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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

Necessity of the research

Hydrogen peroxide is a very interesting reactant due to:

*It can be used as an oxidant or reductant agent.

*It is a green chemical, since water is the sole by-product in the oxidations

*It can be electrochemically synthetized from oxygen in water, so its use and production are clean

However, the electrochemical synthesis presents serious drawbacks

*low solubility of oxygen in water

*sluggish kinetics of the electrochemical reduction

*high alkalinity

It means low current efficiencies and the electrochemical route is not competitive

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

Objectives

Identification of practical electrocatalysts capable of acting as electrode materials in a sonoelectrochemical reactor for the reduction of oxygen (air) to hydrogen peroxide

The determination of the stability of the electrocatalysts in respect of insonation to identify the optimal sonoelectrocatalysts for hydrogen peroxide formation

Design, development and optimisation of a reliable and efficient laboratory bench scale sonoelectrochemical reactor

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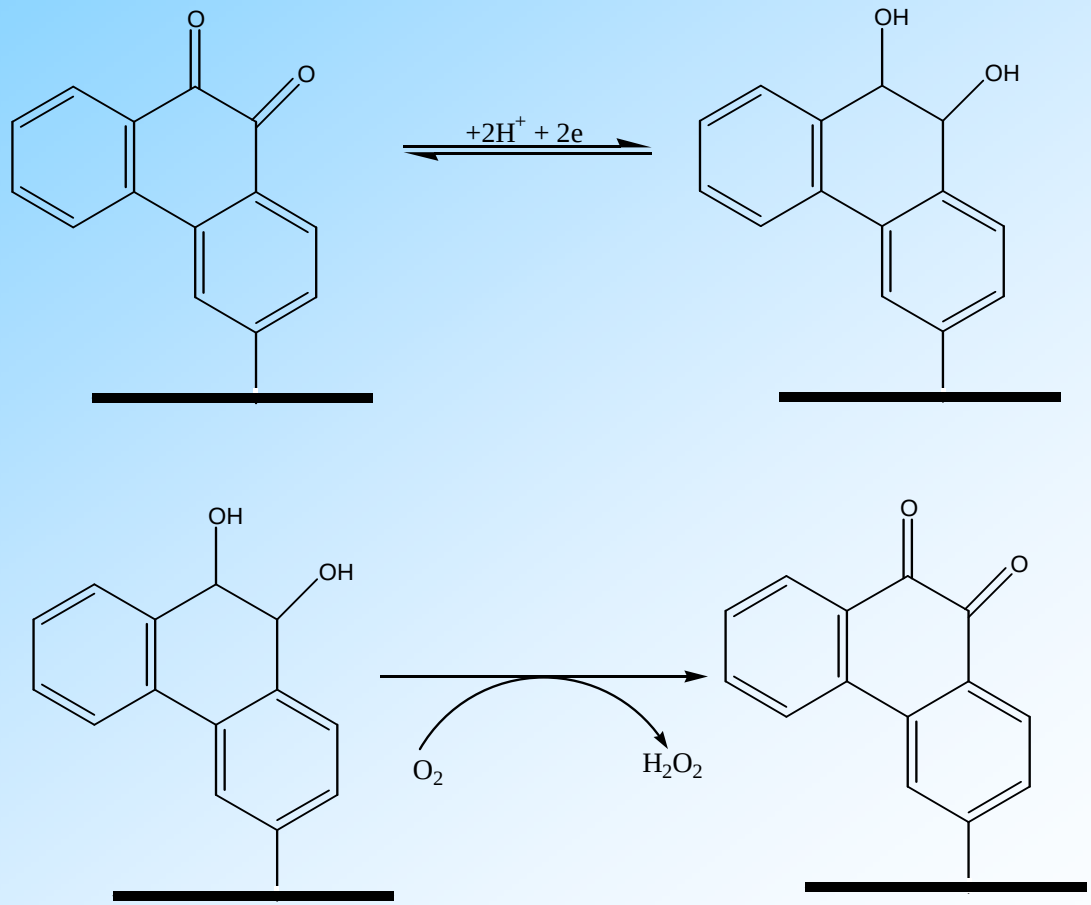
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

(1)Modification of the carbon electrode surface by inmobilization of electrocatalysts
(2)Enhancement of the mass transport by means of ultrasound



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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

From the several kinetics scheme found in literature for the electrocatalytic reduction of dissolved oxygen, it can be suggested:

$$Q(ads) + 2e + 2H^+ \rightarrow H_2Q(ads) \qquad \text{reaction (I)}$$

$$H_2Q(ads) + O_2 \xrightarrow{k} Q(ads) + H_2O_2 \qquad \text{reaction (II)}$$

Where reaction (II) is the rate-determining step. Andrieux and Savéant have derived a theoretical model for an EC′ reaction of a model redox chemically modified electrode to evaluate the catalytic rate constant, k.

C. P. Andrieux and J. M. Savéant *J. Electroanal. Chem.* 1978, 93, 168

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

Previous work:

Work done with two-dimmensional electrodes:

- Glassy carbon
- Edge plane pyrolytic graphite (EPPG)
- Basal plane pyrolytic graphite (BPPG)

Previous work:

