

# Chemistry

- Chemistry is a scientific subject involving elements and compounds which are made up of atoms, ions, molecules
- Chemistry deals with the structure, composition, behaviour and changes these elements and compounds undergo when they react with other substances present in the environment
- **\* Chemistry investigates electron cloud interactions between chemical species – electrons in chemical bonds**

# The main Branches of Chemistry

- General chemistry
- Inorganic chemistry
- Organic chemistry
- Biochemistry
- (physiologically active – pharmaceutical chemistry)
- Medical chemistry
- Analytical chemistry
- Physical chemistry
- Polymer chemistry
- Colloidal and nano chemistry
- Nuclear chemistry
- Quantum chemistry

# 10 branches of chemistry

- Environmental Chemistry—This branch of chemistry focuses on natural systems and what we think of outside of chemistry as the “elements:” air, water and soil;
  - Forensic Chemistry—applying chemistry techniques and instruments to analyze evidence and help solve criminal cases
  - Geochemistry—studying the earth, specifically the physical planet and how it’s made up; you will talk a lot about lava, magma, silicates, which combined with metals form the earth’s crust, and types of silicates like zeolites, as well as analyze samples of the earth’s crust and do geochemical modeling
  - Polymer Chemistry—studying polymers, substances made up of a lot of the same particle chained together over and over again; you’ll mainly study the molecules in plastics, resins, types of rubber and glass, and other textiles
  - Theoretical Chemistry—here is where you use math, physics, computation, and your existing knowledge of chemistry to try to figure out the laws of chemistry that haven’t been written yet. In this branch, you will discover the newest chemical reaction(s) and properties that have yet to be defined.
  - Industrial Chemistry—looking at the makeup of chemicals that help us mass-produce commercial products and create the buildings and structures we need to help society survive, like paints, detergents, batteries, dye, pigments and prescription drugs
  - Thermochemistry—all about heat, but more to the point, the energy released or absorbed in a chemical reactions as well as phase changes like melting or boiling; based on variations on the law of conservation of matter—matter can’t be created or destroyed in any physical process
  - Medicinal or pharmaceutical chemistry—the study of the chemical design of pharmaceuticals, otherwise known as drugs, by picking apart what drugs are made of at the most basic level to find how they are held together, why they work on the human body, and help design new chemical combinations
  - Nuclear chemistry—the area of chemistry that deals with dealing with radioactive materials, how radioactivity transforms matter, and the amazing way that reactions in less-than-microscopic little atoms leads to huge amounts of energy
  - Materials chemistry
- \* Theoretical, computational and practical chemistry

# Branches of chemistry

- Agriculture & Food
- Computational Chemistry
- Paint, Pigments, and Coatings
- Astrochemistry
- Cheminformatics
- Geochemistry
- Nanochemistry
- Personal Care
- Biotechnology
- Crystallography
- Materials
- Nuclear
- Textiles
- Chemical Engineering
- Dyes, Pigments and Inks
- Medicinal
- Oil and Petroleum
- Water

# Branches of chemistry

- Astrochemistry (and cosmochemistry)
- Atmospheric chemistry
- Chemical engineering
- Chemical biology
- Electrochemistry
- Femtochemistry
- Flavor chemistry
- Flow chemistry
- Green chemistry
- Histochemistry
- History of chemistry
- Hydrogenation chemistry

# Branches of chemistry

- Immunochemistry
- Marine chemistry
- Materials science
- Mathematical chemistry
- Mechanochemistry
- Medicinal chemistry
- Molecular biology
- Neurochemistry
- Molecular mechanics
- Nanotechnology
- Natural product chemistry
- Oenology, organometallic chemistry

# Branches of chemistry

- Petrochemistry
- Pharmacology
- Photochemistry
- Physical organic chemistry
- Phytochemistry
- Polymer chemistry
- Radiochemistry
- Solid-state chemistry
- Sonochemistry
- Supramolecular chemistry
- Surface chemistry
- Synthetic chemistry
- Thermochemistry

# Some basic terms in chemistry

## 1. Matter

- Atom
- Element
- Compound
- Molecule
- Substance and mixture
- Mole and amount of substance

## 2. Phase

## 3. Bonding

## 4. Energy

## 5. Reaction

## 6. Ions and salts

## 7. Acidity and basicity

## 8. Redox

## 9. Equilibrium



# Physical chemistry

- Chemical thermodynamics – chemical energy
  - Chemical kinetics
  - Chemical catalysis
  - Electrochemistry
  - Photochemistry
  - Surface chemistry
  - Statistical mechanics
  - Material chemistry
  - Biophysical chemistry
  - Solid-state chemistry
  - Material science
  - Crystallography
  - Nanochemistry
  - Spectroscopy, Microscopy
  - Physical organic chemistry
  - Nuclear chemistry
  - Quantum chemistry
  - Astrochemistry
- \* Physical chemistry has large overlap with molecular physics. Physical chemistry involves the use of infinitesimal calculus in deriving equations
- \* Physical chemistry is a distinct discipline from chemical physics
- \* Chemical engineering, computational chemistry

# Electrochemistry

- PHYSICS

- R,I,V,C,S

-

- electron -

CHEMISTRY

solution, concentration, kinetics, catalysis

diffusion, thermodynamics

-

\* liquid/solid interface

-

\* phase boundary

-

# Electrochemistry

- Electrochemistry is a branch of physical chemistry – the relationship between electrical parameters and chemical changes, with electricity considered as an outcome of a particular chemical change.
- Electrochemistry – analysing and controlling chemical bond creation and breakage
- Liquid/solid interface

# Electrochemistry

- Oxidation and reduction
- Balancing redox reactions
- Acidic medium, basic medium, neutral medium
- Electrochemical cells
- Standard electrode potential
- Spontaneity of redox reaction
- Cell emf dependency on changes in concentration
- Concentration cells
- Battery
- Corrosion
- Sacrificial anodes
- Electroplating, coating
- Sacrificial anodes
- Electrolysis
- Faraday's laws
- Current density, solvent, electrolyte
- OCP at the electrode-equilibrium

# Electrochemistry

- Potential
  - Current
  - Resistivity
  - Conductivity
  - Capacitance
- A, V, R, S, C – can be measured in an electrochemical exp – overall current

# Electrochemistry

- Spontaneous - nonspontaneous reactions
- Faradaic - non Faradaic current
- Capacitive current
- Ohmic drop compensation
- Electron transfer - kinetics
- Number of the electrons involved
- Two electron mechanism
- Redox reaction
- Equilibrium, Ox/REd
- Half-reaction
- Transfer coefficient
- Symmetry factor
- working, reference and counter electrodes
- RHE - not changed with pH
- OCP, OCV
- Reduction and oxidation potentials
- Reversibility of the reaction – fast reactions
- Galvanic-voltaic cell spontaneous reaction
- Electrolytic cell- E needed to drive the elchem r-on
- onset potential, overpotential
- limiting current, polarization curves
- Double-layer, capacitance
- Electrode and ellyte reactions
- hydrodynamic layer - diffusion layer - double layer
- Momentum transfer - mass transfer - heat transfer, flux, coverage

# Electrochemistry

- Charge carriers-ions, electrons
  - Conv curr from + to -, e from - to + circuit
  - Cathode – electrons leave the device (reduct), anode-electrons enter the device
  - - anode + cathode in galvanic cell (battery)  
around the anode there are positive ch.
  - +anode – cathode in the electrolytic cell
  - Cu more el.neg. –steals the e from Zn-batt
  - By changing the cathode and anode-ellysis
- LUMO-HOMO,

# Electrochemistry

- Diffusion, convection, conduction, migration
- Concentration diff, T diff, gradients
- standard kinetic constant  $k^\circ$
- Kinetics
- Heterogeneous catalysis
- Thermodynamics
- Energy (reaction) barrier
- Energy levels
- inert atmosphere, redox species
- Solvents, electrolytes
- Tafel
- Nernst
- Butler-Volmer
- Langmir
- Stern
- Wagner-Traud
- Koutecký-Levich
- Savitsky
- Bourbaix
- Levich
- Randles-Ševčík
- Fourier, Laplace, transfer function
- Coulombic efficiency



# Electrochemistry - methods

- Cyclic voltammetry
- Hydrodynamic voltammetry
- Linear sweep
- Potentiometry
- Amperometry
- EIS
- RRDE
- Linear, wave, pulse, square, sine, triangular signals – techniques
- Polarography - Hg new surface
- Current interrupt , pH-metry, stripping
- Static-dynamic methods,
- Nafion, Teflon, Viton, Buffer
- Corrosion, electroplating, coating
- Potentiostat, galvanostat-high int R-Iconst
- In situ, in operando
- Surface tension
- Inert atmosphere and electrolyte, binder
- Solvent and electrolyte composition
- (Electro)Chemical reactor design
- Laminar – turbulent
- In situ spectroscopy – electrochemistry

