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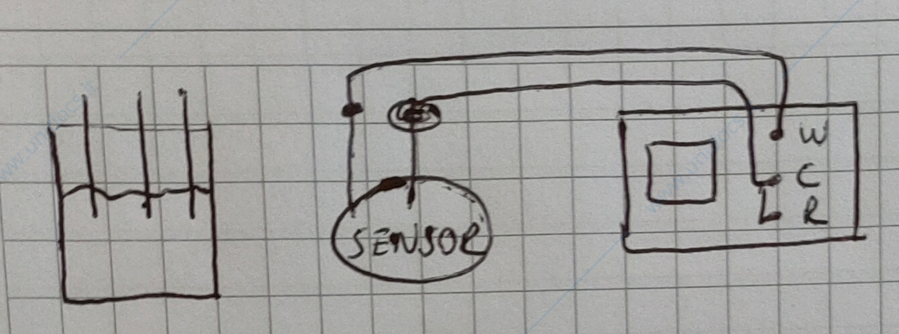
Biosensors Arbizzani 27.10.2022

In some cases, we work with 2 electrodes and in this case, we must use the auxiliary electrode also as the reference electrode, so with voltammetry to measure the potential. You need only a place in which you can put your cable and if you have one of the working electrodes and the other reference electrode, there are no problems. Using the equipment that I showed you last lesson, meaning the potentiostat and galvanostat, usually you have at least 3 places in which you have to put your terminal. One for the working, one for the counter and one for the electrode. What if you have only 2 electrodes like in the Clark cell? You have only 2 electrodes and only 2 terminals. In this case there are no problems, since all the electronics have been developed for that, but if you have other kinds of electrodes, you must try to put your cable in the instrument.



How can I perform the connection between the two? *(First figure)* If I try to do the experiment with the right configuration, the instrument gives error. The instrument will give a message in which it asks for a reference, so at this point what can I do? I simply try to make an external connection between the reference and counter. In this way the instrument knows that there is a reference so there is no problem, and from my side I know that this counter electrode is also used as a reference electrode. For this reason, usually the counter electrode of most sensors is the Ag/AgCl electrode that is also called reference electrode or simply Ag wire. In this case, we can use this also as a reference electrode. Also, for cyclic voltammetry, the use of 3 electrodes is more important, and in the case of cyclic voltammetry – this is a technique that is used specially in lab experiments – I can have a printed screen electrode, a cell with microelectrodes, and I can use the working counter and the reference as well.

Chronoamperometry is obtained by applying a potential, which is a potential in which a reaction occurs, and this reaction should be the one that I am interested in. At this point I can record the current and, as said last time, this current is a mixed current due to Faraday's reaction, but also a current that is due to the separation of the charge that always occurs to every electrode. So, the only way to separate these two kinds of charges is time, because the Faraday current decreases with the square root of vt, and the capacity of current decreases as exponential function of time *(second figure)*. At this point I have two different decreases over time: the very steep decrease of the capacity and the less abrupt decrease of the Faraday; at this point, when I measure the total current, I am sure that after a certain time, I will have only the Faraday current because the capacity current is "eliminated". These are very short times, in the order of milliseconds and even shorter, so usually there are no problems in separating this current if I take the signal after a certain

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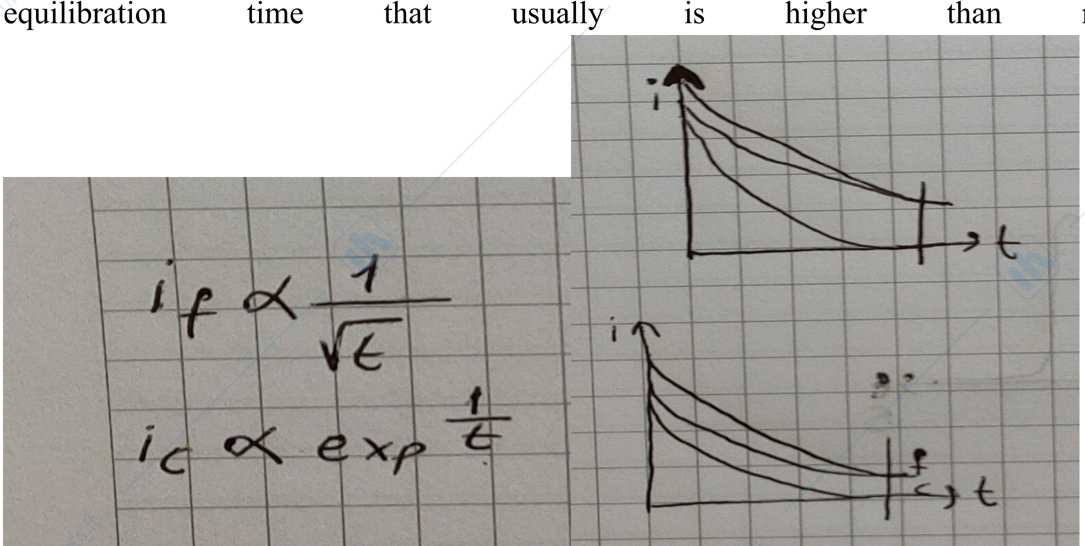
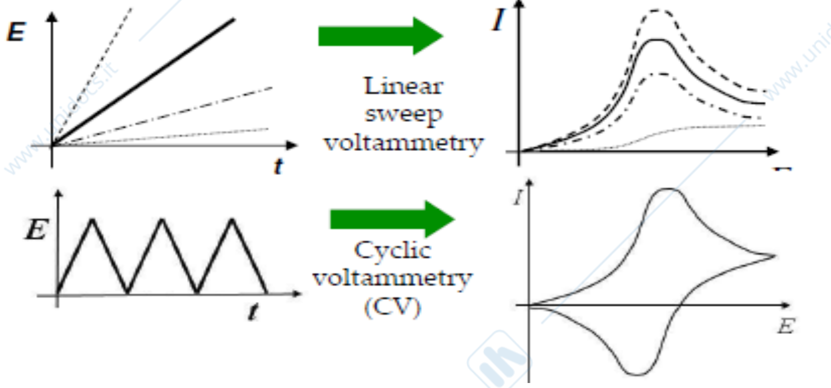
equilibration time that usually is higher than milliseconds.



These are **stationary steady state experiments**, because I apply a potential, and I wait for a situation that is someway steady. When I work with voltammetry, I am in a dynamic situation because the system is evolving during the experiment. Also, in this experiment I start at the point in which nothing happens, then when I increase the potential, and the potential will increase with the linear function of time, I have constant scan rate on this voltammetry, and I see that the signal of the current is increasing. It arrives at a maximum and this maximum indicates the maximum concentration and maximum rate that I can have in my system. After that the response decreases. What happens? It happens what we have seen also in the case of the application of a potential. The concentration of the species that is on the electrode decreases and this is the max rate of exchange of the species. But if I go at a higher potential, I force more of the system to react more, but the diffusion of the species that should react at the electrode is too low and these species arrive on the electrode with a certain slowness, so there is a decrease in the current. So, they arrive but the concentration is not so high and decreases.