A. Salimi et al. Phys. Chem. Chem. Phys. 2003, 5, 3988-3993

B. Sljukic et al. Phys. Chem. Chem. Phys. 2004, 6, 992–997

B. Sljukic et al. Phys. Chem. Chem. Phys. 2004, 6, 4034–4041

B. Sljukic et al. J. of the Iranian Chem. Soc. 2005, 2, 1–25

B. Sljukic et al. Electroanalysis 2005, 17, 1025–1034

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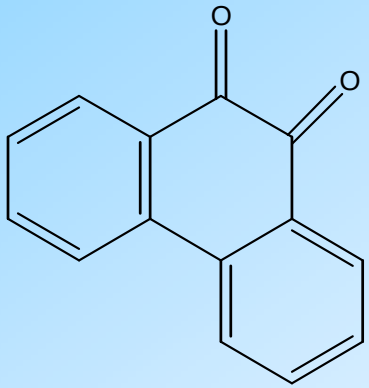
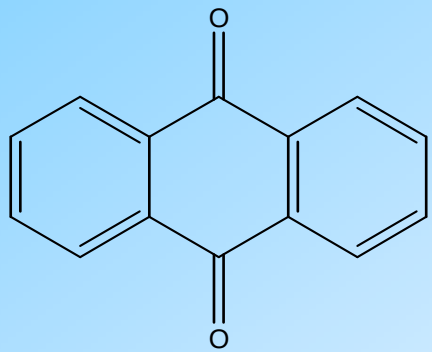
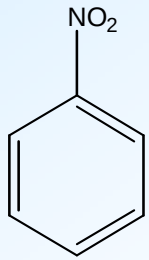
Present work:
Electrocatalysts analyzed



9,10-phenanthraquinone (PAQ)



anthraquinone



nitrobenzene

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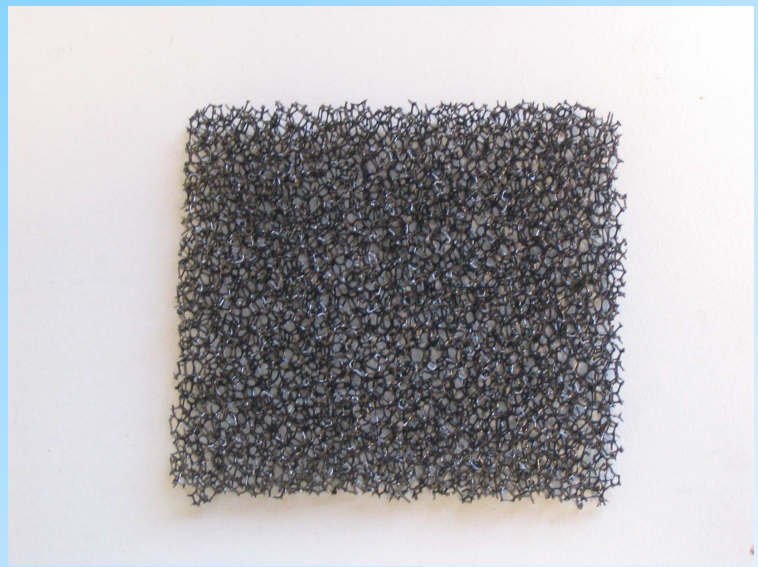
Electrodes to be used: Three-dimmensional electrodes

Reticulated vitreous carbon 10 ppi



Compression Strength	(.28-1.20 MPa)
Tensile Strength	(.17-1.02 MPa)
Modulus of Elasticity	(31-62 MPa)
Shear Modulus	(30.3 MPa)
Hardness	6-7 Mohs
Specific Heat	(1.26 $J \cdot g^{-1} \cdot °C^{-1}$)
Coefficient of Thermal Expansion:	
· 0 - 100°C	($2.2 \cdot 10^{-6} \cdot m \cdot m^{-1} \cdot °C^{-1}$)
· 100 - 1000°C	($3.2 \cdot 10^{-6} \cdot m \cdot m^{-1} \cdot °C^{-1}$)
Bulk Resistivity	($5 \cdot 10^{-2} \cdot$ ohm · cm)
Sublimation Point	(3500°C)
Temperature Limitations:	
· in air	(315°C)
· in non-oxidizing environment	(3500°C)

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Procedure

Different ways of modification of the carbon electrode surface. For all modifications, an **activation step** was carried out as follow:

Cycling between -0.5V and 2.0V at 100 mV s^{-1} in 0.1M H_2SO_4 10 min.
Holding at +1.8V vs SCE in the same solution for 3 minutes

Modifications

Physical **modification**:
electrode is dipped in a 1mM solution of electrocatalyst in acetonitrile and modification by solvent evaporation

Chemical **modification**:
Chemical reduction of the diazonium salts of the electrocatalyst with hypophosphorous acid

Electrochemical **modification** (different among compounds)

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Procedure

Electrochemical modification for PAQ
Cycling between 1.0 to -1.0V vs SCE for five cycles at 10 mV s^{-1} in electrocatalyst solution, pH 10 boric buffer

Electrochemical modification for Anthraquinone (Fast Red AL)
Cycling between 0.65 to -0.45V vs SCE for three cycles at 0.2 V s^{-1} in Fast Red AL solution in acetonitrile, and held at -0.2 V for 10 minutes

Electrochemical modification for Nitrobenzene (Fast Red GG)
Cycling between 0.65 to -0.45V vs SCE for three cycles at 0.2 V s^{-1} in Fast Red GG solution in acetonitrile, and held at -0.2 V for 10 minutes