# Electrochemistry

- Kinetics: Tafelian, Butler-Volmer, Stern or Wagner-Traud kinetics
- Solubility, Dissociation constant, IR compensation,
- Adsorption, Absorption, physi-chemisorption, hydrophilic- hydrophobic
- Uncharged species, non electroactive species, ionophores, ionic shell, complex ions, colloids, surface tension
- An electrode - electrical conductor used to make contact with a nonmetallic part of a circuit.  
Elektron - hodos

# CV

- What happens with the counter electrode
- Why the reduction peak lates after oxidation peak at the CV
- Intersection of lines on the CV – curve crossing
- Sometimes going back doesn't go below 0A current
- Going back line is always lower at the same potential, never the same or higher than the up line
- The thickness of the CV
- Angled CV
- Shift of peaks – harder to oxidize or reduce
- All the CV above X-axis
- Fast elchem processes – peaks are at the same line
- Reversible elchem process – peak separation – no peak shift with scan rate
- CV like a strait angled line
- Peak currents are proportional to the square root of the scan rate – higher scan rate, higher I – diffusion layer thickness
- Quasi reversible
- Reversible processes – peaks shift with scan rate
- Ideal capacitance CV like a rectangle

# EIS

EIS is an essential method for monitoring electrochemical changes of a system in situ with the immersion time, because it provides kinetic and mechanistic information about the corrosion process in the case of passive and active protection or a combination of both [32,33]. Crucially, it provides quantitative information about the processes taking place within the system [34].

This technique is based on the application of a small-amplitude sinusoidal potential perturbation (typically in the range of 5–10 mV) to the working electrode over an extended frequency range (typically, 100 kHz to 10 mHz) using a conventional three-electrode electrochemical cell [35,36]. The current response is a sinusoidal signal of the same frequency but with a different phase and amplitude with respect to the perturbation (Figure 5) [32,33,34,37,38]. The real ( $Z_{re}$ ) and imaginary ( $Z_{im}$ ) components (or modulus  $|Z|$  and phase shift  $\theta$ ) of the impedance ( $Z$ ) are calculated as the complex ratio between the applied potential sinewave ( $V$ ) and the response current ( $I$ ) [32,34,38].

The EIS data are typically presented as a Nyquist plot, where the imaginary impedance component ( $Z''$ ) is plotted against the real impedance component ( $Z'$ ) at each excitation frequency, and the Bode plots display the logarithm of the impedance modulus  $|Z|$  and phase angle ( $\theta$ ) as a function of the logarithm of the applied frequency range [36,39]. Note that Nyquist plots are referred to in this review more extensively than Bode plots.

In order to convert frequency response data to corrosion properties (e.g., resistance and impedance), EIS results are modeled by fitting them to an equivalent electrical circuit consisting of resistors ( $R$ ), capacitors ( $C$ ) or constant phase elements (CPE), inductors ( $L$ ) and Warburg impedance ( $W$ ) connected either in series or in parallel [5,35,38]. Commercial software, for example ZView software (3.0a Scribner Associates, Inc., Southern Pines, NC, USA), may be used for fitting the impedance spectra to the equivalent circuit [40]. The quality of fitting is often evaluated by the chi-squared ( $\chi^2$ ) error value [37]. To be useful, the elements in the equivalent electrical circuit should correlate with the different corrosion processes taking place in the system under investigation.

One of the requirements before impedance analyses is the validation of the EIS data [41]. The application of Kramers–Kronig (K–K) transforms could provide a possible solution to verify electrochemical impedance data with respect to the conditions of the causality, linearity, stability and finity value and the acceptable agreement between the sets of experimental and transformed data confirmed that the system fulfills these conditions.

# EIS

## *Advantages of EIS*

There are several advantages of EIS compared with other methods that are more commonly used for monitoring the corrosion rate, including the following:

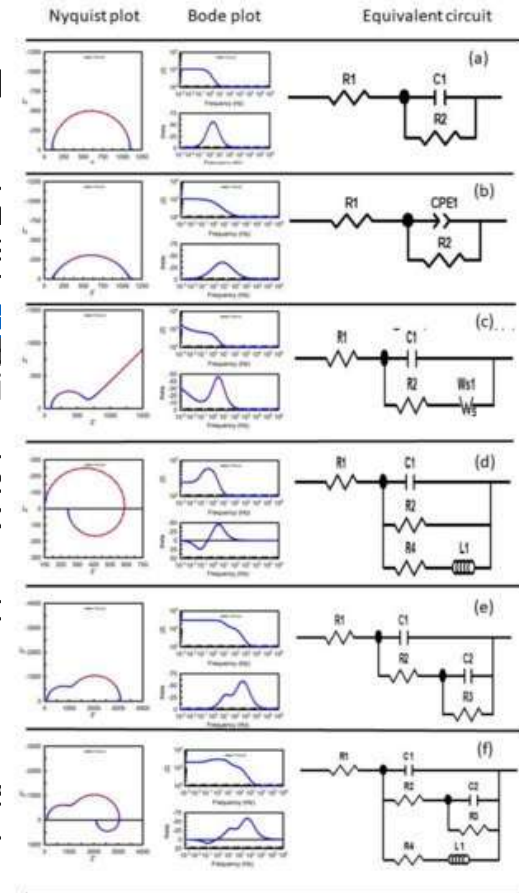
- Frequency-resolved EIS can distinguish among several electrochemical reactions in corrosion science based on their own relaxation times and provide detailed information on their respective kinetics in the form of corrosion rates [40]. In the frequency domain, fast processes, such as the formation of the double electric layer, the presence of ohmic resistance, and charge transfer resistance of electrochemical reactions, occur at high frequencies, while slow processes, such as the formation of adsorbed layers by intermediates of complex electrochemical reactions or diffusion (transport phenomena) in solutions, occur at low frequencies [40,41]. This can be used to calculate the corrosion resistance (i.e., inversely proportional to the corrosion rate), analyze the formation of corrosion or passivation layers on the surface of Mg, indicating whether the corrosive process occurs by activation, concentration, adsorption, or diffusion [5,14,42,43]. Furthermore, it provides information regarding the double layer at the metal/electrolyte and the dielectric properties of the surface oxides [44].
- Compared to polarization curves, EIS uses a small excitation amplitude, causing only minimal perturbation to the corrosion potential. The non-destructive nature of EIS allows real-time measurements of corrosion rates in situ over long periods of immersion [5,42,43] and reduces the number of samples required for measurements.
- EIS allows the determination of much lower corrosion rate values than those measured by non-electrochemical techniques (weight loss or hydrogen evolution).
- The use of EIS gives a reliable and repeatable estimation of the instantaneous corrosion rate of Mg/Mg alloys [13].
- The EIS technique has the ability to study high-impedance systems, such as coatings and linings, high-purity water, and organic coating/metal systems or corrosion in a low-conductive solution [45].

# EIS

## Limitations of EIS

In spite of the obvious advantages of using EIS, there are certain limitations following:

- The major problem with EIS analysis is that, often, different equivalent circuit error values can be used to fit the same EIS data [5,35,41]. Resistance and capacitive model. Thus, the construction of a proper equivalent circuit requires knowledge of the system, the use of complementary characterization techniques, physical chemical analysis, and support by models from published works [5,34,3]. They have validated their proposed equivalent circuits by comparing the corrosion rates of those obtained from weight loss and hydrogen evolution methods. However, this is not always possible.
- Another major limitation of global EIS measurements is its poor lateral resolution over the whole macroscopic electrode surface [46]. This makes it more difficult to study localized reactions in which the specific electrochemical parameters of the micro-defects on the electrode surface [40].
- A major disadvantage of AC impedance measurements is that it is not possible to determine a corrosion rate without prior knowledge of the Tafel slopes values and the exchange current density.
- Instabilities in the Mg corrosion process for Mg, such as relaxation of adsorbed species, can cause dispersion in the impedance values recorded at low frequency.
- Finally, unlike polarization curves, EIS cannot determine changes in corrosion kinetics caused by different alloying elements, microstructures, or solution compositions [5,42].



including the  
 reduced ( $\chi^2$ )  
 choice of  
 corrosion  
 model, and/or  
 et al. [17]  
 compares with  
 aged over  
 corrosion  
 the entire  
 resistance  
 an induce  
 periodic and  
 phases), or

# Electrochemistry - applications

- Corrosion
- Bare Metals
- Coatings
- Galvanic Corrosion
- Hydrogen Embrittlement
- Tribocorrosion
- Corrosion in Air
- Energy Storage
- Batteries
- Fuel Cells
- Photoelectrochemistry
- Photovoltaic and Solar Cells
- General and Physical Electrochemistry
- Electrochemical Sensors
- Nanotechnology
- Fundamental Electrochemistry Research
- Electroanalysis
- Electrosynthesis
- Electrodeposition
- Water purification, neutralization, neuro, recycling, sensors
- Materials Analysis
- Ceramics
- Dielectrics
- Display Technologies
- Ferroelectric Materials
- Energy Devices and Ionic Conductors
- MEMs and NEMs
- Nanomaterials
- Organic Electronics
- Piezoelectric Materials
- Semiconductors and OFET
- Scanning Electrochemical Workstation
- Signal Analysis
- Electronic Measurement
- Frequency Response Analyzer
- Magnetic Measurement
- Mechanical Testing
- Optical Engineering
- TOF-MS Time-of-Flight Mass Spectrometry

