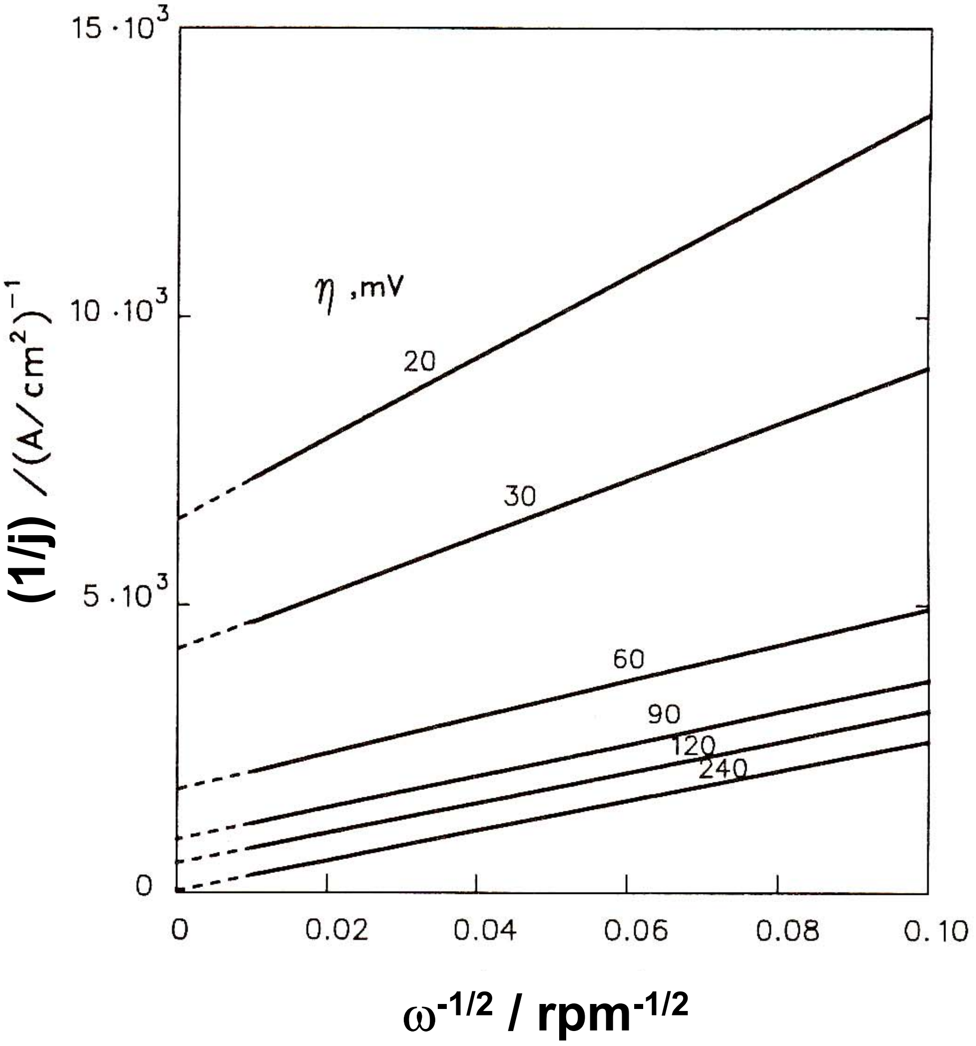
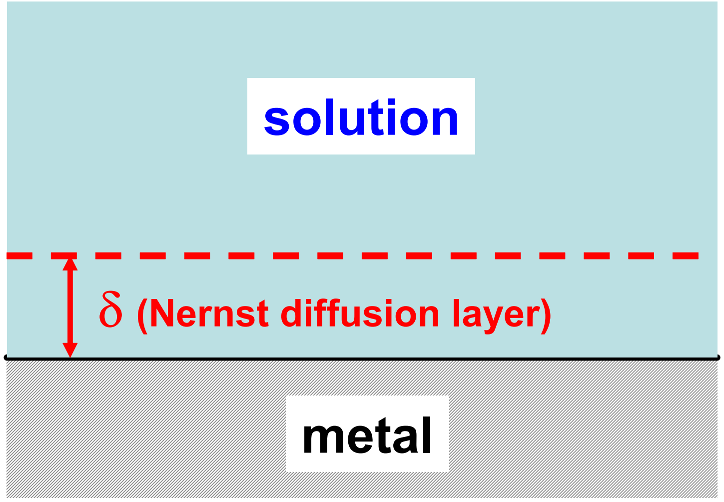
CHEM465/865, 2006-3, Lecture 25+56, Nov. 3, 2006

Hydrodynamic Electrodes and Microelectrodes



So far, we have always been considering (semi-)infinite systems! What does this mean?



- ❑ electrode surface is planar
- ❑ solution: infinite reservoir of electroactive species
- ❑ far away from electrode/solution interface: constant concentrations (bulk concentration)

In this situation:

one relevant length scale in the system →

thickness δ of the Nernst diffusion layer, thickness of the layer adjacent to the electrode in which concentrations deviate significantly from bulk concentrations.