In the first picture, there is a **linear sweep voltammetry**, which means that I start from a certain point of potential (I). The voltage over time increases linearly in the scan rate at a certain value. So, you have a high scan rate. For the high scan rate, I have also a response that is increasing, so the current is higher.

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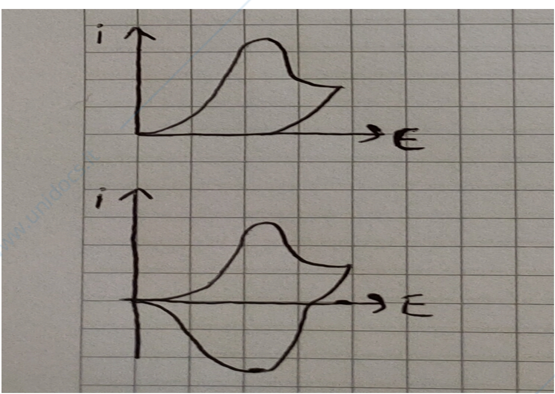
The **cyclic voltammetry** in the figure means that when I arrive at the end of the linear sweep, I come back to the initial value. At this point the curve and the signal come back and the final point is the initial point. In this case it is a positive slope because you go to a higher potential and then it is the opposite slope because you come back to a lower potential. You can see that you have one process here and another process here on the curve graph, this means when you go to higher potential, you oxidize your species, and when you come back, you reduce what you have produced, so you start from species that can be oxidizes, they are oxidized, and here it remains in the oxidation state so you can record the response of the species and you can reduce your species, as it was in the beginning.



I can also have response like this one without the potential. What happens here? The oxidized species that are formed here are not stable so what you have oxidizes could be a gas formation, so you have gas production, or you have some species that precipitate and are not electrochemical reactive. In some cases when you come back, you are not able to see the response, so it means at this potential you have no more initial system and someway you have irreversible transformation. It is important to know this so you can know your system.

Detailed Explanation of it

You start with reduced species. At the top you have oxidation and then you have oxidated species. On the bottom it reduces again and comes back at the beginning. You can do this process any time you want. It is a reversible process. In the other case, you arrive here but at the very end, you cannot go back to the initial system. So, these species are something that remains in solution; they could be non-electroactive species or something that goes out of your system, like a gas, or precipitates and it is no longer reactive. Also, you can have passivation of your electrode, like something that reacts and deposits on your electrode, and in that case, it is your electrode that is no longer able to fill something in the solution because it is covered of a layer that is totally not conductive.

The graph on the bottom is a reverse reaction, whereas on the top is not reverse.

It is useful for cyclic voltammetry because with chronoamperometry, if you put your system at this potential, you see that reaction occurring, but you do not know anything about the stability of what you have produced. In the case of a biosensor, you are probably not interested in this because you only want to know the amount of your analyte in the solution, so you do not care if it is a

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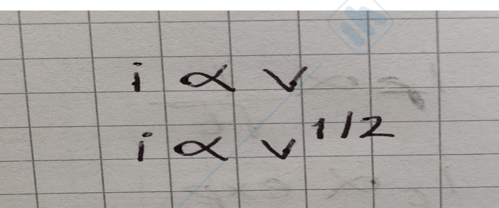
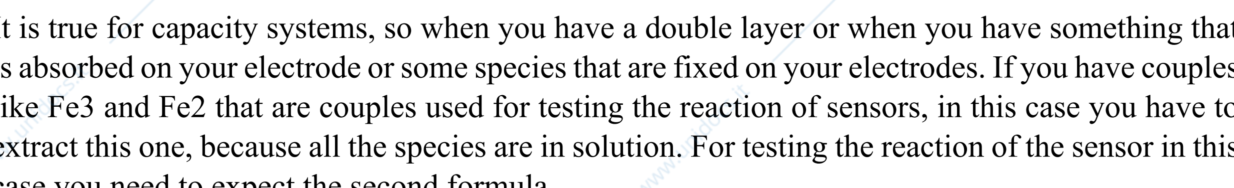
reversible or irreversible reaction, and so on. But if you study some reactions because you want to produce a better sensor, you need to do something like this.

You do not have a linear increase since this is only for reactions occurring in solution, i.e., when you have your analyte dissolved in solution. If you have something on the electrode, and in most cases, it happens, the first formula is true.



It is true for capacity systems, so when you have a double layer or when you have something that is absorbed on your electrode or some species that are fixed on your electrodes. If you have couples like Fe3 and Fe2 that are couples used for testing the reaction of sensors, in this case you have to extract this one, because all the species are in solution. For testing the reaction of the sensor in this case you need to expect the second formula.



There are two main conventions that are the IUPAC convention and the America convention. The **IUPAC convention** places the anodic current, the positive current and the positive potential in the first quadrant. The **American** one is different because you have the reduction, so the negative current, and your potential is increasing but in the negative sense, so you have minus numbers, thus in this case this would be a reduction process. Reduction at the end. The worst is when the two conventions are mixed, because you do not really understand which is the anodic process, the oxidation, the reduction, the sign of the current, and so on.

Note from the teacher: She tries to use the IUPAC in this course but unfortunately, she has to take a lot of figures from American text, and it was not possible to change the picture.

What is the information I take from cyclic voltammetry? From this kind of voltammetry, I get qualitative info given by the potential, because each species that reacts, reacts at a specific potential. I can recognize the different reaction occurring in my system, and I can also have quantitative info related to the current or simply to the area. When do I describe cyclic voltammetry in terms of time?

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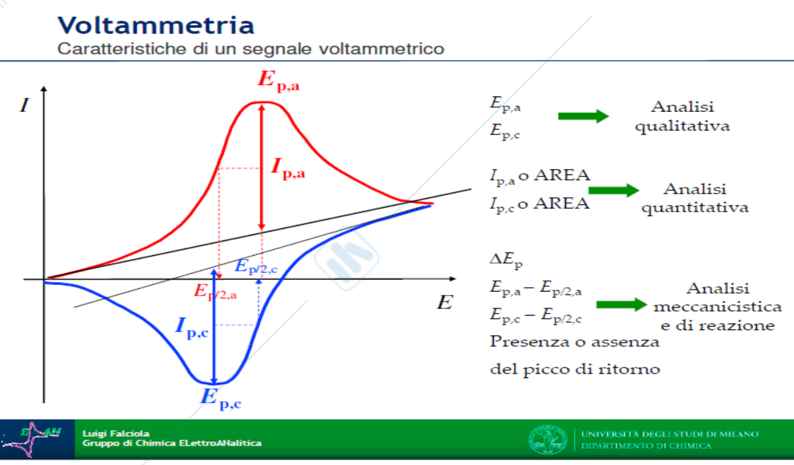

If I have cyclic voltammetry, instead of the voltage I put time on the graph. If it is cyclic voltammetry, I see this one. Time is directly related to the potential, and you can do the integral of the area under, all the area that is at the current that is positive, because in this way you consider the part that is coming back to reach the negative current. The second graph little part is also counted. All this part contributed to the oxidation; until you have a positive current, you have oxidation. Your oxidation stops at the end. Then you have a reduction, because the current changes the sign. While coming back the current changes to negative so it reduces. The current multiplied by time gives a charge, so it is quantitative information because you know how many Columbs are involved in your reaction, and the charge involved is directly proportional to the amount of your analyte.