# Electrochemistry - applications

## ENERGY STORAGE

- Batteries
- Fuel Cells
- Photoelectrochemistry
- Photovoltaic and Solar Cells

## MATERIALS ANALYSIS

- Ceramics
- Dielectrics
- Display Technologies
- Ferroelectric Materials
- Energy Devices and Ionic Conductors
- MEMs and NEMs
- Nanomaterials
- Organic Electronics
- Piezoelectric Materials
- Semiconductors and OFET

## CORROSION

- Bare Metals
- Coatings
- Galvanic Corrosion
- Hydrogen Embrittlement
- Tribocorrosion
- Corrosion in Air

## SIGNAL ANALYSIS

- Electronic Measurement
- Frequency Response Analyzer
- Magnetic Measurement
- Mechanical Testing
- Optical Engineering
- TOF-MS Time-of-Flight Mass Spectrometry
- Scanning Electrochemical Workstation

## GENERAL AND PHYSICAL ELICHEM

- Electrochemical Sensors
- Nanotechnology
- Fundamental Electrochemistry Research
- Electroanalysis
- Electrosynthesis
- Electrodeposition
- extraction of metals, refining of metals
- Electroplating, electrocleaning
- production of chemicals



# Electrochemistry - applications

- Lab on a chip with many sensors
- Water splitting limiting factor in aqueous solution,  $<-0,5\text{V}$  and  $>2,0\text{V}$  vs RHE

### Problems:

- Noisy signal, 220V oscillations, IR compensation,
- Water decomposition red-ox is a limiting factor in aqueous solvents
- Micro and macro systems
- Batteries – environmental and climate change; second battery life

### Other terms:

- EIS – phase angle and shift
- Prof Stojanovic

# Sensors

Other terms:

# Sensors

- Electrochemical sensors are an integral part of our daily lives, making up the largest percentage of all chemical sensors. The sensing mechanisms are based on various electrochemical detection methods, ranging from amperometry to electrochemical impedance analysis. Many of the applications are biochemical and biomedical, where the more generic term, biosensors is often used. The most well-known, and arguably the most impactful, electrochemical sensor to date is the self-monitoring blood glucose meter used to assist diabetics in controlling their blood glucose levels.
- The range of applications where electrochemical sensors are in use and/or under development is far reaching. Some examples include gas sensors, such as those used in homes to detect CO, heavy metal sensors for water quality analysis, and hydrocarbon, alcohol, and ketone sensors for measuring motor oil degradation. Additional examples where electrochemical sensors have been applied, include:
  - Biological/Chemical Warfare (Homeland Security)
  - Food Monitoring
  - Medical Diagnostics
  - Manufacturing
  - Automotive
  - Home/Environmental Monitoring

<https://www.ameteksi.com/applications/general-and-physical-electrochemistry/electrochemical-sensors> - PINCETON

Regardless of the method of detection, the development and utilization of these as transducers continue to expand. Design and optimization of any electrochemical sensor begins with a proof of concept, followed by prototype development, scale-up and commercialization.

- Elchem.methods: CV, LSV, differential + pulse, A, V, R, S, C- can be measured in an electrochemical exp
- Lab on chip with many sensors

What happens at the antigen-antibody interface? Half-elchem cell for each reaction separated by separator !!!!!

What happens at the counter electrode surface? Internal resistance of the battery. When looking at the exp, it doesn't happen.

- **An ideal electrochemical sensor** should have a high performance by achieving high sensitivity, high specificity, selectivity, a wide range of detection, reproducibility in measurements, rapid response (response time) with real-time analysis, multiple uses. It should also be portable, biocompatible, disposable, reusable, user-friendly and environmentally friendly, biodegradable, cost-effective, easily integrable with micro-electronics, with self-calibration and self-cleaning desired, sustainable, lifetime. Nanomaterials should help, as well as ion-selective membranes, ISFET, screen-printed electrodes. Usage should be automated portable, and generally data post-processing plays a very important role in obtaining credible and accurate detection results. Many of those properties are an issue in the real bio (immuno) electrochemical sensors. Linear sensor, response mechanisms, detection limit, measuring range. Interfering and omitting ions, microfluidic devices, repeatability, stability, corrosion, mesoPorousInfluence,
- \*\*\*low output impedance, high signal-to-noise ratio, long linear range, Nernstian response,
- Sistem sa 10 razlicitih vrsta molekula funkcionise – Au-H<sub>2</sub>O-COO-enzim-secer-H<sub>2</sub>O<sub>2</sub>-Lakton-O<sub>2</sub>-Na<sup>+</sup>
- Sistem sa 15 razl vrsta molekula ce tesko funkcionisati MSN—aminopropyl-2xlinkeri-Pt/Au/Pd-enzim-secer
- Celijske medijume je elchem CV nemoguće analizirati
- A lot of knowledge, will, ideas, and motivation needed, communication, and a lot of literature reading - videos

- WHAT ARE WE DETECTING
  - Elchem.methods: CV, LSV, stripping + differential + pulse, A, V, R, S, C – can be measured in an electrochemical exp
  - Voltammetric (I vs V), potentiometric (V vs t), chronoamperometric (I vs t), Impedimetric ( $R_e$  vs  $I_m$ , magnitude (phase) vs Hz), conductometric ( $1/R$  vs t), coulometry (q/t vs t)
  - Electrochemical parameters - potential window...
  - Purity of electrolytes and substrates
  - which material for substrate to use – GC, Au, Pt,
  - REF el
  - Nanomaterials
  - Study of elchem reaction and kinetics
- 
- Types of R compensation modes and electronic filters; inert atmosphere,
  - organic solvents - wider electrochemical window, aprotic conditions, high solubility/stability for many organometallic or air-sensitive compounds
  - Wire connections

<https://pubs.acs.org/action/doSearch?AllField=immunosensors> - ACS search – immune

<https://onlinelibrary.wiley.com/action/doSearch?field1=AllField&text1=immunosensors&field2=AllField&text2=&field3=AllField&text3=&Ppub=> - angewandte Wiley

<https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781118354162> - very good book about biosensors and techniques

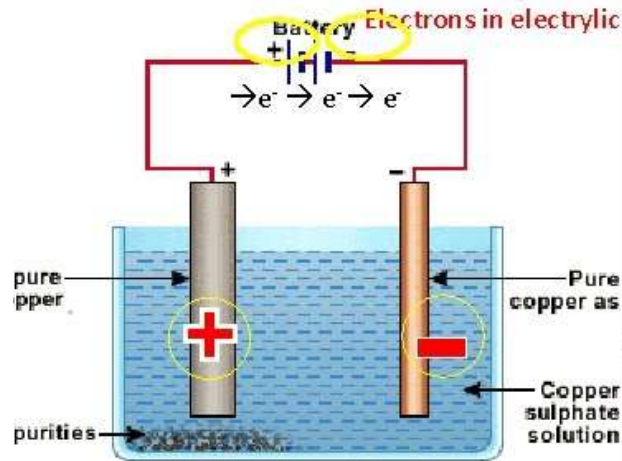
- EU projects !!!

## What's the difference?

Battery in one.

Electrons in galvanic flowing from - to +

Electrons in electrolytic flowing from + to -  $e^- \rightarrow$



Experimental set up for the electrolytic refining of copper.