Essentially, always the same basic competition

rate of the electrode reaction vs. rate of mass transport to the surface

k^0

$$k_{\text{diff}} = \frac{D}{\delta}$$

Want to understand how a certain electrochemical system would perform in an experiment? Start by having a look at the two relevant constants, k^0 and k_{diff}!!! This will tell you which process is the most important one.

- **Rate of reaction k^0: fixed (electrode material, crystallographic surface structure, solution, redox couple); range of variation: 10 cm/s to 10^{-14} cm/s!!.**
- **Diffusion coefficients: also fixed system; vary in narrow range, ~ 10^{-5} cm^2/s (aqueous solutions)**
- **Only parameter that you can somehow control: thickness of the diffusion layer, δ**

Hydrodynamic devices: control δ

Microelectrodes:

another length scale, the **radius of the electrode**

If you

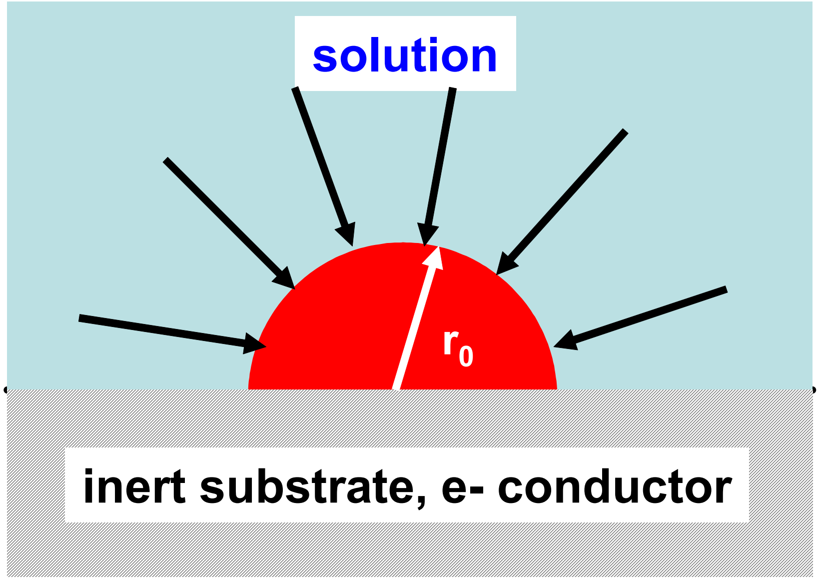
- understand these principles,
- know how to describe the corresponding phenomena (Butler-Volmer equation, diffusion-equation, convection, ...)
- know how to apply this to real systems (e.g. DME, RDE)
- know how to circumvent problems with mass transfer (control δ)

... then you have already a good understanding of some of the main topics in electrochemistry!

What is a microelectrode

Conventional definition: at least one dimensions < 25 μm

Consider: hemispherical electrode with radius r_0 .



What is the interplay of reaction and diffusion at such an electrode?

Diffusion of electroactive species (concentration c, spherical symmetry):

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right\}$$

(for definiteness: consider cathodic reaction)

Initial condition: $t = 0 \Rightarrow c = c^{\infty} \left(= c^{b}\right)$ uniform

Boundary conditions:

(1) far away: $t \geq 0 \Rightarrow c = c^{\infty}$ at $r \to \infty$

(2) at electrode surface:

balance of reactant fluxes:

activation controlled flux = diffusion controlled flux

$$t > 0 \Rightarrow \quad j_{\text{ac}} \quad = \quad j_{\text{diff}} \quad \text{at} \quad r = r_0$$

$$\Rightarrow nFk^0\, c(r,t)\Big|_{r=r_0} \exp\left(-\frac{(1-\alpha)F\left(E - E^0\right)}{RT}\right) = nFD\frac{\partial c}{\partial r}\Big|_{r=r_0}$$

$$\Rightarrow \quad \kappa\, c(r,t)\Big|_{r=r_0} = \frac{\partial c}{\partial r}\Big|_{r=r_0}$$

We introduced a parameter

$$\kappa = \frac{k^0}{D}\exp\left(-\frac{(1-\alpha)F\left(E-E^0\right)}{RT}\right)$$

which is a ratio of the corresponding rates.

Mathematical manipulations → exact solution for the concentration as a function of r and t :

Eq. (#)

$$\frac{c(r,t)}{c^\infty}=1-\frac{r_0}{r}\frac{\kappa r_0}{1+\kappa r_0}\left\{\text{erfc}\left(\frac{r-r_0}{\sqrt{4Dt}}\right)-\exp\left(\frac{r-r_0}{r_0}(1+\kappa r_0)+(1+\kappa r_0)^2\frac{Dt}{r_0{}^2}\right)\text{erfc}\left(\frac{r-r_0}{\sqrt{4Dt}}+(1+\kappa r_0)\sqrt{\frac{Dt}{r_0{}^2}}\right)\right\}$$

This looks ugly, but you can use it under all conditions!