The current is a little bit difficult to validate. The evaluation of the current should be done after you have removed the base line. First you need to find the base line and subtract the value of the base line to your current. An example: if you want to know the anodic current here, this is not simply the height of the peak, because the peak is not finishing at zero but at the end. So, you must do a base line starting from the beginning, which is tangent to the initial part of the cyclic voltammetry, and in the middle part you must subtract the system (effective current of your system). The same is for the reduction peak. First you see that you must take the base line starting from the turnout rate step and this is the peak cathodic reaction (the bottom blue is the peak). Thus, just to do the area is easy in order to have a quantitative idea of the system.

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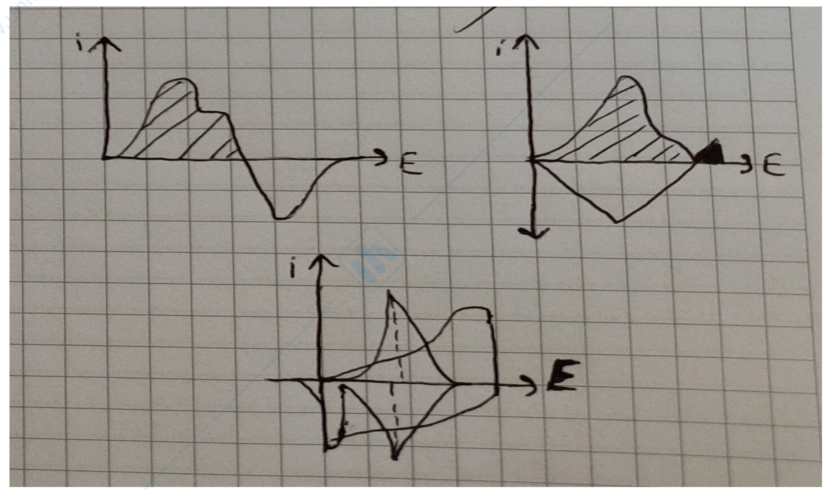
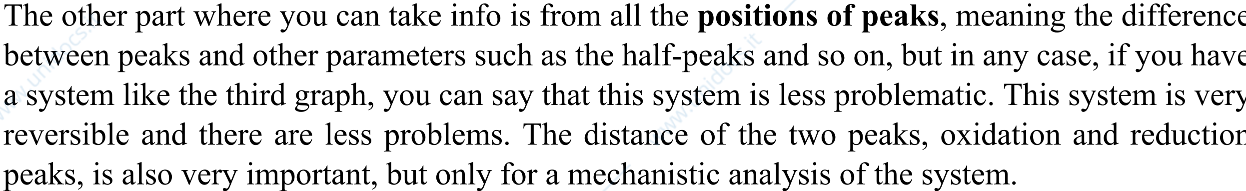


The other part where you can take info is from all the **positions of peaks**, meaning the difference between peaks and other parameters such as the half-peaks and so on, but in any case, if you have a system like the third graph, you can say that this system is less problematic. This system is very reversible and there are less problems. The distance of the two peaks, oxidation and reduction peaks, is also very important, but only for a mechanistic analysis of the system.

In the case of reversible electrochemical processes in semi-infinite diffusion conditions, the peak current intensity is proportional to the square root of the scan rate by the Randles-Sevcik equation:



$$i_p = 0.4463\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A D_O^{1/2} C_O^* v^{1/2}$$

We have an expression of the peak current in function of several parameters, such as Faraday constant, gas constant, temperature, the number of electrons, area, while the last part is related to the diffusion, so there are the parameters related to diffusion. We have the concentration of the oxidized species, and in this case this reaction is a reduction reaction. Then v is the scan rate. The square root of the scan rate is for systems that have the species in solution. When I have substances that are absorbed or deposited on the surface of the electrode, the peak current will be proportional to v instead of $v^{1/2}$. The diffusion coefficient is inside the reaction. In the case of chronoamperometry, we also have diffusion coefficient because the species should arrive at the electrode and should react, specifically if the system is not steep.

When we use a linear square voltammetry, we know that the limit of the concentration we can detect is not very low, since we arrive at 10^(-5)-10^(-6) M. We have separability of 1-400, which means that if you have 2 species and you have signals that are near, you can see the two species only if the concentration of one is not 400 more than the concentration of the other. You have good separability in this way. The resolution is usually 40-50 mV, which means that if you have two signals, two species that we add in the voltage range, you can detect quite well the two peaks, but you can also have something in which you cannot quite well distinguish them and understand what the potential is, or in the worst case you cannot determine at all if there is a species. Of course, in

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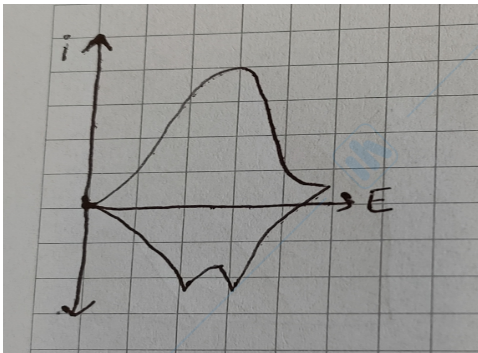
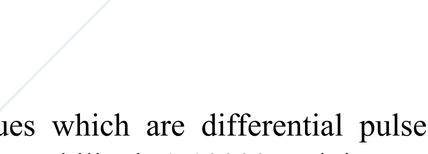
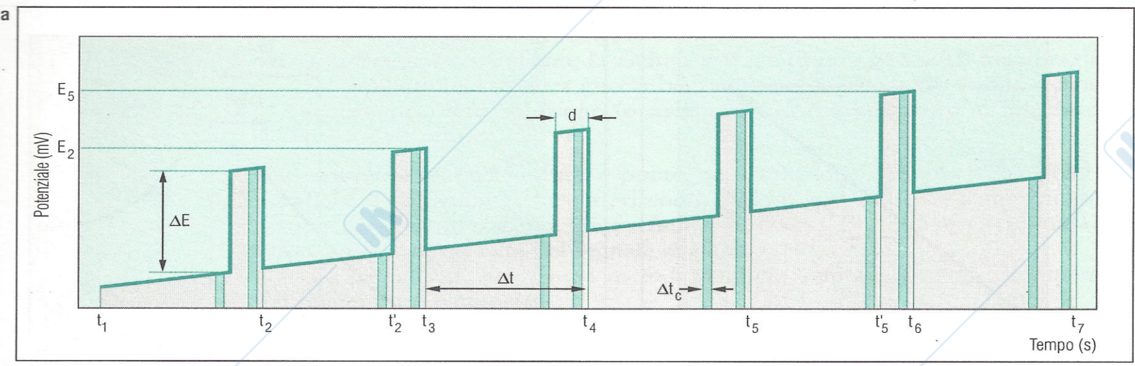
this case, if you have a difference in concentrations of your species, you can have the separability of the peaks, otherwise there is not this possibility.