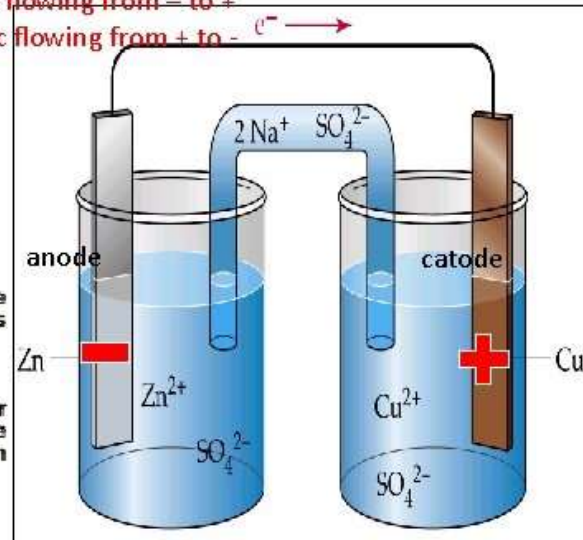
Electrolytic Cell

a Fat Red Cat ate an Ox

Use Table J, but opposite

**More active metal = cathode = negative**

**Less active metal = anode = positive**



Galvanic Cell

A Fat Red Cat ate an Ox

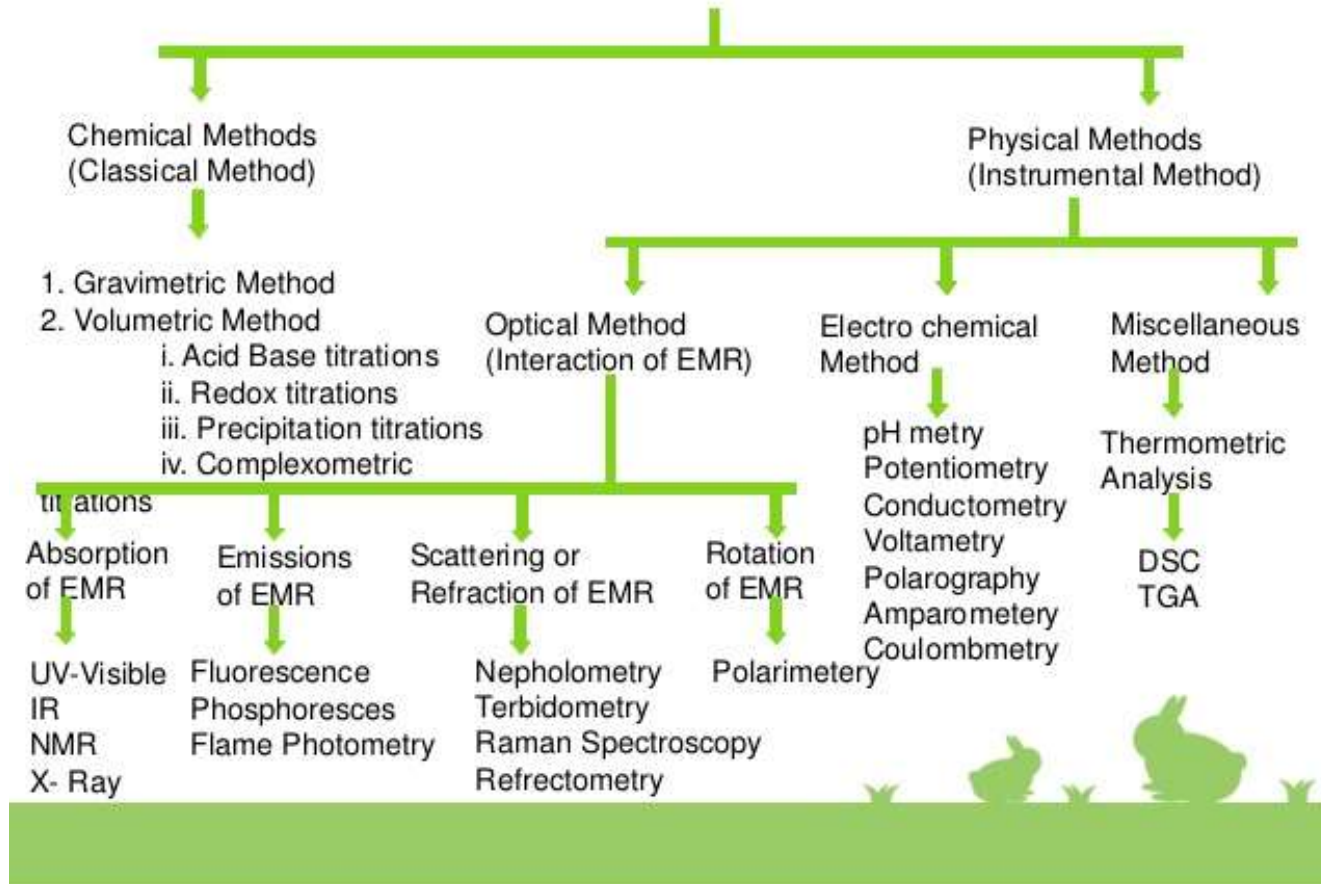
Use Table J

**More active metal = anode = negative**

**Less active metal = cathode = positive**



# - ANALYTICAL TECHNIQUE



■ OBERACHER ET AL.