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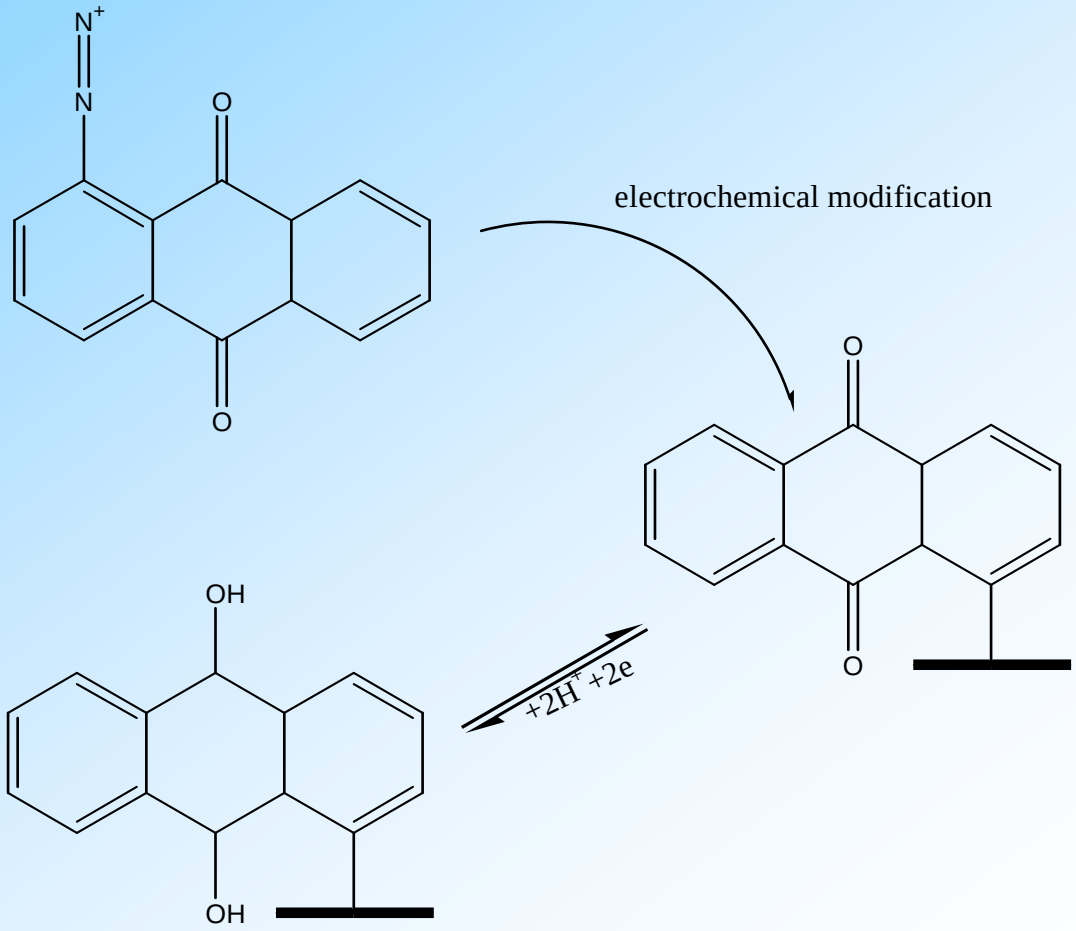
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Procedure



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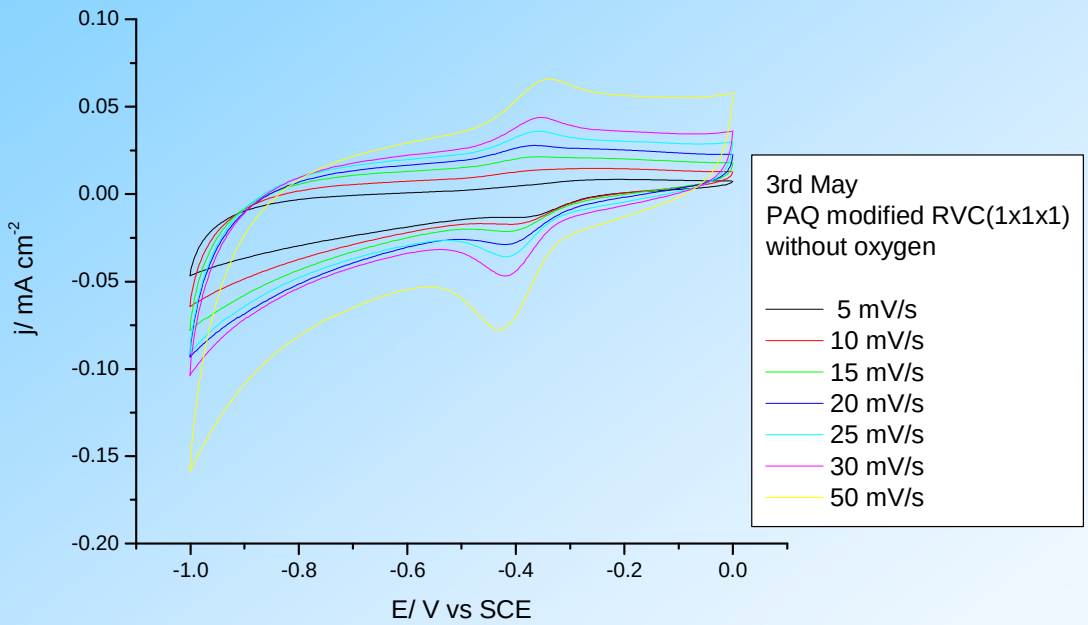
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Characterization fo the coverage of the modification

The modified electrode is placed into a pH 10 buffer solution and is investigated voltammetrically by means a scan rate series



9,10-phenanthraquinone (PAQ)
Physical modification

A pair of well-defined redox peaks corresponding to the reversible reduction of the surface confined quinone species is observed at -0.4 V vs SCE

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Characterization fo the coverage of the modification

The surface concentration of the electrocatalyst adsorbed on the reticulated vitreous carbon electrode, Γ, can be calculated from the following equation

$$\Gamma = \frac{Q}{nFA}$$

Γ: is the surface coverage in mol cm^{-2}
n: number of the electrons per reactant molecule
F: Faraday constant
A:electrode area
Q: is the charge obtained from integration of the cathodic peak