It’s the general solution (reaction + diffusion).

Cathodic current:

Eq.(##)

$$j = -j^C = nFD\kappa\, c(r,t)\big|_{r=r_0}$$

$$= \frac{nFDc^\infty}{r_0}\left\{\frac{\kappa r_0}{1+\kappa r_0} + \frac{(\kappa r_0)^2}{1+\kappa r_0}\exp\left((1+\kappa r_0)^2\frac{Dt}{r_0^{\,2}}\right)\mathrm{erfc}\left((1+\kappa r_0)\sqrt{\frac{Dt}{r_0^{\,2}}}\right)\right\}$$

Depends on κ, D, r_0, **and** t

Eqs.(#) and (##): valid for arbitrary κ **(and thus** E**).**

Recall:

- **Planar electrode: time-dependence of the diffusion limited current density given by Cottrell-equation**
- **Current density** j_{diff}**: decreases continuously with time, never reaching a steady state value**

Reaction and diffusion at spherical electrode:

steady state solution exists!

Limit $t \to \infty$ **in Eq.(##)** → **steady state current density**

$$j_{\text{ss}} = \frac{nFDc^\infty}{r_0}\frac{\kappa r_0}{1+\kappa r_0}$$

Do we get the correct limiting cases? How large is j_{ss} for different values of κr_0?

- $\kappa r_0 << 1$ (limitations prevail):

$$j_{ss}^{\bullet\kappa r_0 <<1} = nFk^0c^\infty \exp\left(-\frac{(1-\alpha)F\left(E-E^0\right)}{RT}\right)$$

  i.e. we get the well known Butler-Volmer case, diffusion limitations not important – expected result!

- $\kappa r_0 >> 1$ (limitations prevail):

$$j_{ss}^{\bullet\kappa r_0 >>1} = \frac{nFDc^\infty}{r_0}$$

  i.e. we get the diffusion-limited current density at a spherical electrode – expected and correct!

The general equation reproduces the correct limiting case – we can have some confidence, that it is correct!

You see that r_0 is the characteristic length scale!

Next, let's consider when the time is finite, but large. How does the system approach the steady state?

First let's consider another question:

In this context, when can we say "t is large"?

"Large time" means that the argument of the "exp" and "erfc" functions in Eq.(##) should be large,

$$\left(1+\kappa r_0\right)^2 \frac{Dt}{r_0{}^2} >> 1 \Rightarrow t >> \frac{r_0{}^2}{D\left(1+\kappa r_0\right)^2}$$

The latter criterion will be always fulfilled, as long as

$$t >> \frac{r_0{}^2}{D}$$

This is the condition of "large t".

Depends on diffusion coefficient and electrode radius.

Example:

Radius $r_0 = 1\ \mu\text{m}$ and diffusion coefficient $D \approx 10^{-5}\,\text{cm}^2\text{s}^{-1}$

$\Rightarrow$ "large t" means

$$t >> 10^{-3}\,s$$

Now, what is the correction to the steady state solution for large, but finite t?

We get

$$j = j_{ss}\left\{1 + \frac{\kappa r_0}{1+\kappa r_0}\frac{r_0}{\sqrt{\pi D t}}\right\}$$

- $\kappa r_0 << 1$ (**limitations are most severe):** **correction due to finite time is insignificant**
- $\kappa r_0 >> 1$ (**limitations are most severe):** **we get**

$$\boxed{j_{ss}^{\kappa r_0 >> 1} = nFDc^{\infty}\left\{\frac{1}{\sqrt{\pi D t}} + \frac{1}{r_0}\right\}}$$

This is the result that you will usually find in the textbooks.

- **Short times: spherical diffusion resembles the solution for planar diffusion (Cottrell equation)**
- **At times** $t >> \frac{r_0^{\,2}}{\pi D}$ **for which** $\delta >> r_0$ **: finite size of the electrode matters – steady state solution**

Table: diffusion-limited current densities for various electrode sizes in the μm and sub-μm range

$D = 2.0 \cdot 10^{-5}$ cm^{2}s^{-1}, $c_{ox}^{b} = 0.01$ mol l^{-1}, $n = 1$

r_0 / μm	$t_0 = \frac{r_0^{\,2}}{\pi D}$ / s	$j_{\mathrm{diff}} = \frac{nFDc_{\mathrm{ox}}^{\mathrm{b}}}{r_0}$ / Acm^{-2}
100	1.6	$2.0 \cdot 10^{-3}$
1	$1.6 \cdot 10^{-4}$	0.2
0.01	$1.6 \cdot 10^{-8}$	20

Small electrodes:

- large diffusion-limited current densities, steady state rapidly reached
- wide range over which current-potential relationships can be obtained under activation-controlled conditions

Why does the spherical electrode have a steady state?