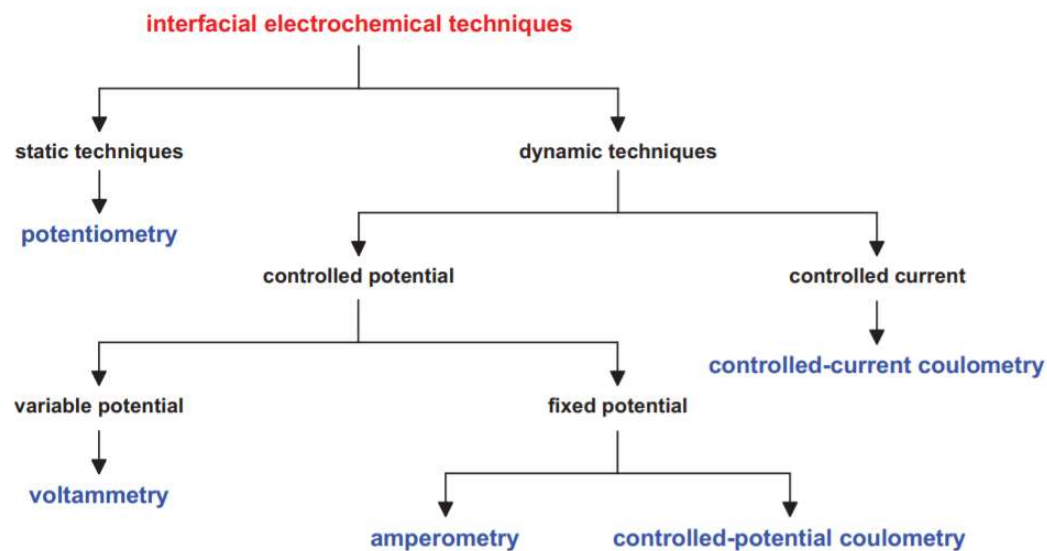
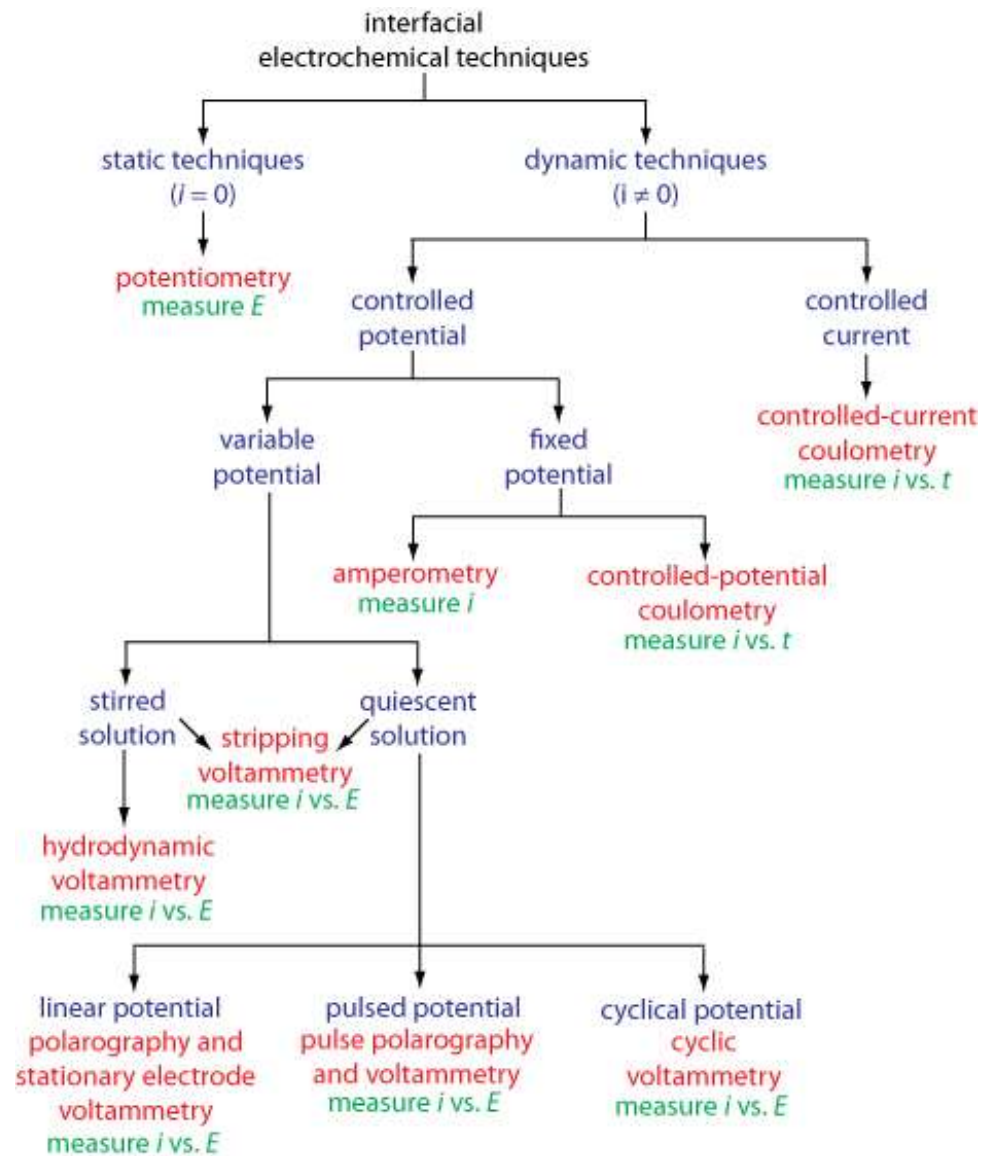
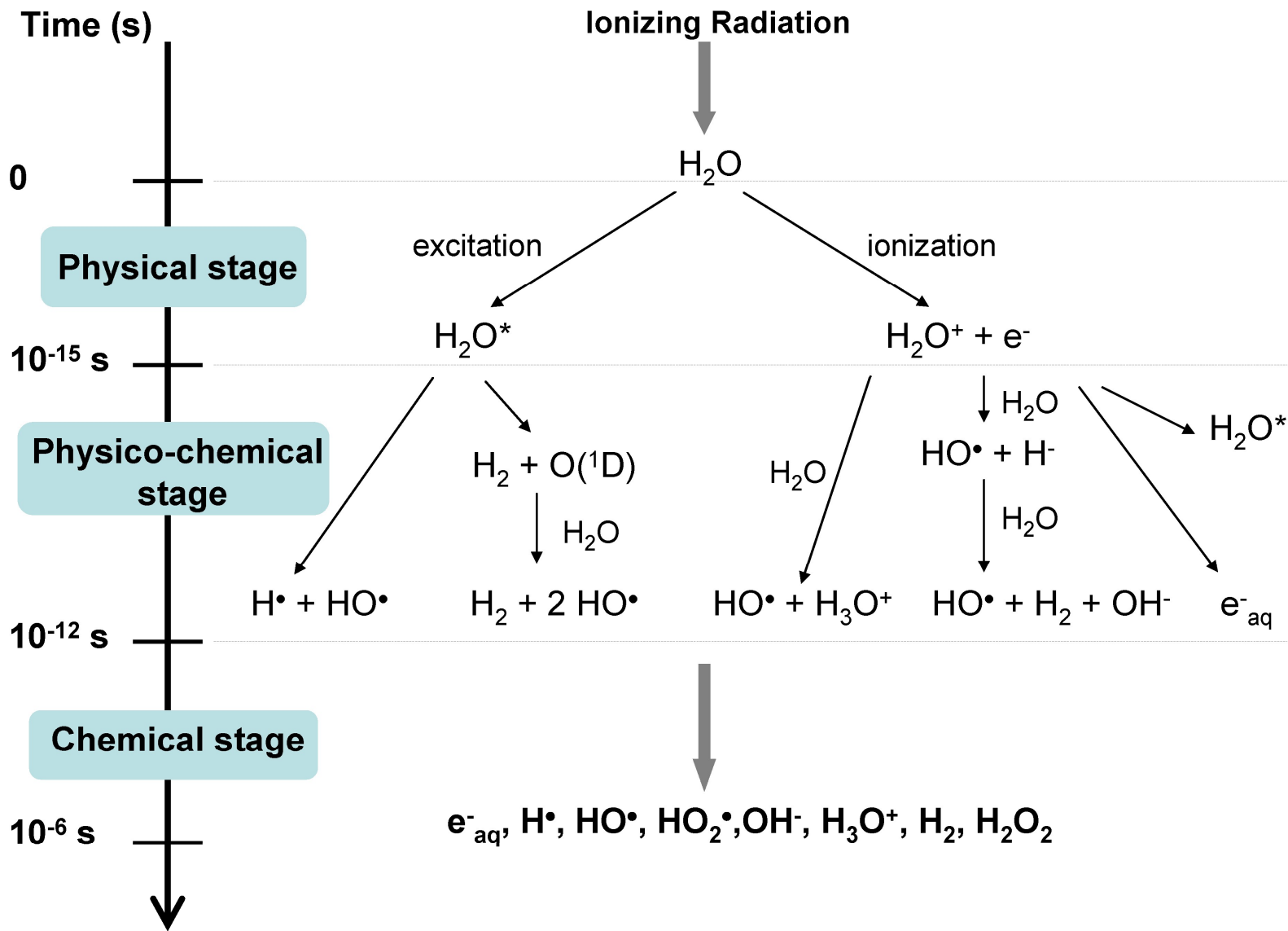
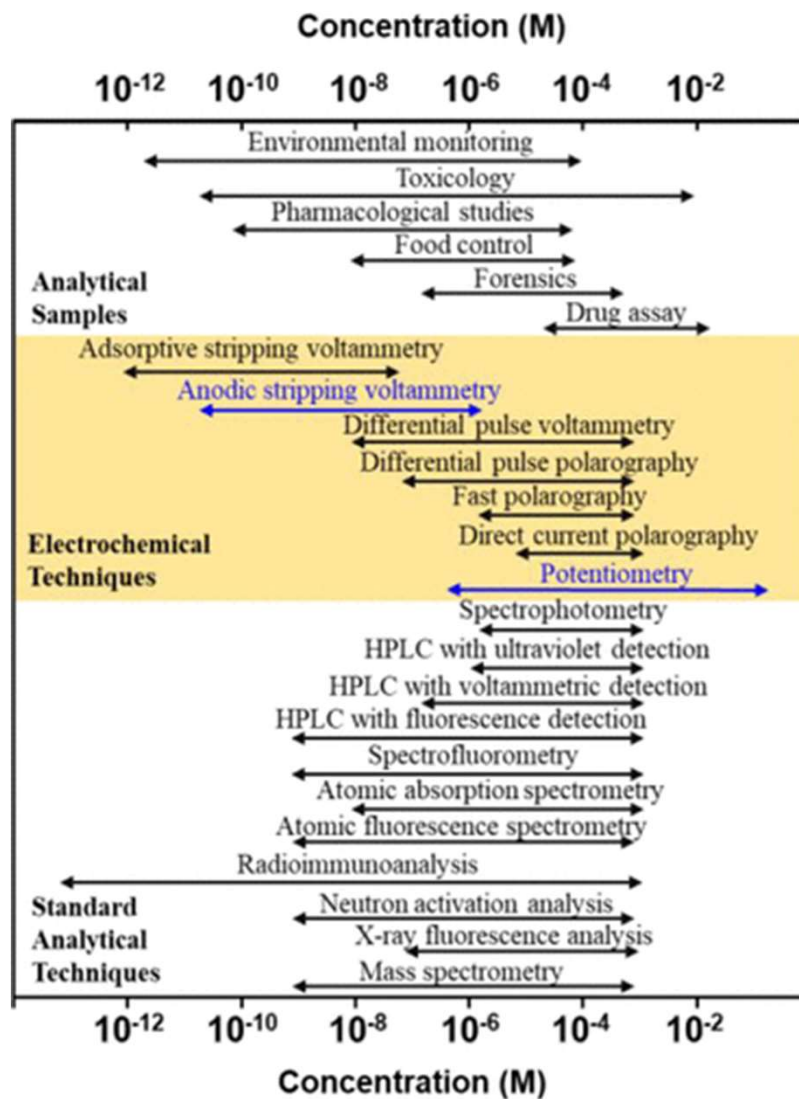


FIGURE 1. The family tree of interfacial electrochemical techniques.

In coulometry the analyte is completely converted from one electroanalytical methods may suffer from the problem that







### Voltammetry (SWASV) and linear sweep anodic stripping voltammetry (LSASV).

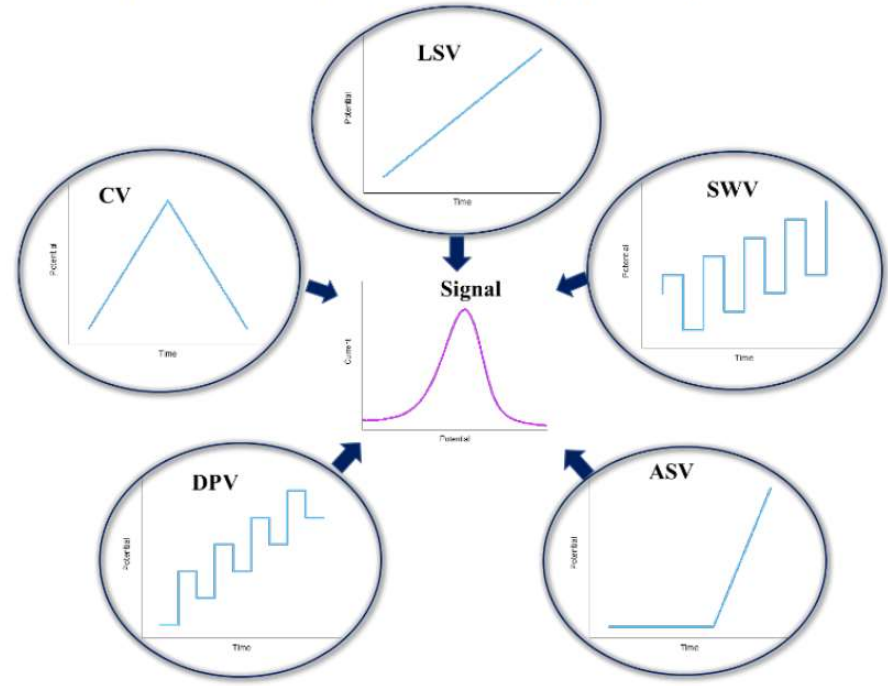


Figure 1: The graphs of potential vs time for some voltammetry techniques to produce a signal.

