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XXXVII Cycle

# Non-enzymatic Electrochemical Sensors: Effects of Chemical and Crystallographic Features

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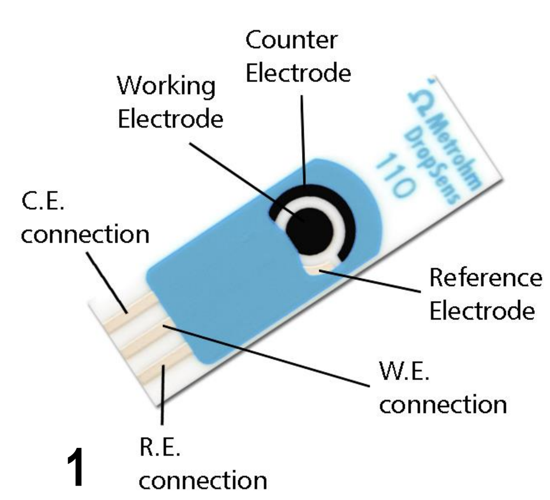
## Research context and motivation

- Several methods have been proposed for **sensing various biomolecules**. However, they (titrimetric, liquid chromatography, chemiluminescence, capillary electrophoretic, water analysis etc.) are **time consuming** and require **cumbersome equipment.**
- **Electrochemical sensors** have consequently attracted more attention due to their **low cost**, ease of use, and **high sensitivity**.

- Disposable **screen-printed carbon electrodes (SPCEs)** as **non-enzymatic** electrochemical sensors
- **Surface modification**
- Simple design, low-cost fabrication
- **Smart sensing, on-site or point-of-care (POC)** measurements
- **No enzymes** required
- Room temperature storage, high operational lifetime



1


2


3

From metrohm dropsens [1], palmsens [2-3].

## Addressed research questions/problems

- Marcus [1956] developed a model to **calculate the rate constant** due to electron transfer at an interface which was generalized by Tachiya and Murata [1992].
- The first order rate constant k is given by

$$k = \frac{4\pi^2}{h} \frac{J^2}{(4\pi k_B T\lambda)^{1/2}} exp\left[-\frac{(\Delta G + \lambda)^2}{4 k_B T\lambda}\right]$$

$$J^2 = {J_0}^2 exp[-\beta\{R-(a+b)\}]$$

$$\lambda = \frac{e^2}{2}\left({\epsilon_{op}}^{-1} - {\epsilon_s}^{-1}\right)\left(\frac{1}{a}+\frac{1}{b}+\frac{2}{R}\right)$$

h – Plank constant, **J – transfer integral**
$J_0$ – J with $\beta$ – decay parameter = 0
**R – donor, acceptor distance**
**a and b – the radii of the donor and the acceptor**
$k_B$ – the Boltzmann constant, T – the temperature
**λ** – the **reorganization energy**, e – electronic charge
$\epsilon_{op}, \epsilon_s$ – optical, static dielectric constants of the solvent
$\Delta G$ – the **Gibbs free energy**

k → J, $\lambda$ → R, a, b → **Size, geometry**
J, $\lambda$ → **Crystal structure, chemical composition**

## List of attended classes

- 01UKGKI – Synthesis methods to tailor the surface, and the structural properties of advanced materials (11/05/2022, 5 credits)
- 02UKHKI – Applied spectroscopic methods (13/06/2022, 6 credits)
- XXXXXX – The 2nd Training school on Modelling and Characterization of CNM composites (16/06/2022, 4 credits)
- 01MQLKI – X-ray diffraction by materials (06/07/2022, 5 credits)
- XXXXXX – Short course on Electrochemistry (01/07/2022, 1.5 credits)
- XXXXXX – Soft skills (03/12/2022, 10 credits)
- 01DOJRV – Computational (opto) electronics (exam pending, 3.6 credits)
- 01UILIY – Catalysis and biocatalysis: fundamentals (27/09/2022, 4 credits)
- XXXXXX – School on micro-nano technologies (23/09/2022, 3 credits)