Diffusion layer grows in thickness with t, but volume from which reactant in solution is drawn grows faster than δ

Microelectrode-Arrays

Advantage of microelectrodes:

- ☐ **large limiting current density**
- ☐ **controlled by radius r_0**
- ☐ **microelectrodes with radii $r_0 = 25 - 0.25\ \mu\mathrm{m}$ can be easily prepared**
- ☐ **larger current densities and overvoltages can be studied with them compared for instance to RDEs**

Disadvantage: tiny currents that have to be detected!

Consider:

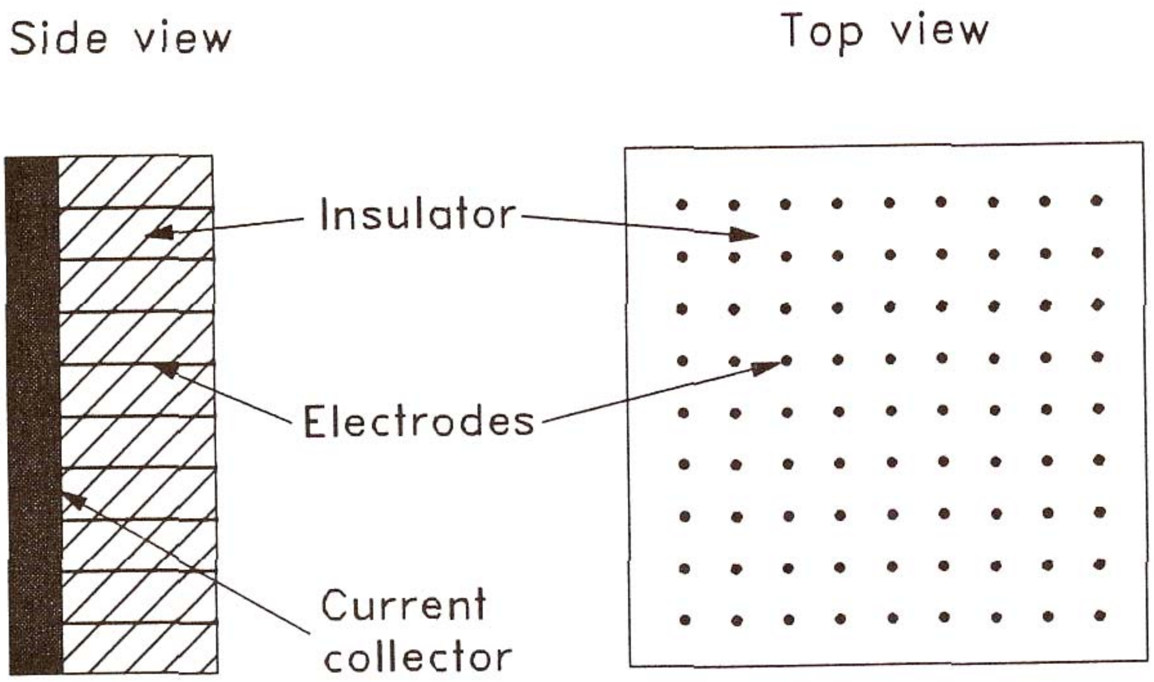
hemispherical electrode with $r_0 = 1\ \mu\mathrm{m}$ at $j = 1\ \mathrm{mA\ cm^{-2}}$

→ total current to be detected is $I = jA_s = j2\pi r_0^2 = 63\ \mathrm{pA}$!!!

Measurable with modern equipment, but difficult and poor signal-to-noise ratio.

Solution: arrays of microelectrodes

Individual electrodes isolated from each other at the electrode|solution interface, but connected to a common current collector.



Two geometric length scales:

- **radius of each electrode,** r_0
- **separation between electrodes,** L

Consider (again…): mass transport and reaction

Equations (BV and diffusion) could be formulated as before.

Here, let's consider only a qualitative discussion.

Question to start with: How large is the diffusion-length δ **compared to** r_0 **and** L**?**

Three cases can be distinguished:

- $\delta \le 0.3 r_0$: diffusion similar to planar diffusion at individual microelectrode; diffusion layers not overlapping; diffusion fields only exist in close proximity of microelectrodes.

  Diffusion-limited current density

  $$j_{\text{diff}}(t) = nFc^{\infty}\sqrt{\frac{D}{\pi t}}\left(\frac{2\pi r_0{}^2}{L^2}\right)$$ Cottrell-equation

  Includes real-to-apparent surface area ratio: surface area $2\pi r_0{}^2$ of one hemispherical electrode per surface area L^2 of substrate).