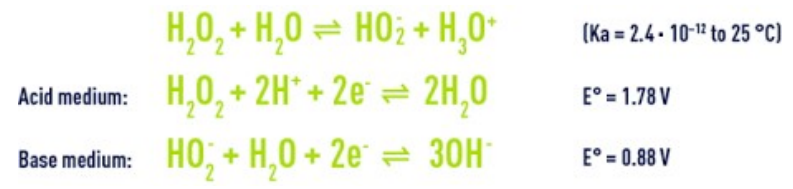


	$E^\phi$ (V)
<b>One electron reduction</b>	
$O_2 + e^- \leftrightarrow \bullet O_2^-$	-0.33
$\bullet O_2^- + e^- + 2H^+ \leftrightarrow H_2O_2$	+0.94
$H_2O_2 + H^+ + e^- \leftrightarrow \bullet OH + H_2O$	+0.38
$\bullet OH + H^+ + e^- \leftrightarrow H_2O$	+2.33
<b>Two electron reduction</b>	
$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2$	+0.30
$H_2O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$	+1.35
<b>Four electron reduction</b>	
$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	+0.82

Half-reaction	Electrode potential (V vs. NHE) pH = 7 at 25 °C <sup>a</sup>
$O_2 + e^- = O_2^{\bullet -}$	-0.18
$H_2O_2 + e^- + H^+ = HO^\bullet + H_2O$	+0.39
${}^1O_2 + e^- = O_2^{\bullet -}$	+0.81
$O_2^{\bullet -} + e^- + 2H^+ = H_2O_2$	+0.91
$HO_2^\bullet + e^- + H^+ = H_2O_2$	+1.05
$H_2O_2 + 2e^- + 2H^+ = 2H_2O$	+1.35
$HO^\bullet + e^- + H^+ = H_2O$	+2.31
$g\text{-}C_3N_4(\text{CB}_{\text{edge}} \text{ potential})$	-1.27 <sup>b</sup>
$g\text{-}C_3N_4(\text{VB}_{\text{edge}} \text{ potential})$	+1.39 <sup>b</sup>

Anodic reaction	Reactant	Standard potential	Reaction
$OH^\bullet$	$H_2O$	2.85 V	$H_2O \rightarrow OH + H^+ + e^-$
$O^\bullet$	$H_2O$	2.42 V	$H_2O \rightarrow O + 2H^+ + 2e^-$
$O_3$	$H_2O$	2.08 V	$H_2O + O_2 \rightarrow O_3 + 2H^+ + 2e^-$
$H_2O_2$	$H_2O$	1.78 V	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$
$Cl_2$	$Cl^-$	1.36 V	$2Cl^- \rightarrow Cl_2 + 2e^-$
$O_2$	$H_2O$	1.23 V	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Cathodic reaction	Reactant	Standard potential	Reaction
$H_2$	$H_2O$	0.00 V	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
$H_2O_2$	$O_2$	-0.15 V	$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$

Source: Kraft, A.; et al.: Electrochemical water disinfection, In: Transworld Research Network, 2003; P 27-55

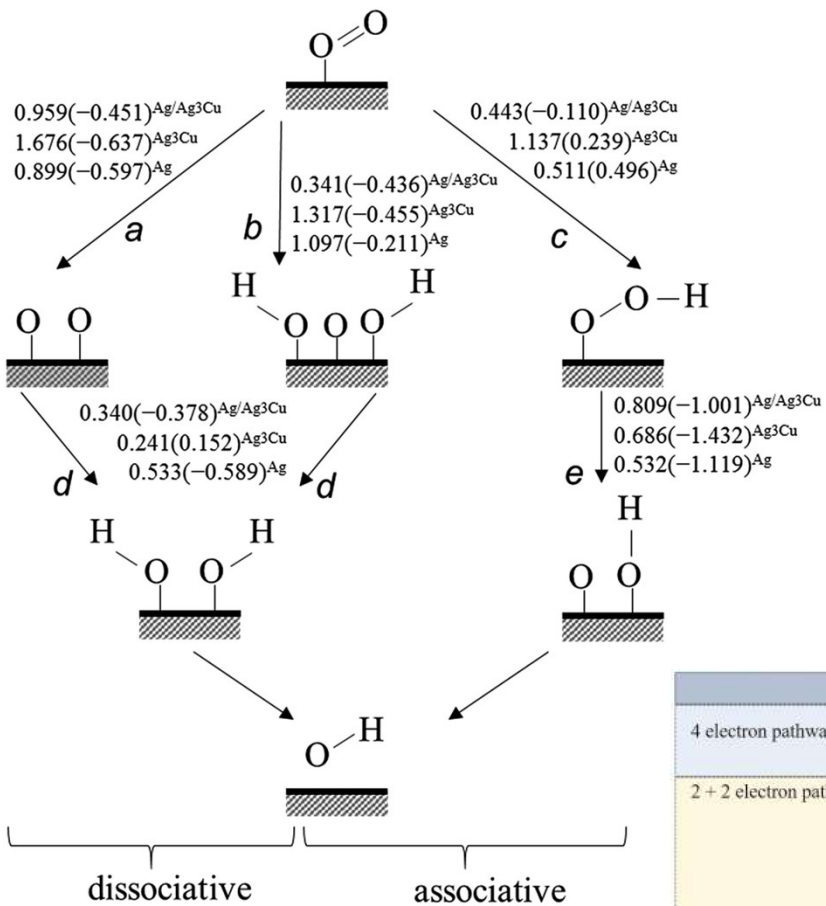


Half-reaction	Redox couple	Redox potential <sup>a)</sup> (E <sub>0</sub> ) [V]
$O_2 + e^- \rightarrow \bullet O_2^-$	$O_2/\bullet O_2^-$	-0.16
$\bullet O_2^- + 2H^+ + e^- \rightarrow H_2O_2$	$\bullet O_2^-/H_2O_2$	0.89
$H_2O_2 + H^+ + e^- \rightarrow H_2O + \bullet OH$	$H_2O_2/\bullet OH$	0.38
$H_2O + h^+ \rightarrow H^+ + \bullet OH$	$H_2O/\bullet OH$	2.32
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	$O_2/H_2O_2$	0.28

### Redox-Potentials

${}^1O_2 + e = O_2^{\bullet -}$	+ 0.64 V
${}^3O_2 + e = O_2^{\bullet -}$	- 0.33 V
$O_2^{\bullet -} + e + 2H^+ = H_2O_2$	+ 0.89 V
$H_2O_2 + e + H^+ = OH^\bullet + H_2O$	+ 0.38 V
$OH^\bullet + e + H^+ = H_2O$	+ 2.33 V
$CH_3OO^\bullet + e + H^+ = CH_3OOH$	+ 1.05 V

<sup>a)</sup>pH = 7.0.



Electrolyte	ORR reactions	Thermodynamic electrode potential at standard conditions, V
Acidic aqueous solution	$O_2 + 4H^+ + 4e^- \rightarrow H_2O$	1.229
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.70
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76
Alkaline aqueous solution	$O_2 + H_2O + 4e^- \rightarrow 4OH^-$	0.401
	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.065
	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.867
Non-aqueous aprotic solvents	$O_2 + e^- \rightarrow O_2^-$	a
	$O_2^- + e^- \rightarrow O_2^{2-}$	b

a, b: The thermodynamic potentials for the 1-electron reduction reaction to form a superoxide, and its further reduction to  $O_2^{2-}$ , are not listed in Table 2.1 because their values are strongly dependent on the solvent used.