## Novel contributions

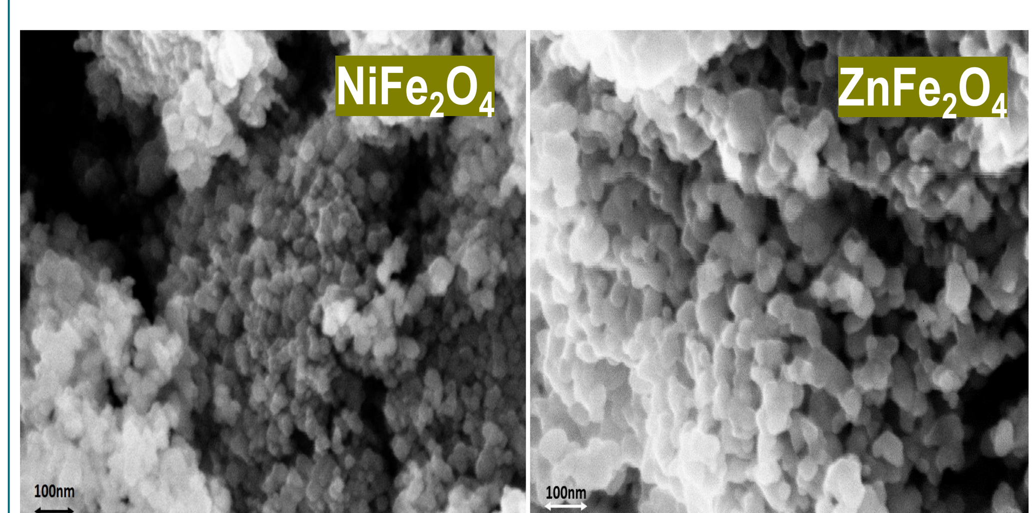
- **Spinel structure** ↔ **Inverse spinel structure**
  $(A_{th}(B_2)_{oh}O_4)$ $(B_{th}(AB)_{oh}O_4)$
  → J, λ → k
  **Shape, geometry, chemical composition** → J, λ

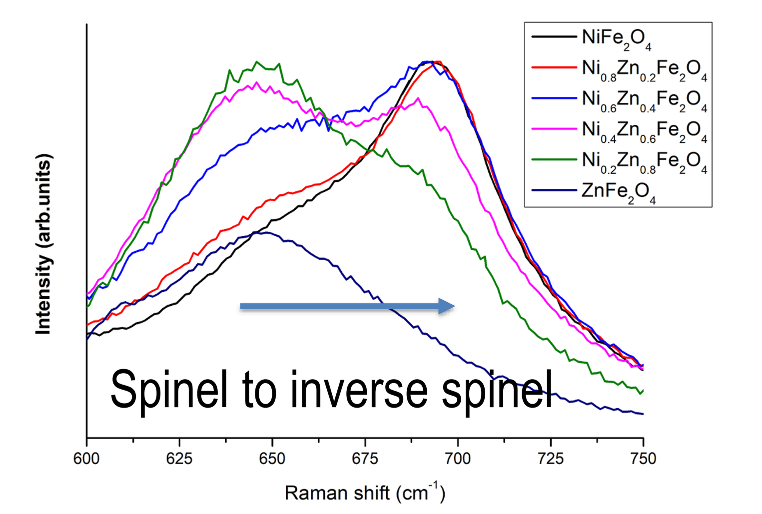
A = $Zn^{+2}$, $Fe^{+2}$, $Ni^{+2}$
B = $Fe^{+3}$, $Cr^{+3}$, $Bi^{+3}$