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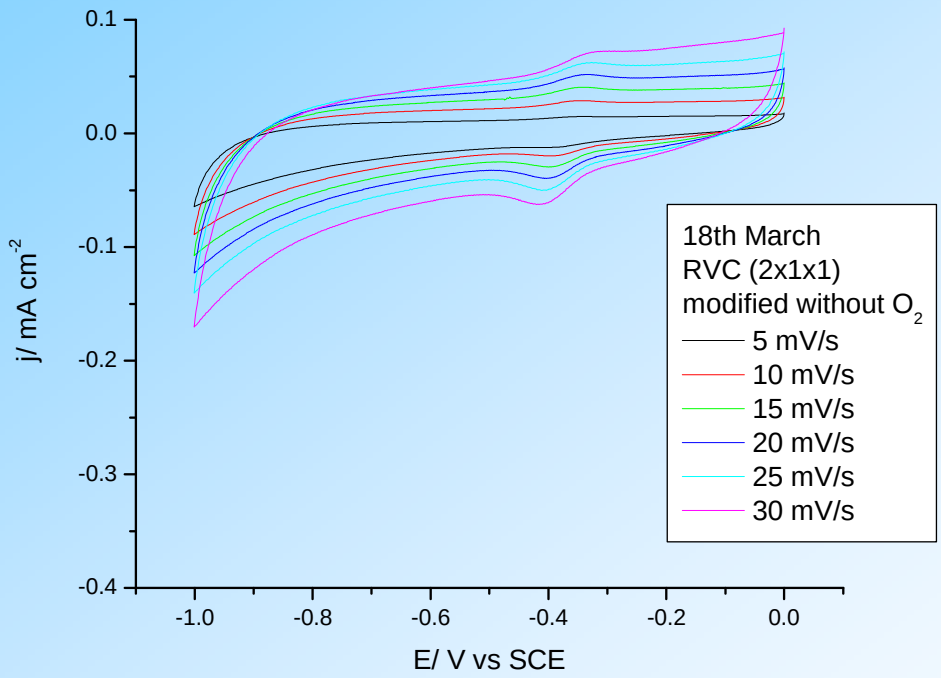
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results for PAQ and physical modification:



υ/ mV/s	I_{peak}/A	Charge/C	Γ/mol cm^{-2}
5	-0.170 10^{-3}	0.890 10^{-3}	3.30 10^{-10}
10	-0.279 10^{-2}	0.818 10^{-3}	3.03 10^{-10}
15	-0.414 10^{-2}	0.875 10^{-3}	3.24 10^{-10}
20	-0.555 10^{-2}	0.850 10^{-3}	3.14 10^{-10}
25	-0.700 10^{-2}	0.988 10^{-3}	3.66 10^{-10}
30	-0.870 10^{-2}	1.153 10^{-3}	4.26 10^{-10}

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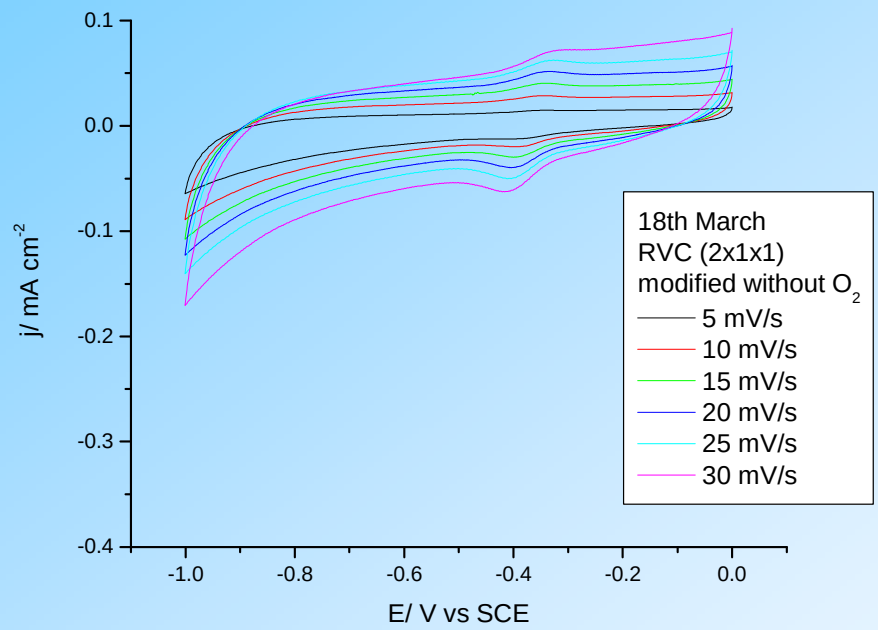
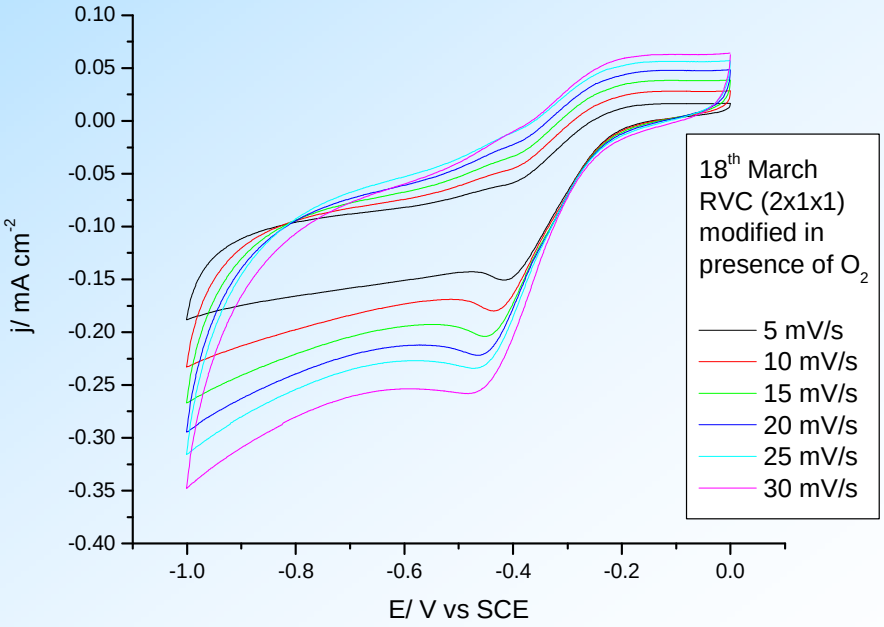
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Voltammetry in absence and presence of oxygen





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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Electrocatalysis of the oxygen reduction