To have better separability, we must use the pulse techniques which are differential pulse voltammetry and square wave voltammetry. In these cases, the separability is 1-10000, so it is very high. The resolution is the same, but it will decrease a lot the detection need.

Differential Pulse Voltammetry (DPV)



The concept is the same. I have (usually) linear voltammetry. I start from potential. I arrive to another potential with the scan rate that is linear, so 20 mV per second or even one or two volt per second. The difference is that during the scanning I perform some very short pulses, not very high in potential. The difference in potential is around 5-50mv. These are at the regular time and the pulse time is 40-60 ms, so very short. This pulse is repeated every 0.5-5 seconds. During this voltammetry your reaction occurs normally, but during the pulse you have a different response. First, I must know where I must take the signal of the current because in the other case, I know that I must evaluate the voltammetry, take the peak, and I can have all info I want. But here I obtain the same peak, but it is a little bit different because I do not consider the total current but the difference in the current with each pulse. The two values that I consider are the first (green) value before the pulse and the last after the pulse. Thus, I take these two values for each pulse, and I do the difference. At the end I can have a plot dv and e graph. I have these kinds of results: very sharp peak that starts at d near 0 and finishes at near 0 with a very good shape. This is very interesting because I increase the separability a lot.

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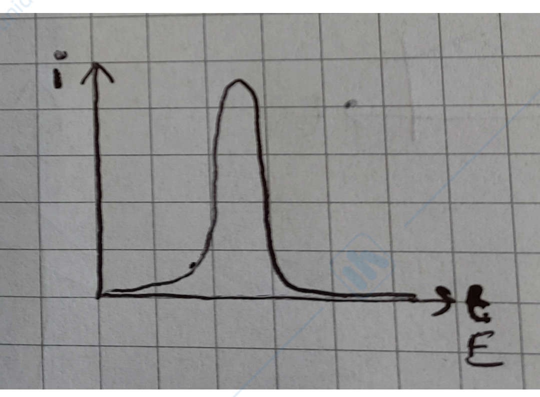

In the first current, nothing happens at the third green graph. I have the first point similar to the second one. The Faraday current is 0 in both cases before and after the pulse. Also, I totally eliminate the capacity current. When I am in point 5, I take the value where I have no pulses, so I have simply the value of the current at that specific potential. When I do the pulse, the current increases because I give a positive pulse and then decrease. If I take the current at the very end, it is the Faraday current, and it should be a little bit higher than the first one, because the potential is higher. So, increasing the potential increases also the current.

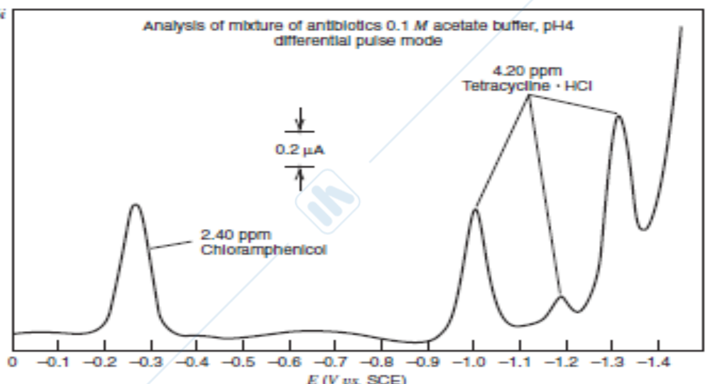

Figure 7.3.19 Differential pulse polarogram for a mixture of tetracycline and chloramphenicol. $\Delta E = -25$ mV. [From Application Note AN-111, EG&G Princeton Applied Research, Princeton, NJ, with permission.]

Here you have emiction of antibiotics. You can see the 3 different kinds of responses from tetracycline and chloramphenicol.

Square Wave Voltammetry (SWV)

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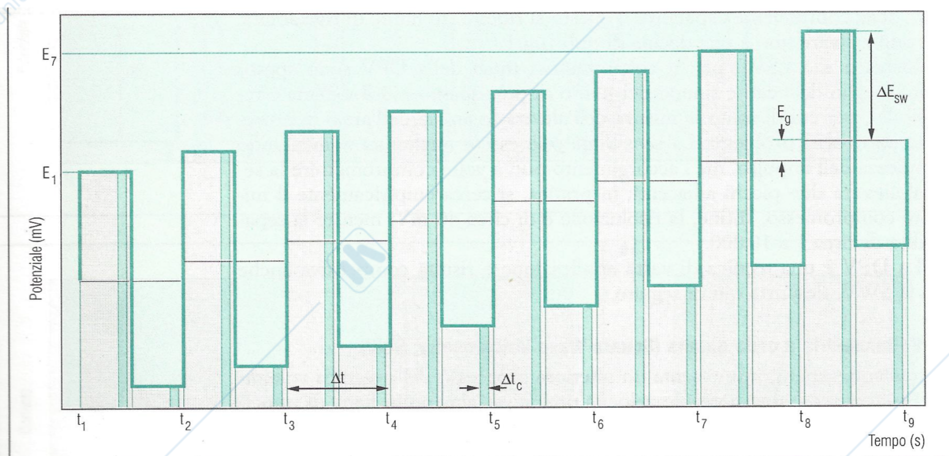
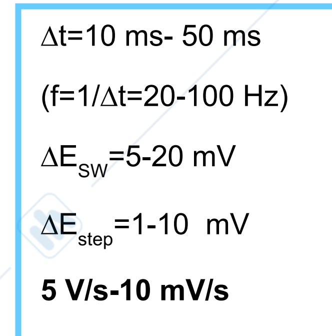
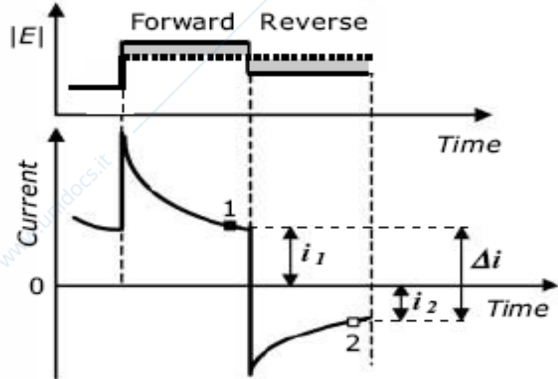




The square wave is very similar to pulse voltammetry. The only difference is that you apply a pulse in the higher and little bit lower potential. Then you have your linear increase, and you apply a small square wave voltage and, after that, a small square wave in the opposite direction. So, the time is the same, meaning the direction of the course and the interval of the course are the same as in the other. What has changed? It changes the point at which I take the current. Even in this case it is a delta, so a difference, and I have the same kind of response, but I take the points at the end of the positive pulse and at the end of the negative pulse. If I do the difference, given that in one case I have a positive current and in the other I have a negative current, it will give the doubling of the current, because you have a positive current minus minus another part of the current, and the values are similar. So, you double your signal, and this is the reason why the square wave voltammetry is more sensitive than the other one because you double your current signal. In one case you increase the work process, but if you apply the current in the other sense, you decrease your current and you provoke the reverse reaction. So, you have these 2 kinds of current profiles.