th – **tetrahedral site**
oh – **octahedral site**

## Adopted methodologies

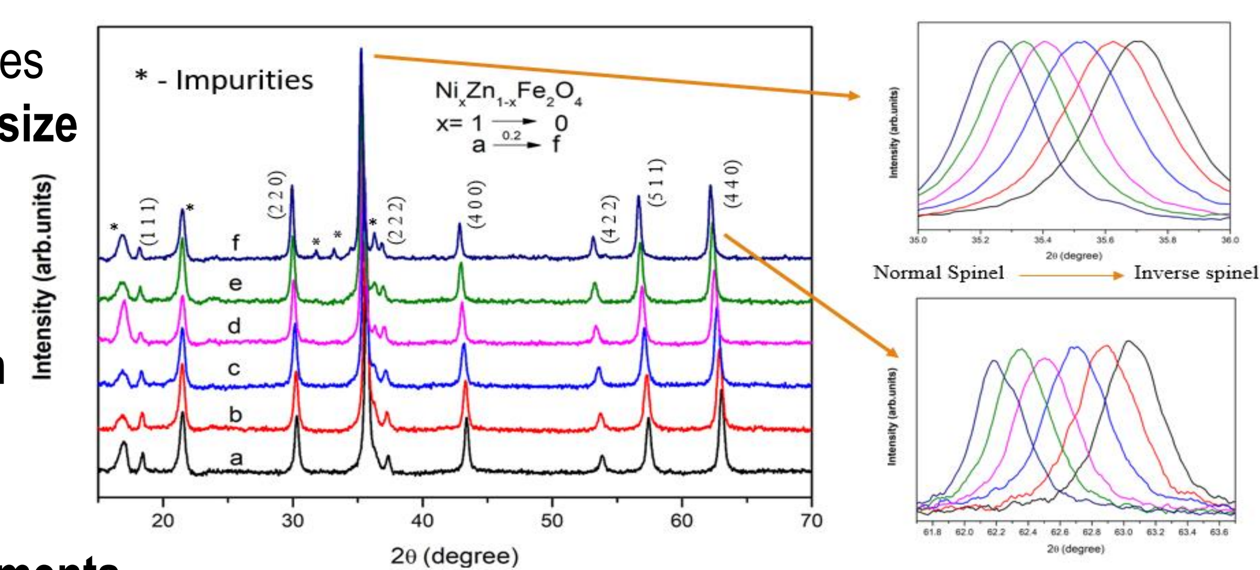
- Spinel and inverse spinel-based nanoparticles **were synthesized** by **autocombustion**.
- Characterized by **FE-SEM, Raman spectroscopy, and X-ray diffraction (XRD)**.