Using the Andrieux and Savéant method, the catalytic rate constant are obtained

From the voltammetry in presence of oxygen for the modified electrode and using the following equation:

$$I_P = yFAC_{bulk}D^{1/2}\left(\frac{F\nu}{RT}\right)^{1/2} \rightarrow y$$

we obtain "y" from the plot I_p vs $\upsilon^{1/2}$ This value is used via the theoretically derived curve provided by Andrieux and Savént to determine "x". Once we know "x", we obtain the rate constant k, or kΓ, with the following equation:

$$x = \log\left[\frac{k\Gamma}{D^{1/2}\left(F\upsilon/RT\right)^{1/2}}\right] \rightarrow k$$

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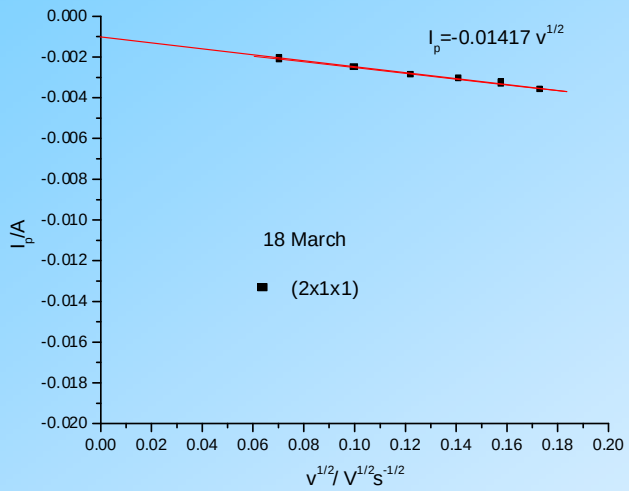
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound Identification of electrocatalysts

Results for PAQ and physical modification:



	Absence of oxygen			Presence of oxygen	
υ/ mV/s	I_{peak}/A	Charge/C	Γ/mol cm^{-2}	I_{peak}/A	I^c_{peak}/A
5	-0.170 10^{-3}	0.890 10^{-3}	3.30 10^{-10}	-0.211 10^{-2}	-0.194 10^{-2}
10	-0.279 10^{-2}	0.818 10^{-3}	3.03 10^{-10}	-0.252 10^{-2}	-0.226 10^{-2}
15	-0.414 10^{-2}	0.875 10^{-3}	3.24 10^{-10}	-0.285 10^{-2}	-0.249 10^{-2}
20	-0.555 10^{-2}	0.850 10^{-3}	3.14 10^{-10}	-0.310 10^{-2}	-0.264 10^{-2}
25	-0.700 10^{-2}	0.988 10^{-3}	3.66 10^{-10}	-0.328 10^{-2}	-0.269 10^{-2}
30	-0.870 10^{-2}	1.153 10^{-3}	4.26 10^{-10}	-0.361 10^{-2}	-0.285 10^{-2}

(Γ=3.03 10^{-10} mol cm^{-2}) the chemical rate constant: 2.34 10^3 M^{-1} s^{-1}

Γk=7.09 10^{-4} cm s^{-1}

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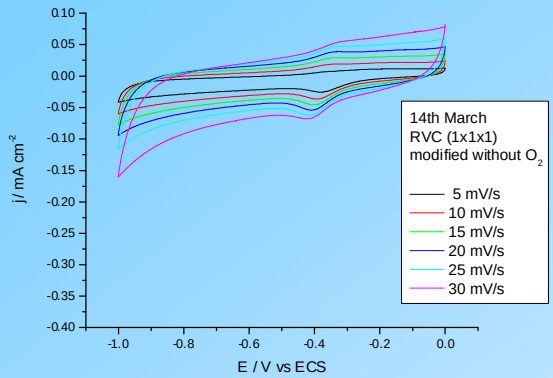
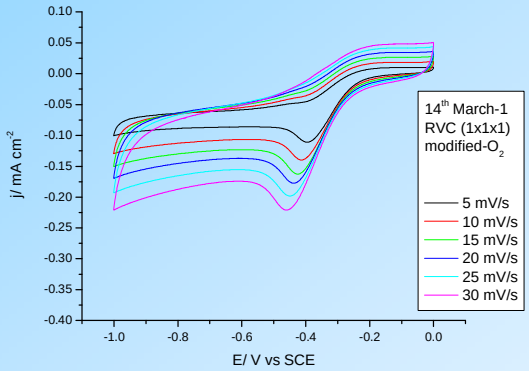
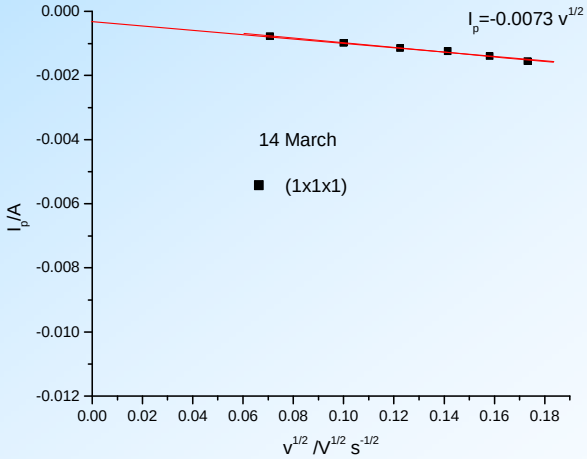
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results:PAQ physical adsorption







	Absence of oxygen			Presence of oxygen	
υ/ mV/s	I_{peak}/A	Charge/C	Γ/mol cm^{-2}	I_{peak}/A	I^c_{peak}/A
5	-0.178 10^{-3}	2.501 10^{-3}*	1.85 10^{-9}	-0.078 10^{-2}	-0.603 10^{-3}
10	-0.256 10^{-3}	1.693 10^{-3}	1.25 10^{-9}	-0.098 10^{-2}	-0.738 10^{-3}
15	-0.321 10^{-3}	1.337 10^{-3}	9.90 10^{-10}	-0.114 10^{-2}	-0.840 10^{-3}
20	-0.379 10^{-3}	1.026 10^{-3}	7.60 10^{-10}	-0.124 10^{-2}	-0.893 10^{-3}
25	-0.436 10^{-3}	0.889 10^{-3}	6.58 10^{-10}	-0.139 10^{-2}	-0.990 10^{-2}
30	-0.475 10^{-3}	0.623 10^{-3}	4.61 10^{-10}	-0.155 10^{-2}	-1.100 10^{-2}