We can see that the difference in current is shown as a negative current, but this depends only on the signs of the currents according to the two different conventions used. Still, you can see that the response is very similar to the other. You can also see that the two currents are not the same: you have one current that is for the forward reaction (i1) and another current for the backward reaction (i2). i1 (forward) is higher than i2 (reverse) in absolute value. Why is there this difference between the two currents? Why is the forward current higher than the reverse current for all the points? Why is the reverse current always a little bit lower than the other? The reason (apart from the sign)

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is because we produce something near the electrode – there is the increase production of the species – and with this current you consume the species, but it could happen that part of species go far from the electrode, because your reaction occurs in the same electrode, so you produce something; when a certain current occurs, you have production of your species and some of these species that you have produced are no more near the electrode, and with the reverse reaction you can re-oxidize just that part, because the others are far from the electrode, even if you have a very short time.

Case Study 2

ZnO Nanowire Arrays on 3D Hierachical Graphene Foam: Biomarker Detection of Parkinson's Disease

Hong Yan Yue,[†,‡,§,#] Shuo Huang,[⊥,#] Jian Chang,[†,‡] Chaejeong Heo,[‖] Fei Yao,[†,‡] Subash Adhikari,[†,‡] Fethullah Gunes,[‡] Li Chun Liu,[‡] Tae Hoon Lee,[†,‡] Eung Seok Oh,[¶] Bing Li,[†,‡] Jian Jiao Zhang,[§] Ta Quang Huy,[†,‡] Nguyen Van Luan,[†,‡] and Young Hee Lee[†,‡,*]

They wanted to detect specific biomarkers that are uric acid (UA) and dopamine (DA). They also detected ascorbic acid (AA), which is always present and could have interfered with the electrochemical behavior of the two biomarkers. The technique they selected was the **differential pulse voltammetry**. They wanted to improve the electrode in terms of conductivity, to make the reaction faster, and in terms of area, for which they tried to increase the area of the electrode. They made a specific design for the electrode, using an **ITO (indium tin oxide) glass**. This is a very specific glass, and the ITO layer is a very conductive layer. They add, to this glass, **3D structures of graphene**, which also facilitate the diffusion and the conductivity. They also enrich these structures of graphene with **zinc oxide**, which helps increase the surface area of the electrode. Thus, the key features for the structural design are:

- large surface area with 3D graphene structures to facilitate ion diffusion because it is a dimensional structure
- high conductivity from 3D graphene foam
- active sites of ZnO surface for high selectivity, also helps to increase the surface area of the electrode.

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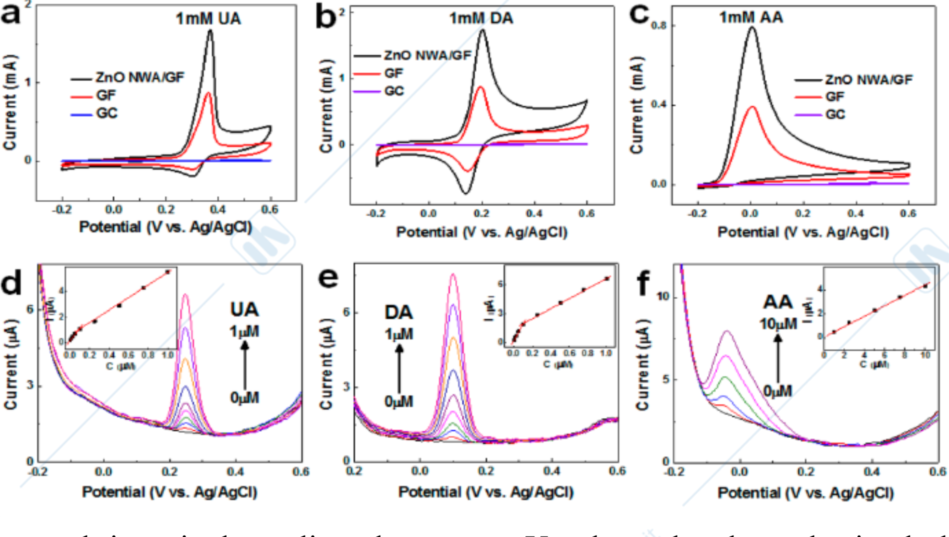
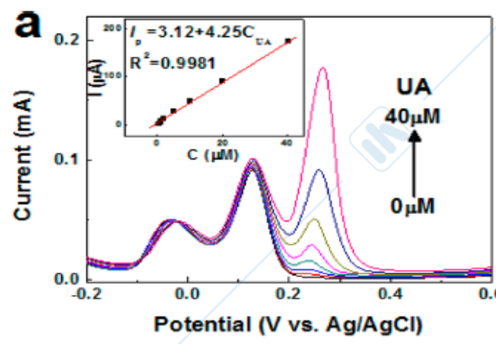
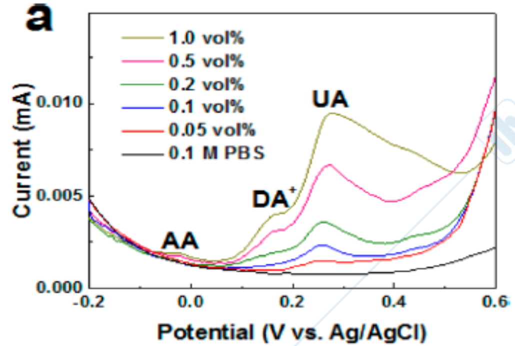


The first graph is a single cyclic voltammetry. You have the electrode simply based on **glassy carbon**, which is a typical material used as an electrode and to make comparisons (in a way it can be said that it is used as a reference). So, you see that with a simple glassy carbon electrode, you have a very flat response, you cannot detect anything. On the other hand, if you have graphene, you increase your response a lot. On the other hand, you do not have a good response and not a good reversibility. However, in this case, you do not really care, because you just want to know if this biomarker is present; so, you just want to oxidize it and the other responses are not interesting. When ZnO is applied to your graphene, you see another increase in the current. Thus, the electrode is improved. There is also a big part that remains constant after the decrease of the voltammetry and this constancy is mainly due to the capacitive effect of the current on the graphene. ZnO can create a stable double layer of charge, and this double layer can be seen when there is not more reaction. For this reason, it is important to use a technique that eliminates the capacitive response, otherwise you should subtract this from all the current.

If you consider the current, uric acid and dopamine are quite similar. Dopamine is more reversible in terms of reaction. On the other hand, we have a big current, but no backward response from AA, which means that it is a species that reacts, and the reaction is irreversible. If you consider the current, you see that it is quite similar to that of uric acid, at the same concentration, and a little bit slower than that of dopamine. It is important that they react at potentials that are not very similar, specifically in the case of AA.