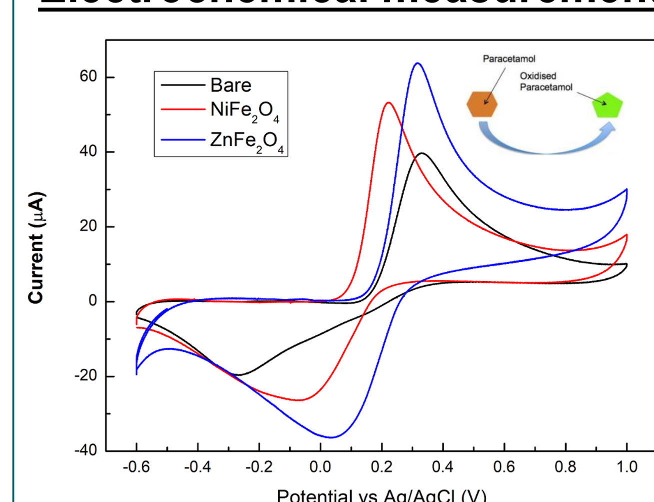



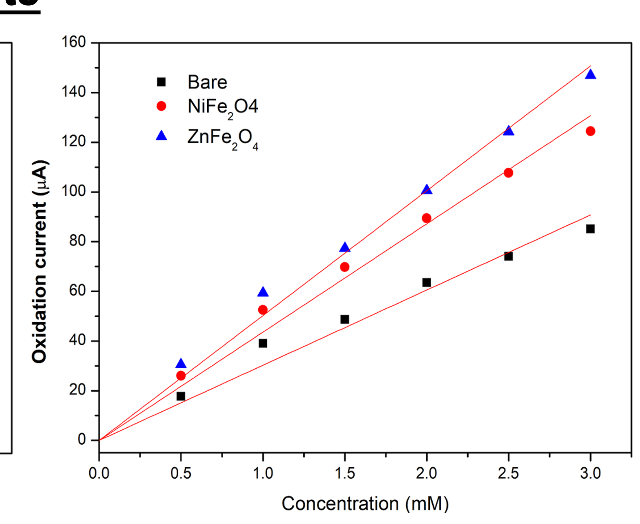

**Spherical shaped** particles with an average **particle size 30 – 40 nm**

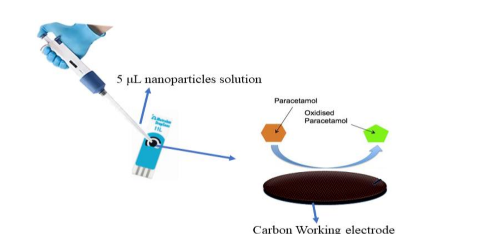
The **transition** from spinel to inverse spinel **has been observed** in both Raman spectra and XRD spectra.




**Electrochemical measurements**



**Ferrites nanoparticles modified SPCEs** as electrochemical sensors

Cyclic voltammograms of 1mM **paracetamol in 0.1M PBS pH 6.9** (left), and calibration curves (right).

| Electrode | Oxidation Potential (mV ± SEM) | Oxidation Current (µA ± SEM) |
|---|---|---|
| Bare | 326.80 ± 0.73 | 39.11 ± 0.16 |
| $NiFe_2O_4$ | 246.6 ± 3.2 | 51.53 ± 0.80 |
| $ZnFe_2O_4$ | 307.0 ± 6.0 | 59.17 ± 0.63 |

SEM – standard error mean

| Electrode | Sensitivity (µA/mM ± SEM) | $\Delta E_p$ (mV ± SEM) |
|---|---|---|
| Bare | 30.2 ± 1.0 | 594.4 ± 1.2 |
| $NiFe_2O_4$ | 43.6 ± 1.1 | 290.6 ± 1.3 |
| $ZnFe_2O_4$ | 50.26 ± 0.98 | 278.3 ± 2.7 |

**$\Delta E_p$ – Peak to peak separation**

## Conclusions

- Successful synthesis and characterization of **ferrites-based nanoparticles**.
- Preliminary **electrochemical sensing** and **calibration** measurements were performed.
- Results were presented at **Nanoinnovation conference 2022** as a **poster** in Rome.

## Future works

- Completion of electrochemical measurements
- Computational approach
- Chemical composition (same crystal structure)
- Size, shape, and orientation

} **Effect on k**

## Submitted and published works

- Cantarella, G., **Madagalam, M.**, ..., Lugli, P.,"Laser-induced, Green and Biocompatible Paper-based Devices for Circular Electronics", *Advanced materials* (submitted), August 2022.
- **Madagalam, M.** , La Torraca, P., ..., Lugli, P., "Screen-Printed Flexible Circular and Rectangular Silver Spirals for Planar Electrodynamic Loudspeakers: A Comparative Study of Pressure Frequency Response", *IEEE EDTM conference*, 2022.
- **Madagalam, M.** , Catania, F., Bartoli, M., Tagliaferro, A., and Carrara, S., "Nanostructured Bismuth Electrodes for Non-Enzymatic Paracetamol Sensing: Development, Testing, and Computational Approach", *MDPI, Chemistry Proceedings*, 2021.
- **Madagalam, M.**, Bartoli, M., Tagliaferro, A., and Carrara, S., "Bismuth-nanocomposites modified SPCEs for non-enzymatic electrochemical sensors", *IEEE Sensors Journal*, vol. 21, no. 9, 2021, pp. 11155-11162.

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