$k = 6.05\ 10^{2}\ M^{-1}\ s^{-1}$

$\Gamma k = 7.56\ 10^{-4}\ cm\ s^{-1}$

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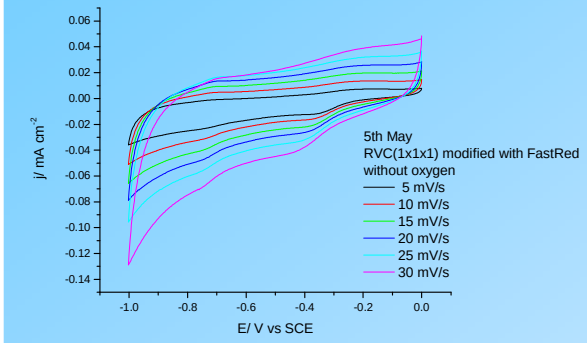
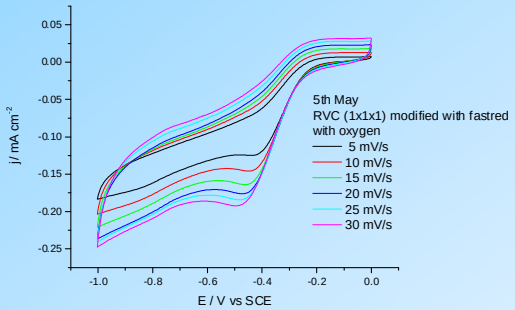
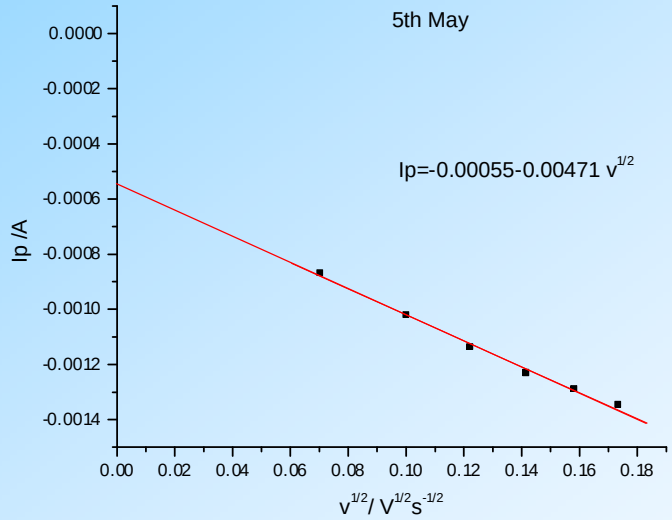
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results:Anthraquinone (Fast Red AL) Chemical modification







$k = 1.05\ 10^{3}\ M^{-1}\ s^{-1}$

$\Gamma k = 3.97\ 10^{-4}\ cm\ s^{-1}$

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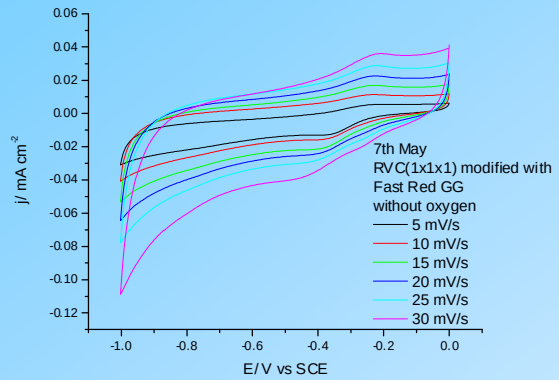
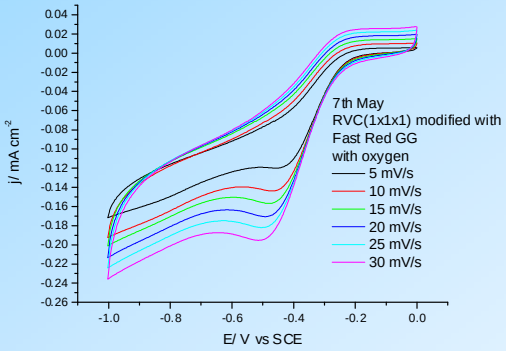
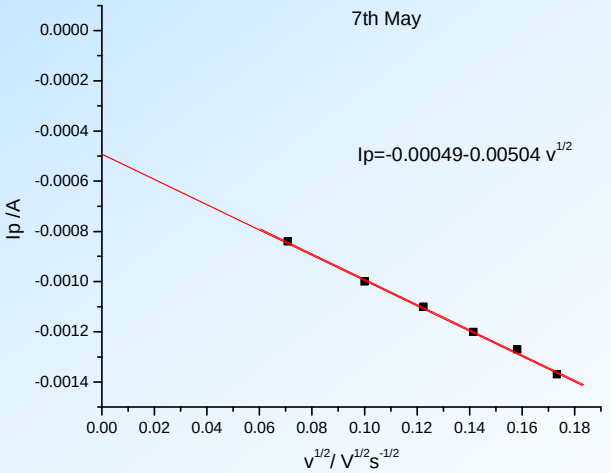
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound Identification of electrocatalysts