- $3r_0 < \delta \le 0.3L$: spherical diffusion to individual microelectrodes, no overlap of diffusion fields. Diffusion-limited current density

  $$j_{\text{diff}}(t) = \frac{nFDc^{\infty}}{r_0}\left(\frac{2\pi r_0{}^2}{L^2}\right)$$

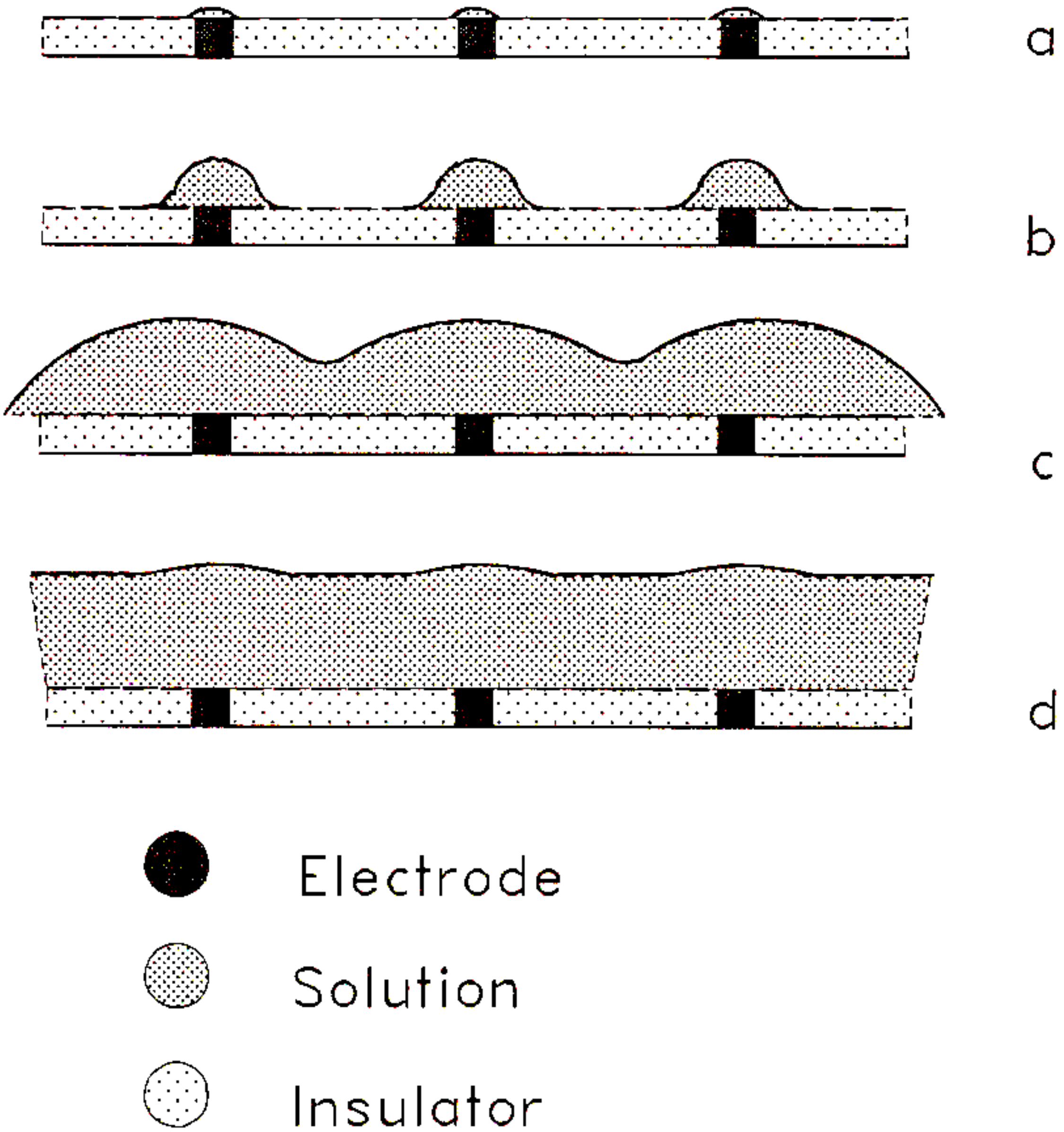
- $3L \le \delta$: overlap of diffusion layers of the electrodes; individual electrodes not resolved!