DPV measurements for mixed UA, DA, and AA. DPV curves for the ZnO NWA/GF electrode at varying concentrations of (a) UA in a mixture of 100 μM AA and 15 μMDA; theUA concentrations from the bottom are 0, 0.5, 1, 2.5, 5, 10, 20, and 40 μM.



DPV measurements in serum of patients from Parkinson's disease (PD). (a) DPV curves of different volume fractions of PD serum in a 0.1 M PBS solution (pH 7.4) for a ZnO NWA/GF electrode.

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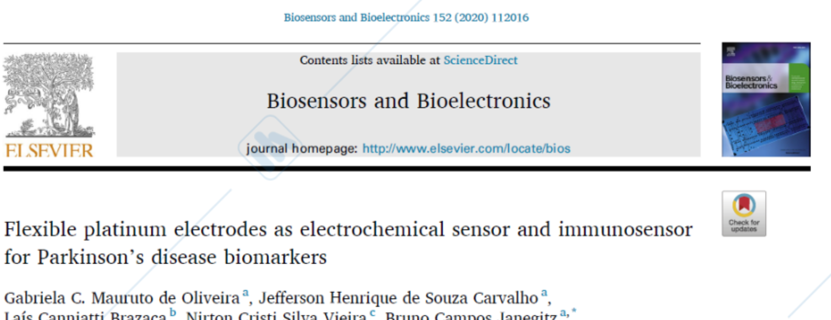
With differential pulse voltammetry, you can see what happens when you increase the concentration from 0 to 1 µM of uric acid. You see that there is corresponding increase in the current and the signal is very clean so you can evaluate the current very well. In the case of dopamine, you have a good signal as well, with the same range of concentration. Also, with AA you have a good response to different concentrations up to 10 µM.

It is interesting to see what happens when you have all three substrates in the system. In this case you have uric acid from 0 to 40 µM. The two peaks of dopamine and ascorbic acid are quite well separated. In this case you have your system but with a real sample that is the serum of your patient. You can see that ascorbic acid is not so dramatic as the other case; dopamine and uric acid can also be both seen.

Case Study 3



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Flexible platinum electrodes as electrochemical sensor and immunosensor for Parkinson's disease biomarkers

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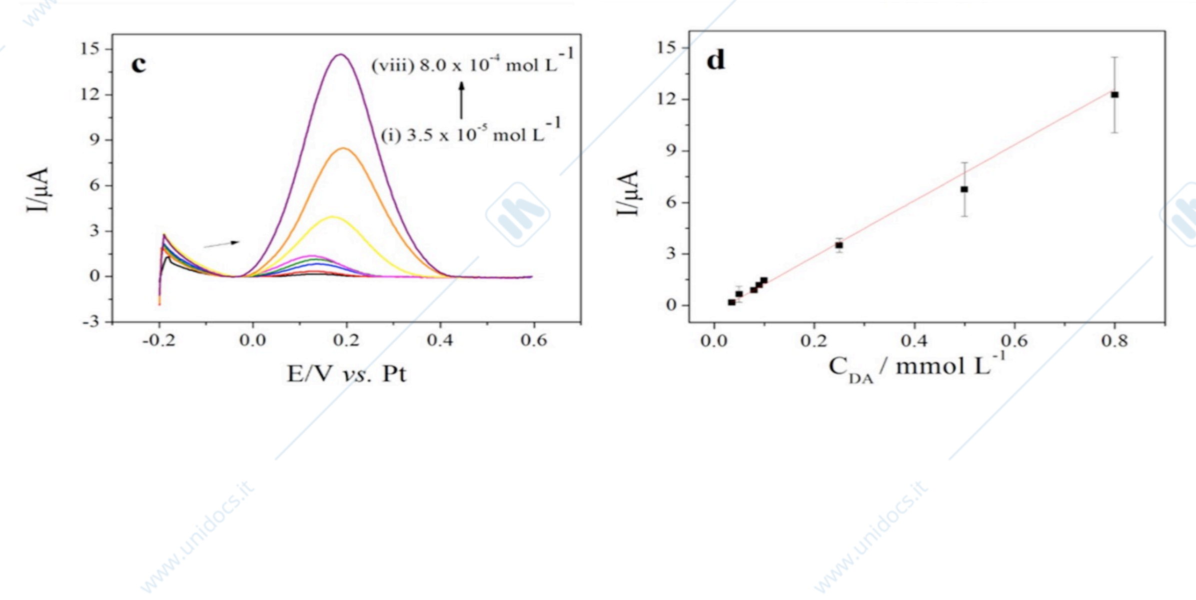
Here we use **flexible platinum (inert) electrode**. Platinum electrodes were fabricated on the bio-based polyethylene terephthalate (Bio-PET) substrates for the development of flexible electrochemical sensors (biomarkers) for the detection of Parkinson's disease biomarkers.



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c) Square-wave voltammograms obtained in 0.20 mol L^{-1} phosphate buffer (pH 6.5) in the presence of different dopamine concentrations: (i) $3.5\cdot10^{-5}$; (ii) $5.0\cdot10^{-5}$; (iii) $8.0\cdot10^{-5}$; (iv) $9.0\cdot10^{-5}$; (v) $1.0\cdot10^{-4}$; (vi) $2.5\cdot10^{-4}$; (vii) $5.0\cdot10^{-4}$; (viii) $8.0\cdot10^{-4}$ mol L^{-1}; (d) Analytical curve obtained for the detection of dopamine. SWV parameters: ΔE_S =0.005 V; a = 0.02V and f: 25 Hz.

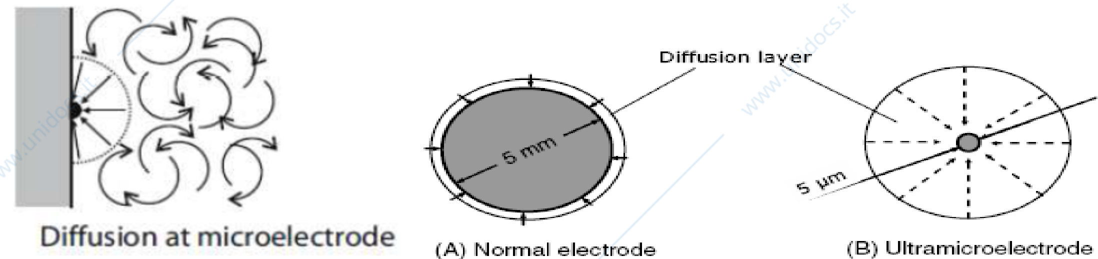
You have the calibration curve. Platinum can be used because they are **screen printed electrodes**, and the amount of material used is very low. However, usually, these kinds of electrodes were made using carbon, not noble metals like platinum. You can see that the response is equal to the last one.

Macroelectrodes, microelectrodes, arrays of microelectrodes

What are the differences in the shape of the electrodes? What is the main effect of the shape on the electrode? The shape and the dimensions of the electrode mainly affect the resistance, the capacity behavior, and the diffusion.