Results:Nitrobenzene (Fast Red GG) Chemical modification







$k = 8.02\ 10^{2}\ M^{-1}\ s^{-1}$

$\Gamma k = 4.35\ 10^{-4}\ cm\ s^{-1}$

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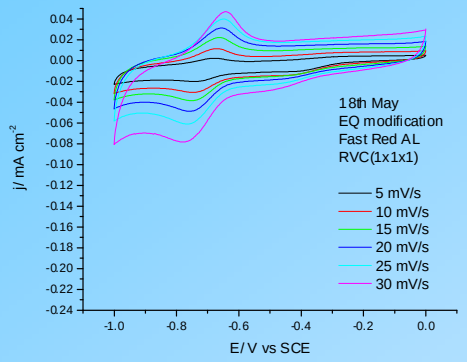
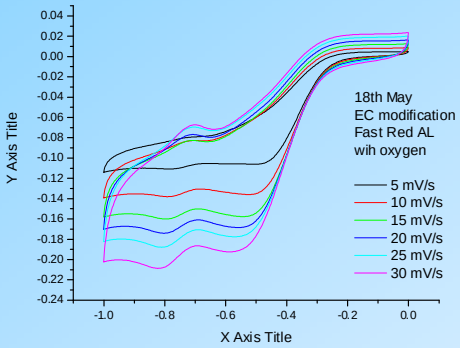
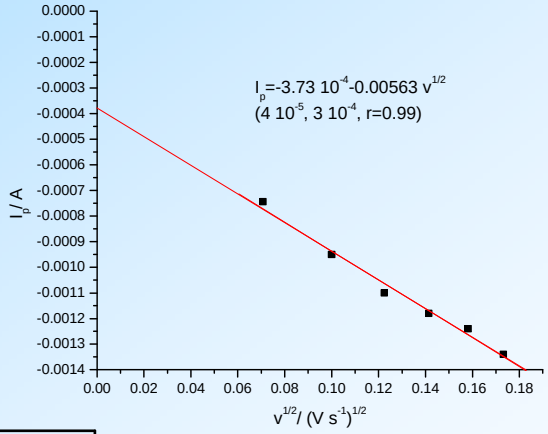
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results:Anthraquinone (Fast Red AL) Electrochemical modification







	Absence of oxygen					Presence of oxygen
υ/ mV/s	I_{peak}/A	Charge/C	Charge*/C	Γ/mol cm^{-2}	Γ*/mol cm^{-2}	I_{peak}/A
5	-0.141 10^{-3}	8.28 10^{-4}	1.73 10^{-3}	6.13 10^{-10}	12.77 10^{-10}	-0. 074 10^{-2}
10	-0.214 10^{-3}	8.34 10^{-4}	1.31 10^{-3}	6.17 10^{-10}	12.85 10^{-10}	-0. 095 10^{-2}
15	-0.270 10^{-3}	8.94 10^{-4}	1.10 10^{-3}	6.62 10^{-10}	13.79 10^{-10}	-0. 110 10^{-2}
20	-0.341 10^{-3}	9.24 10^{-4}	1.07 10^{-3}	6.84 10^{-10}	14.25 10^{-10}	-0. 118 10^{-2}
25	-0.426 10^{-3}	9.51 10^{-4}	1.06 10^{-3}	7.04 10^{-10}	14.67 10^{-10}	-0. 124 10^{-2}
30	-0.548 10^{-3}	9.51 10^{-4}	1.06 10^{-3}	7.04 10^{-10}	14.67 10^{-10}	-0. 134 10^{-2}

$k = 8.22\ 10^{2}\ M^{-1}\ s^{-1}$

$\Gamma k = 5.07\ 10^{-4}\ cm\ s^{-1}$

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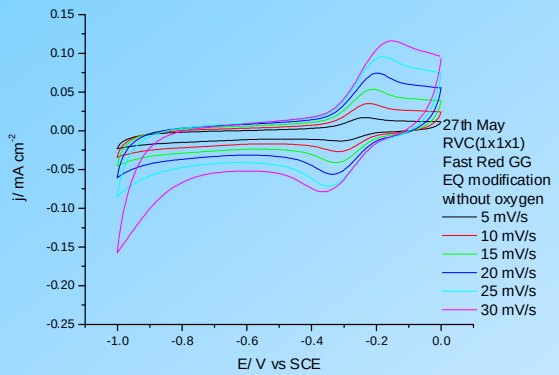
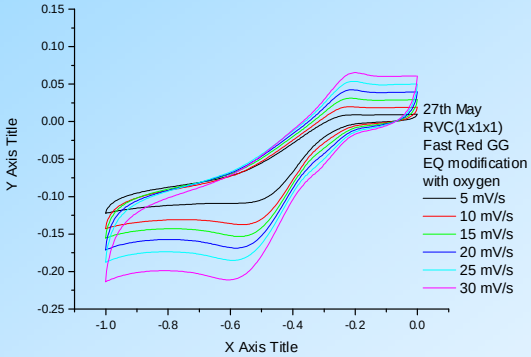
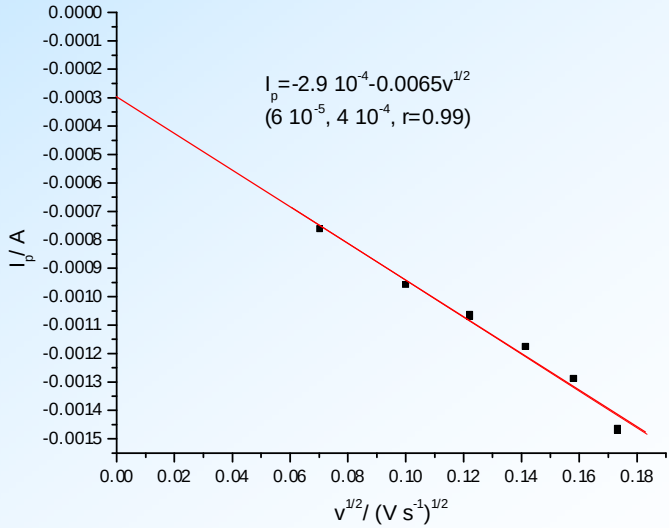
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results:Nitrobenzene (Fast Red GG) Electrochemical modification