  → expression for planar diffusion, involving full surface of the substrate,

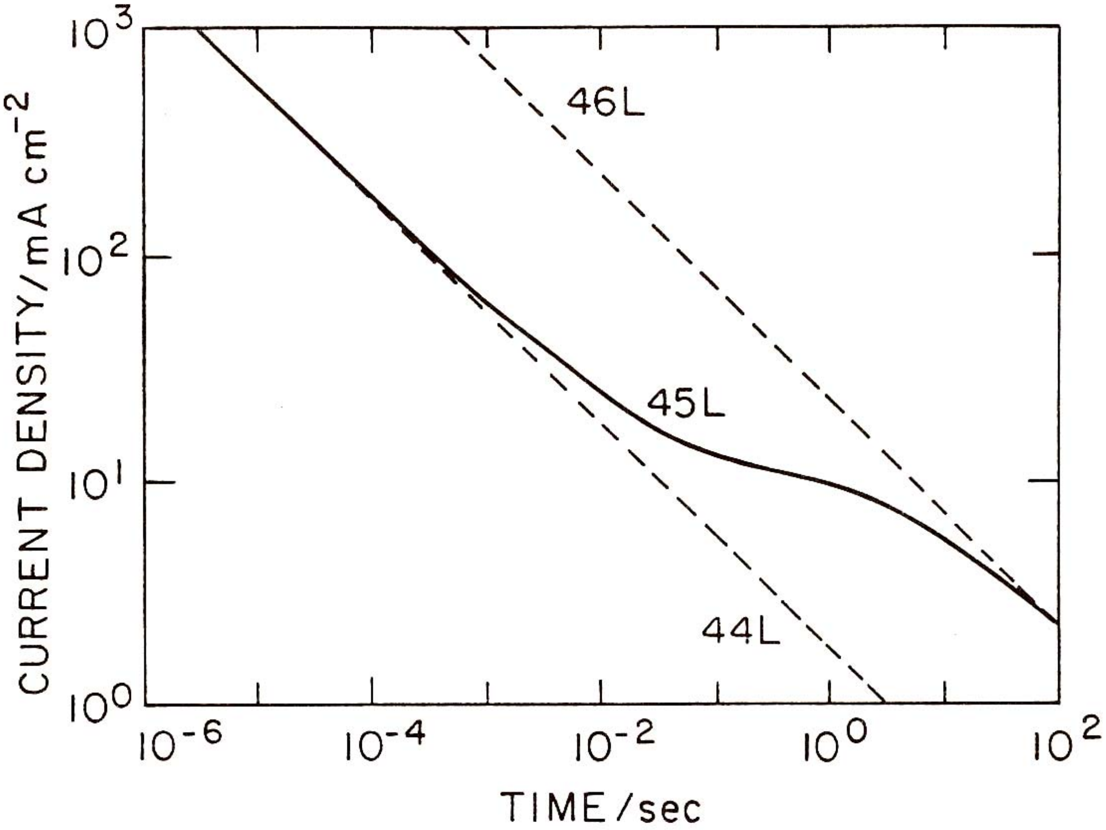
  $$j_{\text{diff}}(t) = nFc^{\infty}\sqrt{\frac{D}{\pi t}}$$

Interesting interplay of surface geometry and kinetics!

Time-evolution of the diffusion field is shown in the subsequent figure



Variation of diffusion-limited current density with time



Summary: microelectrode arrays achieve tradeoff between two objectives:

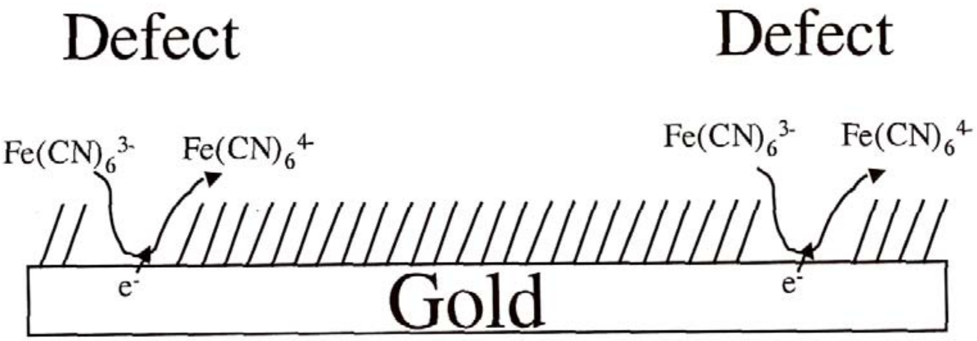
1. **large electrode surface area (large currents) – large ratio r_0/L**
2. **small overlap of diffusion fields of individual microelectrodes, i.e. utilize the advantage of the small electrode size – small ratio r_0/L**

In practice, the following range is a reasonable choice:

$\frac{r_0}{L} \sim 0.03 - 0.1 \Rightarrow$ **active area 0.1–1% of total surface area**