ORR Pathways in Acidic Media		
4 electron pathway:	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E^\circ = 1.229 \text{ V vs SHE}$
2 + 2 electron pathway:	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	$E^\circ = 0.695 \text{ V vs SHE}$
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$E^\circ = 1.770 \text{ V vs SHE}$
	$2H_2O_2 \rightarrow 2H_2O + O_2$	
ORR Pathways in Basic Media		
4 electron pathway:	$O_2 + 2H_2O + 4e^- \rightarrow 2OH^-$	$E^\circ = 0.401 \text{ V vs SHE}$
2 + 2 electron pathway:	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	$E^\circ = -0.065 \text{ V vs SHE}$
	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	$E^\circ = 0.867 \text{ V vs SHE}$
	$2HO_2^- \rightarrow 2OH^- + O_2$	

<i>Alkaline media</i> : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (Four-electron process)
$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ (Two-electron process)
$H_2O + HO_2^- + 2e^- \rightarrow 3OH^-$
<i>Acid media</i> : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (Four-electron process)
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (Two-electron process)
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

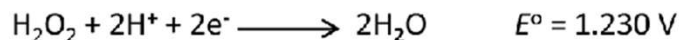
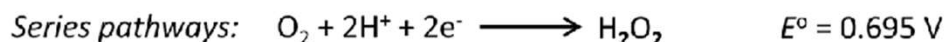
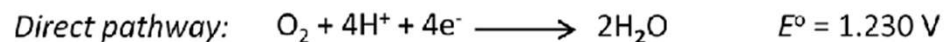


reduced intermediates, ozone, and singlet dioxygen

Half-reaction	$E^{\circ}$ ' (vs NHE) at pH 7 in V at 25 °C
$O_2 + e^- = O_2^{\cdot -}$	-0.18
$O_2(g) + e^- = O_2^{\cdot -}$	-0.35
$^1O_2 + e^- = O_2^{\cdot -}$	+0.81
$^1O_2(g) + e^- = O_2^{\cdot -}$	+0.64
$O_3 + e^- = O_3^{\cdot -}$	+1.03
$O_3(g) + e^- = O_3^{\cdot -}$	+0.91
$O_2^{\cdot -} + e^- + 2H^+ = H_2O_2$	+0.91
$HO_2^{\cdot} + e^- + H^+ = H_2O_2$	+1.05
$O_2 + 2e^- + 2H^+ = H_2O_2$	+0.36
$O_2(g) + 2e^- + 2H^+ = H_2O_2$	+0.28
$H_2O_2 + e^- + H^+ = HO^{\cdot} + H_2O$	+0.39
$H_2O_2 + 2e^- + 2H^+ = 2H_2O$	+1.35
$O_2 + 4e^- + 4H^+ = H_2O$	+0.85
$O_2(g) + 4e^- + 4H^+ = H_2O$	+0.81
$HO^{\cdot} + e^- + H^+ = H_2O$	+2.31

1 M aqueous conditions unless otherwise noted.

### Acidic medium



### Alkaline medium

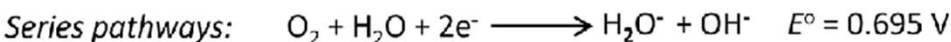
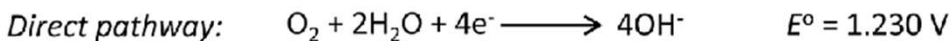


Figure 3: Reactions of hydrogen peroxide

1. in absence of metal catalyst ( $Fe^{++}$ )	
$H_2O_2(aq) \rightarrow H_2O(aq) + 1/2O_2(g)$	
$H_2O_2(aq) \rightarrow OH^{\cdot}(aq) + OH^{\cdot}(aq)$	
$H_2O_2(aq) \rightarrow OH^{\cdot}(aq) + OH^{\cdot}(aq)$	
$H_2O_2(aq) \rightarrow H^{\cdot} + OOH^{\cdot}$	
$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$	
2. in presence of metal catalyst ( Fenton reaction)	
A/ Oxidising agent in acidic medium	
$Fe^{++} + H_2O_2 \rightarrow Fe^{3+} - OH^{\cdot} + H_2O$ (1a)	
$Fe^{3+} + H_2O_2 \rightarrow Fe^{++} + OH^{\cdot}$ (1b)	
$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^{\cdot} + H_2O$ (1)	
$^{\cdot}OH + H_2O_2 \rightarrow OOH^{\cdot} + H_2O$ (2)	
$^{\cdot}OOH + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+$ (3)	
$2H_2O_2 \xrightarrow[\text{catalase}]{\text{Fe}} 2H_2O + O_2$ (4)	
B/ Oxidizing agent in alkaline conditions:	
$Fe^{2+}(aq) + HO_2^{\cdot -}(aq) + H_2O(l) \rightarrow Fe^{3+}(aq) + 3OH^-(aq)$	
[OH <sup>-</sup> — Hydroxyl ion; OH <sup>·</sup> — Hydroxyl radical; OOH <sup>·</sup> — perhydroxide radical Fe <sup>3+</sup> - OH <sup>·</sup> - Ferryl radical ]	

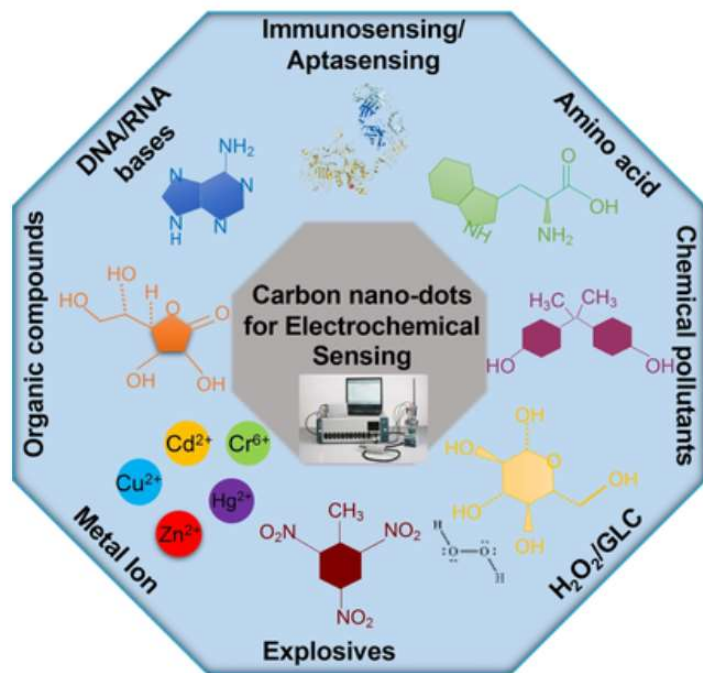
Electrolyte	Reaction pathway	Reaction potential (V vs. NHE)	
Alkaline electrolyte	4e <sup>-</sup> pathway:		
	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.401	
	Peroxide pathway:		
	$O_2 + H_2O + 2e^- \rightarrow HO_2^{\cdot -} + OH^-$	-0.065	
Acidic electrolyte	Peroxide pathway:	$HO_2^{\cdot -} + H_2O + 2e^- \rightarrow 3OH^-$	+0.867
		Or	Decomposition
	4e <sup>-</sup> pathway:		
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229	
	Peroxide pathway:		
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	+0.67		
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.77	
	Or	Decomposition	



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### Electrochemical Science Advances

[In Situ One-Step Electrochemical Preparation of Graphene Oxide Nanosheet-Modified Electrodes for Biosensors](#)

Fanwu Zeng, Zhenhua Sun, Xiaoguang Sang, Dermot Diamond, King Tong Lau, Xiaoxia Liu, Dang Sheng Su

ChemSusChem

[Electrochemical Sensors and Biosensors Based on Graphene Functionalized with](#)

## Abstract

This Review presents the latest advances in designing electrochemical sensors by using

- Cleaning polishing – elchem Nature – electrode pretreatment
- Eldep Au Pt on Au Pt
- Antibodies + EIS LSV, PM-CA
- Methyl blue, ferrocene, K3/K4FeCN6 1:0 1:1 0:1
  
- Spectroscopies and microscopies – in situ
- All the scientific devices and techniques?
- GC, MS, TG-DSC, ISP-OES, UV-VIS, FTIR, Raman, Elchem (CV, CA, LSV, EIS, pulse, differential, square-triangular, anodic-cathodic, with time, with Hz, voltage-current-conductivity-resistivity-capacitance)

### Bioelectrochemical sensors: (lab on chip)

- Metabolyte sensors – biomolecules
  - Pathogen detection – bacteria viruses and fungi – immunosensors
  - Aptasensors – pathogen
  - Cancer biomarker electrochemical biosensors
  - flavours and sweeteners – electronic nose and tongue
- 
- NPK sensors in agriculture
  - Pesticide detection
  - Heavy metal detection in water
- 
- Drug detection
  - Purity of pharmaceutical raw materials
- 
- ISFET, quantum dots
  - sample collection, sample treatment, analyte-specific reaction, signal generation and detection on a single platform

# Comsol simulations

- Energy balance
- Mass balance
- Transfer phenomena - Mass transfer, Heat transfer, Momentum transfer
- Diffusion, convection, conduction, irradiation (Transport, transfer)
- Electrochemical methods
- Partial differential equations, Nabla operator, Laplace
- Time and frequency domain-change
- Chemical reactions, Electrochemical kinetics, charge transfer
- Kinetics-equations, constants, equilibrium, thermodynamics
- Catalysis, redox, electrics (R,I,V,C,S; AC-DC, sine-square,  $\lambda$ ,  $v$ , ampl,  $\omega$ ),
- liquid/solid interface, phase boundary, double layer,
- Standard electrode potential, spontaneity of redox reaction
- Tafel, Nernst, Butler-Volmer, Langmir, Stern, Wagner-Traud, Koutecký-Levich
- Savitsky, Bourbaix, Levich, Randles-Ševčík, Fourier, Laplace, transfer function
- Coulombic efficiency
- Fluid dynamics - Flows-laminar-turbulent
- Osmosis, dialysis, electrophoresis, capillary effects, surface tension,
- Derivates, gradients-pressure-T-concentration
- Bernoulli, Reynolds, Van der Waals,
- Cartesian, Spherical, Cylindrical coordinates

# Comsol simulations

- Fluid dynamics
- Thermodynamics
- Mass transport
- Charge transfer
- Chemical reaction
- Electrochemical kinetics

- Finite element analysis
- DFT



Integrated Graphene

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Product Code NCZSPE101

Diameter of WE 2 mm, 3 mm, 4 mm, 5 mm

Size of RE 0.5 x 1 mm

Ratio CE/WE Surface Area 4/1

Shape Rectangle

Overall Dimension 50 x 10 mm

Thickness 0.5 mm

Thickness of Coated Material 10 µm

Working Electrode Graphite/Gold/Graphene/CNT/Platinum/Silver/Pdot-PSS, Prussian Blue (customization possible)

Counter Electrode Graphite/Gold/Silver

Reference Electrode Ag/AgCl

Substrate Valox FR1

Packaging 10, 40, 50, 100, 200, 500, 1000 Pcs etc.