Macroelectrodes have a large electrode surface with respect to the diffusion layer (very thin, in the order of nanometers). The diffusion can be considered directly perpendicular to the surface. Contribution of the diffusive transport to the margins of the non-significant active zone, not very high current densities.

Microelectrodes have a small electrode surface. The diffusion is spherical. Contribution of the diffusive transport to the edges of the active zone, high current density and short response times. Disadvantage: Low currents in absolute value (femto- or nano-ampere). But, if you have a low area, you have reduced capacitance, because also the capacitance is proportional to the area. You reduce also the ohmic drop of your system (resistance) which is proportional to your current. This means that you can use 2 electrode configurations without problems and use with systems that are not so conductive, such as organic solvents. If you have a very low resistance, you have a very low ohmic drop (iR=V).



Where can I detect the highest current, 5 mm or 5um? Highest current density……. In the B, you have very small area, so the current is low, because the current is proportional to the area. But if you divide your current by the area, the highest current density is higher than A.

Microelectrodes are disc electrodes. They have very thin wires (with a diameter of 5µM) that are embedded in glass or in a specific polymer. **Microelectrode arrays** are composed of many microelectrodes. In general, microelectrode arrays have higher currents than single microelectrodes. The spacing between the microelectrodes is important because it influences the

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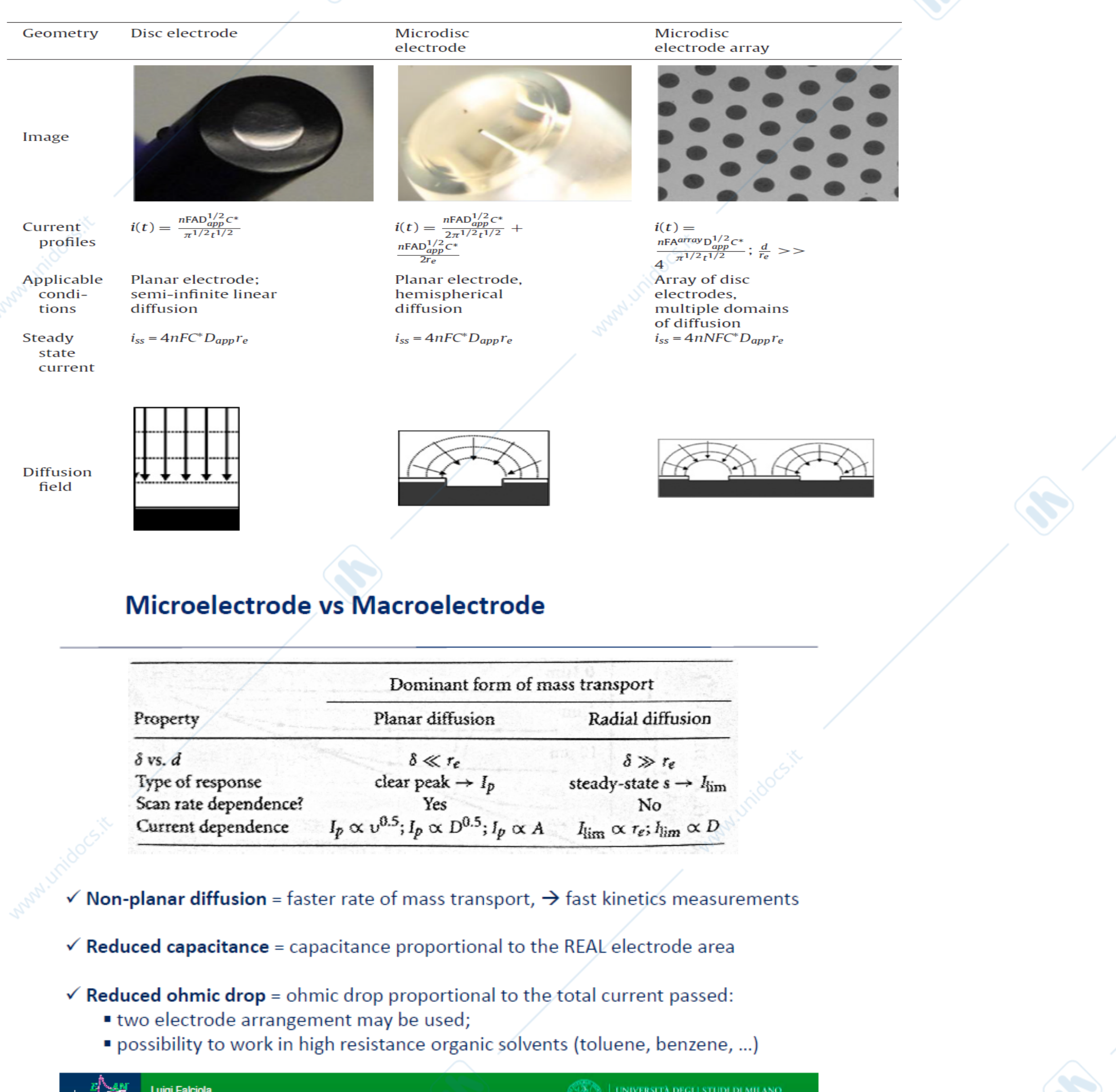
shape of the diffusion layers and their interaction. You can have different diffusion layers, one near the other. If they are far apart, they do not interfere with each other. On the other hand, if you have a good overlapping, you can have a diffusion that is linear as it is for the macroelectrode. You can arrive at a response that is very similar to the flat electrode. Also in this case, the interesting thing is that, if you have a good array, you should arrive at the same response as if all the surfaces were active for the reaction, while, in reality, you have a limited consumption of platinum.



Geometry	Disc electrode	Microdisc electrode	Microdisc electrode array
Image			
Current profiles	$i(t) = \frac{nFAD_{app}^{1/2}C^*}{\pi^{1/2}t^{1/2}}$	$i(t) = \frac{nFAD_{app}^{1/2}C^*}{2\pi^{1/2}t^{1/2}} + \frac{nFAD_{app}^{1/2}C^*}{2r_e}$	$i(t) = \frac{nFA^{array}D_{app}^{1/2}C^*}{\pi^{1/2}t^{1/2}}; \frac{d}{r_e} >> 4$
Applicable conditions	Planar electrode; semi-infinite linear diffusion	Planar electrode, hemispherical diffusion	Array of disc electrodes, multiple domains of diffusion
Steady state current	$i_{ss} = 4nFC^*D_{app}r_e$	$i_{ss} = 4nFC^*D_{app}r_e$	$i_{ss} = 4nNFC^*D_{app}r_e$
Diffusion field			

Microelectrode vs Macroelectrode

Property	Dominant form of mass transport: Planar diffusion	Radial diffusion
δ vs. d	$\delta \ll r_e$	$\delta \gg r_e$
Type of response	clear peak $\rightarrow I_p$	steady-state s $\rightarrow I_{lim}$
Scan rate dependence?	Yes	No
Current dependence	$I_p \propto \upsilon^{0.5}; I_p \propto D^{0.5}; I_p \propto A$	$I_{lim} \propto r_e; I_{lim} \propto D$

Sphere electrode is for chronoamperometric measurement. There is a part that depends on time and a part that is not dependent on time. When you have this part that increases and becomes higher than the radius of your electrode, given that it is at the denominator, it can be neglected, and your equation is dependent only on the radius of your electrode.