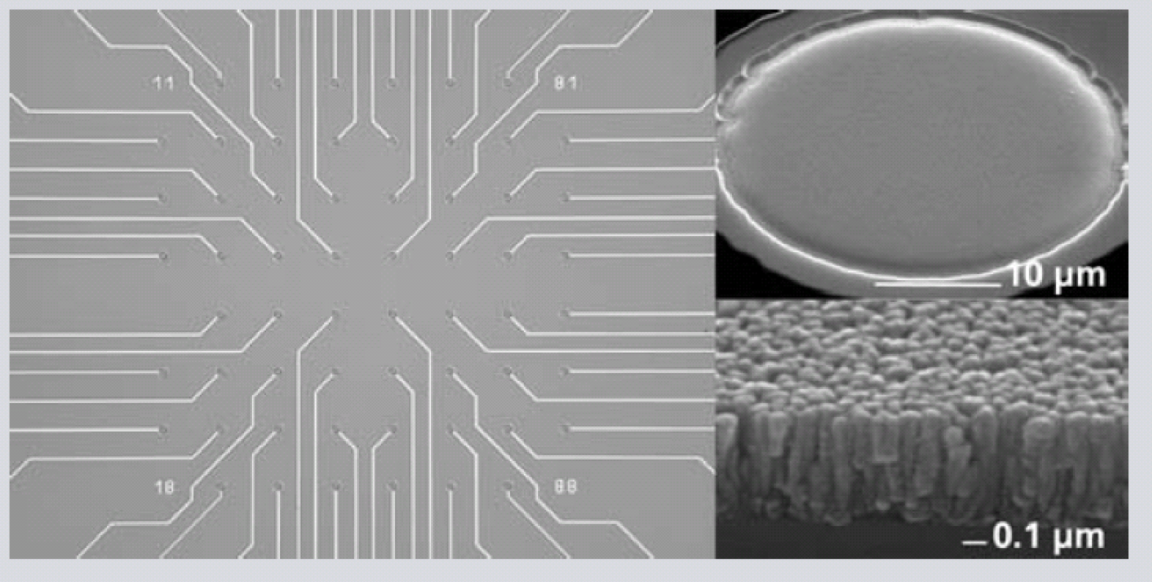
Applications of Microelectrode Arrays

- **defects in self-assembled monolayers on metal electrodes**

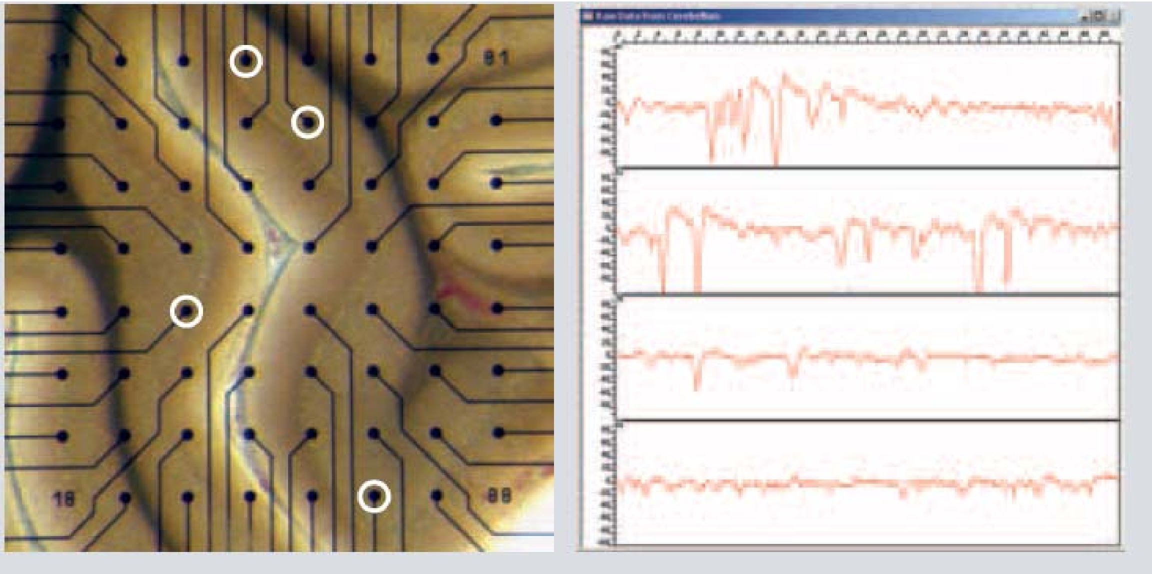


Electron transfer: only at the defects, not at monolayer-coated areas

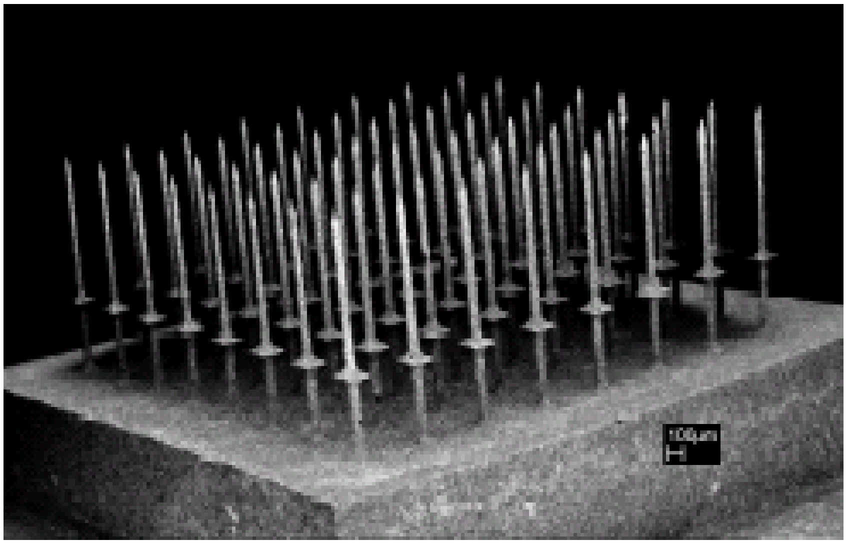
- **neurophysiology and pharmacology**
- **electrical activities and responses to stimuli of cells and tissues**
- ***in vitro* studies on neurons, heart cells, retina, or muscle cells**
- **study spatio-temporal pattern of responses**
- **about 60 – 120 individually addressable electrodes, each with diameter of ~10 μm**
- **fabrication: e.g. using photolithography**