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Chemical Name: Molybdenum Disulfide Powder

Purity: > 99.99%

Diameter: 20 nm to 10 µm (Size Customization possible)

Form: Powder/Dispersion (nano and micron Particle size)

Product Number: NCZAM102

CAS Number: 1317-33-5

Purity: > 99.99%

Size: ≤ 10 nm (Size Customization possible)

Concentration: 0.5 to 1 mg/ml (Customization possible)

Form: Powder/Dispersion

Product Number: NCZAM112

CAS Number: 12058-18-3

Purity: > 99.99%

Diameter: 0.2-5 µm, mainly concentrate in 1µm-3µm

Thickness: ~ 1 nm

Form: Powder/Dispersion

Product Number: NCZAM104

CAS Number: 1317-33-5

BASI RESEARCH PRODUCTS

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Screen Printed Electrodes

Performing diagnostic sensing or basic electrochemistry education research nowadays call for portable, disposable sensors that are cheap, reliable and functional. BASI's wide array of screen-printed electrodes is now available in 2 mm diameters and compatible with both BASI and PalmSens instruments. Compact and disposable, these units provide electrochemical cell systems with various configurations for the lab on the go.

AC1 (\*NEW SIZE AVAILABLE\*)

This screen printed amperometric sensor has three electrodes and is formed on a corundum base. It is 2.54 cm long, 0.73 cm wide, 0.63 mm thick, and weighs 0.5 grams. The available diameters of the working electrode area are 1.00 mm, 2.00 mm or 4.00 mm (±0.05 mm). There is a silver electrical contact at the end of each sensor and this conductive path is covered by a dielectric protection layer. They can be ordered in multiples of 20 sensors. The PALM-SPEHOLDER-2MM is an appropriate adapter for these sensors.

Part Number	Description
SP-1101	AC1 (1mm Gold Working; Silver/Silver Chloride Reference)
SP-1102	AC1 (2mm Gold Working; Silver/Silver Chloride Reference)
SP-1104	AC1 (4mm Gold Working; Silver/Silver Chloride Reference)
SP-1111	AC1 (1mm Gold Working; Silver Reference)
SP-1112	AC1 (2mm Gold Working; Silver Reference)

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	Gold Screen Printed Electrodes (3-electrodes)	Gold Screen Printed Electrodes Product No NRE-49003 CAS NA Diameter of WE 2 mm Size of RE ...
	Screen Printed Carbon Electrode (3-electrodes)	Screen Printed Carbon Electrode Product No NRE-49004 CAS NA Diameter of WE 2 mm Size of RE ...
	Screen Printed Electrodes Biosensors (3-electrodes)	Screen Printed Electrodes Biosensors Product No NRE-49005 CAS NA Diameter of WE 2 mm Size of RE ...
	Sensor Screen Printed Electrodes (3-electrodes)	Sensor Screen Printed Electrodes Product No NRE-49006 CAS NA Diameter of WE 2 mm Size of RE ...

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## Products Overview

Conductive Technologies (CT) has been a leader in high volume manufacturing of electrochemical sensors for the medical device and institutional markets. CTI continues to be a key contract manufacturer of disposable glucose test strips and electrochemical sensors for a wide range of diagnostic tests. Our extensive capabilities uniquely position us to design and develop the next generation of disposable diagnostic biosensors, MPOCT (multiplexed point of care testing) sensors and wearables. The biosensors market is expected to experience a 9% compounded annual growth rate through 2022. This expansion has brought us a diverse set of

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**PalmSens** Compact Electrochemical Interfaces

For Research OEM / Embedded For Corrosion

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Gold  
Gold Interdigitated  
Platinum  
Platinum Gold Alloy  
Silver

CE Material  
Graphene  
Platinum

RE Material

**CTI Phase Zero Sensors**

**ItalSens IS-C**

**Integrated Graphene Gli-Sens**

**ItalSens Gold SPE**

**ItalSens IS-HM**

**ZP Glucose Sensor Test Kit**

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AC1 Dwe = 4 mm Electrochemica...

AC1 Electrochemical sensor

AC1 Sw = 6.8 mm2...

AC1 AChE Electrochemical sensor

AC1.GOD Electrochemical sensor

AC13 Electrochemical sensor

AC1P Electrochemical sensor

AC2 Electrochemical sensor

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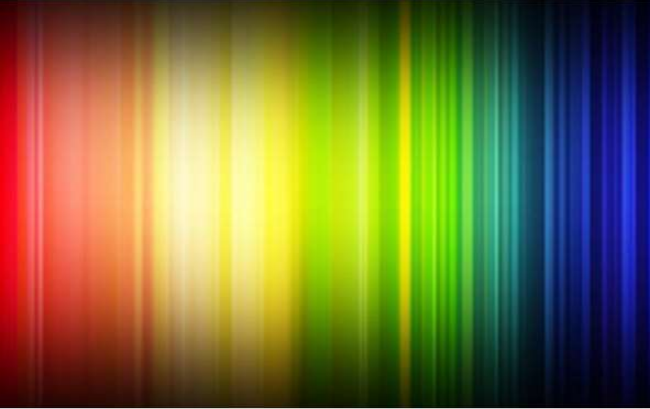
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Sep 6, 2021 Article

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Home Researching Communicating Advising Experience

## Researching

Throughout my academic career, I've been fortunate to contribute to a wide variety of research directions, including graph representation learning, computational biology, medical imaging, cross-modal learning, reinforcement learning, explainable AI, and deep learning on low-power/embedded systems. A detailed list of relevant publications is provided below.

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# Artificial intelligence

## Petar Velickovic

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Graph Attention Networks  
by Petar Veličković, Guillem Cucurull, Arantxa Casanova, Adriana Romero, Pietro Liò and Yoshua Bengio in ICLR (2018)

Multi-omics data integration using cross-modal neural networks  
by Ioana Biza, Petar Veličković, Ilus Xiao and Pietro Liò in ESANN (2018)

Using deep data augmentation training to address software and hardware heterogeneities in wearable and smartphone sensing devices  
by Akhil Mathur, Tianlin Zhang, Soumya Bhattacharya, Petar Veličković, Leonid Joffe, Nicholas D. Lane, Fahim Kwassar and Pietro Liò in IPSN (2015)

Scaling health analytics to millions without compromising privacy using deep distributed behavior models

X-CNN: Cross-modal convolutional neural networks

Viral: Real-world competing process simulations on multiplex

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## Biosensing

- a. Artificial intelligence in biosensors;
- b. Ingestible, implantable and wearable biosensors;
- c. Smartphone-based biosensors;
- d. The evolution of biological recognition elements in biosensors;
- e. Microfabrication and printing techniques in biosensors;
- f. Nanomaterials and smart surfaces in biosensors;
- g. Technological advancements in biosensor actuators.

- Bioelectronics (including biocomputing, bio-fuel and photovoltaic cells, and electronic noses)
- Commercial biosensors, manufacturing and markets
- DNA chips, and nucleic acid sensors and aptasensors
- Enzyme-based biosensors
- Immunosensors
- Lab-on-a-chip and multiplexed sensors
- Microfluidics and immobilization technology
- Smartphone diagnostics, wearable biosensors and personal mobile health
- Nanobiosensors, nanomaterials & nanoanalytical systems
- Natural & synthetic receptors (including MIPs)
- Organism-, and whole cell- and organ-based biosensors
- Printed biosensors and microfabrication
- Proteomics, single-cell analysis and cancer-cell detection
- Signal transduction technology
- Single molecule detection
- Theranostics, implantable and ingestible sensors
- CRISPR-based biosensors
- Novel transducers
- Implantable and ingestible sensors
- Synthetic biology for biosensors