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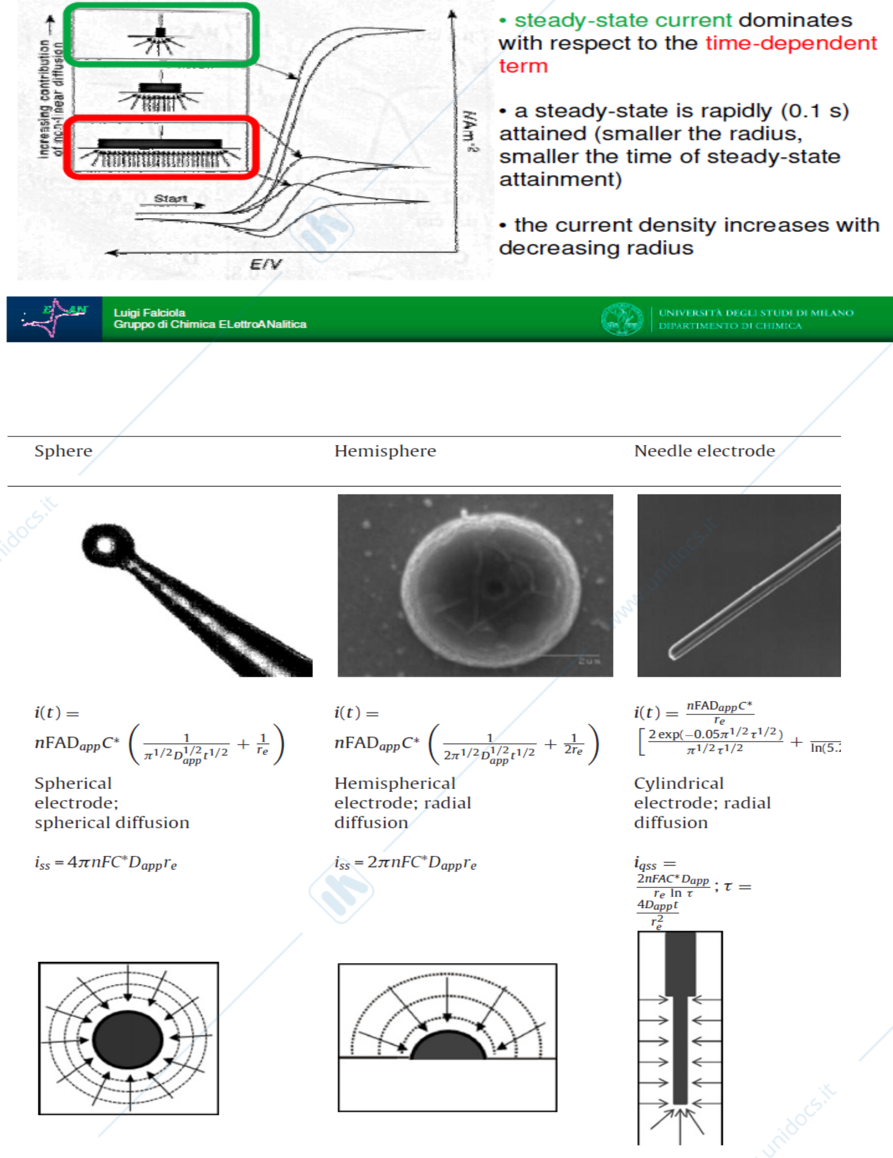

Sphere	Hemisphere	Needle electrode
$i(t) = nFAD_{app}C^* \left(\frac{1}{\pi^{1/2}D_{app}^{1/2}t^{1/2}} + \frac{1}{r_e}\right)$	$i(t) = nFAD_{app}C^* \left(\frac{1}{2\pi^{1/2}D_{app}^{1/2}t^{1/2}} + \frac{1}{2r_e}\right)$	$i(t) = \frac{nFAD_{app}C^*}{r_e}\left[\frac{2\exp(-0.05\pi^{1/2}\tau^{1/2})}{\pi^{1/2}\tau^{1/2}} + \frac{1}{\ln(5.}\right.$
Spherical electrode; spherical diffusion	Hemispherical electrode; radial diffusion	Cylindrical electrode; radial diffusion
$i_{ss} = 4\pi nFC^*D_{app}r_e$	$i_{ss} = 2\pi nFC^*D_{app}r_e$	$i_{qss} = \frac{2nFAC^*D_{app}}{r_e \ln \tau}$; $\tau = \frac{4D_{app}t}{r_e^2}$

In **interdigitated electrodes**, you have one working electrode on one side and one counter electrode on the other side and they are interdigitated, so you have the alternation of the working and the counter and so on. So, at the electrodes, different potentials are applied, which means that if you have a certain difference in potential between the two electrodes, you have the oxidation of the species, and the oxidated species come in solution, but at the other electrode you have the reduction of the species. This is a cycle, and, in this way, you can improve your signal, because you can have continuously your reaction. There is not 100% efficiency, but you can have this loop for a certain amount of time and you can have the magnification of your signal.

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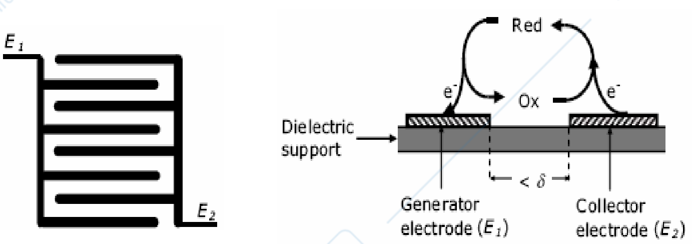

Amperometric Biosensors

Pros

- Linear response between current and concentration: current is proportional to the concentration of analyte.
- More sensitive than potentiometric biosensors
- Miniaturization is possible

Cons

- The analyte is consumed because there is a current that passes through the system, which means that there is a reaction, and its diffusion influences the response: at high concentration, the reaction is faster.
- The measurements are performed at specific potentials in the case of chronoamperometric measurements, but even when you do a voltametric measurement, you see that species will react at specific potentials. What you must take care is that other substances that react in the same potential range are not present, otherwise you will also see these other responses.
- The anode material is consumed reducing its usage time, particularly when using Ag/AgCl thin films in two-electrode systems where Ag/AgCl acts as a counter electrode.

If you have an amperometric biosensor, if you put your potential at 0.4 for the detection of uric acid, you are quite sure to see uric acid. However, in the response of both dopamine and uric acid, you cannot determine the concentration because it is a mixed signal of the two substances.

For the preparation of the Ag/AgCl reference electrode you can simply put the Ag wire in a solution of silver nitrate, an acid solution, and you put the silver as anode and the platinum wire as cathode electrodes and apply a current. You obtain a very thin layer on the wire (miniaturized reference), and you can use this electrode after conditioning it in distilled water.

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