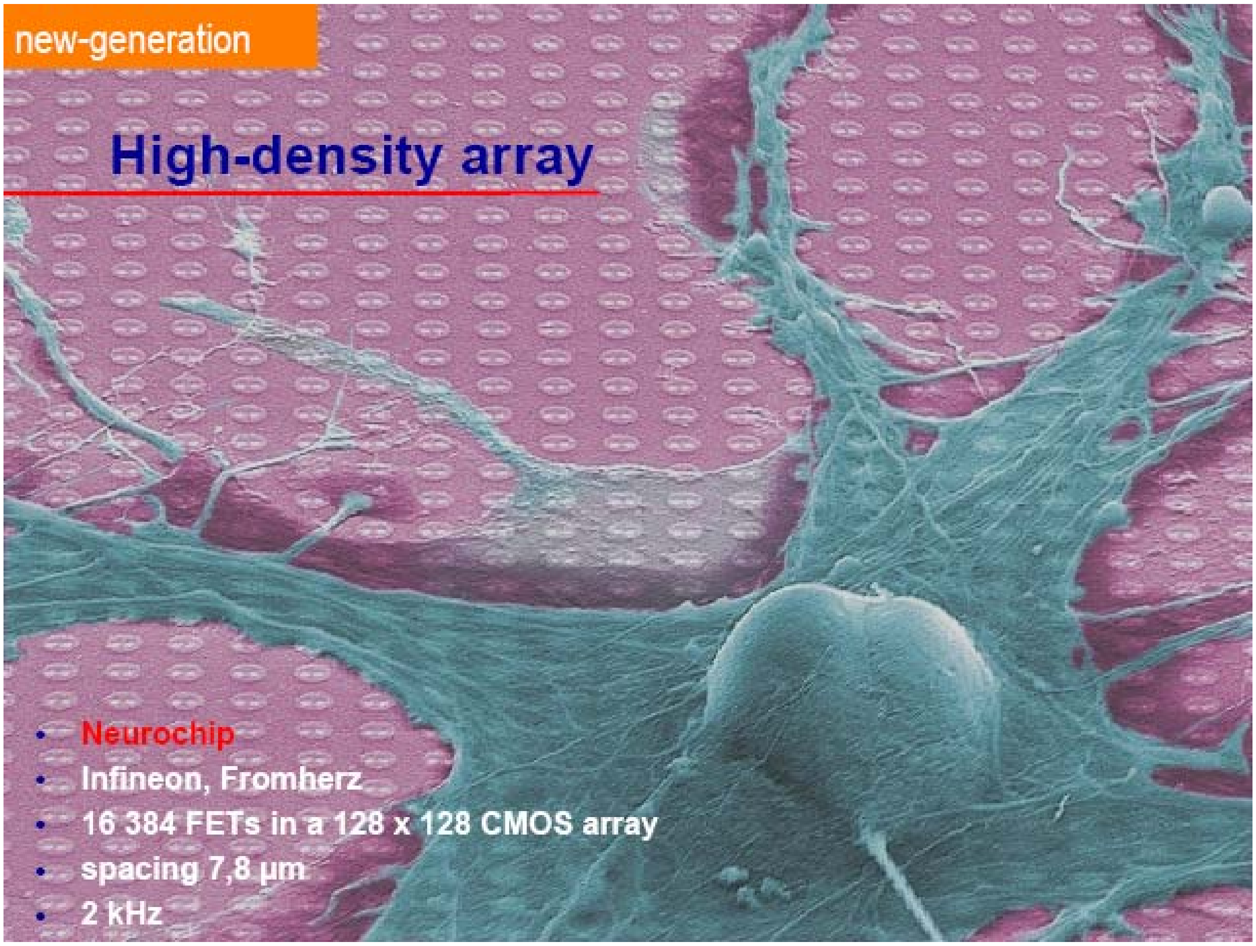
(diameter: ~10 μm, center to center distance ~100 μm, substrate integrated 8x8 array)



(acute slice of cerebellum, electrical response at highlighted points)



(electrical discharge machined microelectrode array)



new-generation

High-density array

- Neurochip
- Infineon, Fromherz
- 16 384 FETs in a 128 x 128 CMOS array
- spacing 7,8 µm
- 2 kHz