$k = 3.87\ 10^{2}\ M^{-1}\ s^{-1}$

$\Gamma k = 6.31\ 10^{-4}\ s^{-1}\ cm^{-1}$

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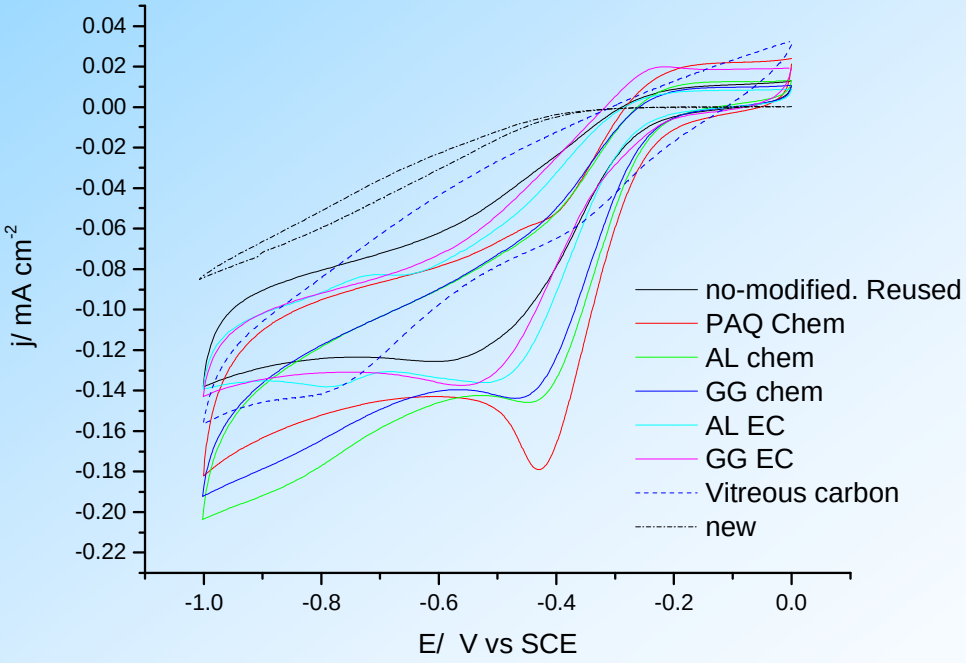
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Final results

Voltammetry in presence of oxygen



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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound Identification of electrocatalysts

Conclusions

9-10 phenantraquinone is a good electrocatalysts capable of acting as electrode materials in a electrochemical reactor for the reduction of oxygen (air) to hydrogen peroxide

Physical adsorption is shown as the best modification method

Electrochemical modification presents better coverages than chemical modifications

Activation step presents an interesting activity for oxygen electrochemical reduction

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

State of the art

Cathodic reaction: $O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^-$

Anodic reaction: $2OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e$

Global reaction: $\frac{1}{2} O_2 + H_2O \rightarrow H_2O_2$

Drawbacks of the synthesis

- Slow kinetics
- Current efficiency not higher than 40%
- High alcalinity

Parasitic reactions:

Cathodic reduction of hydrogen peroxide: $2H_2O_2 + 4e \rightarrow 4OH^-$

Anodic oxidation of hydrogen peroxide $H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e$

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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

Equiptment

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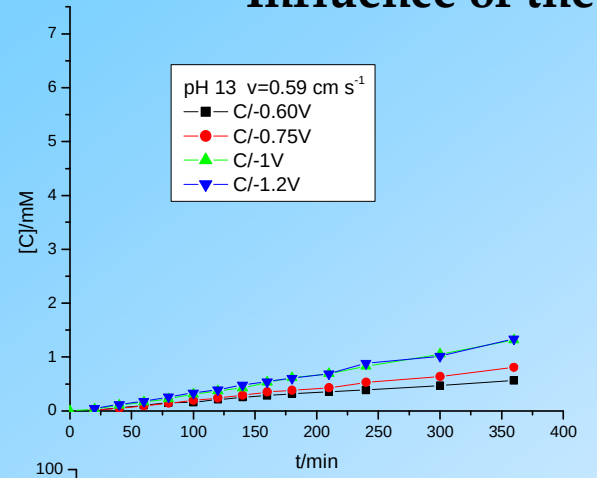
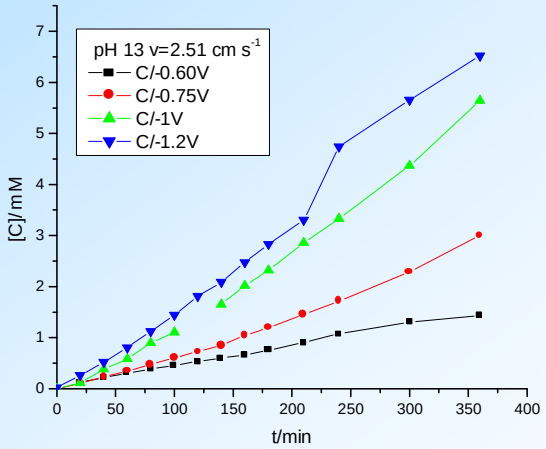
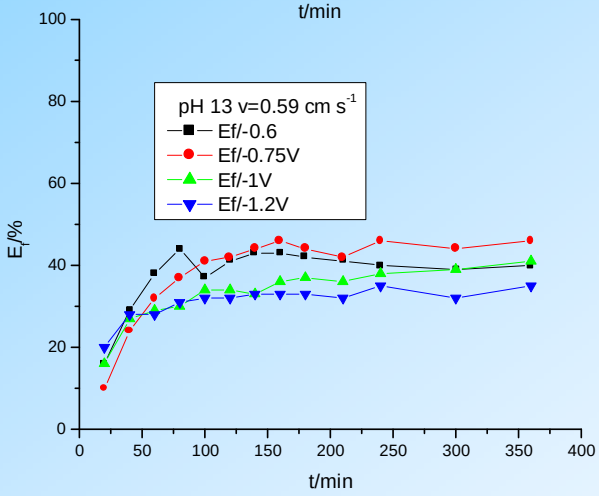
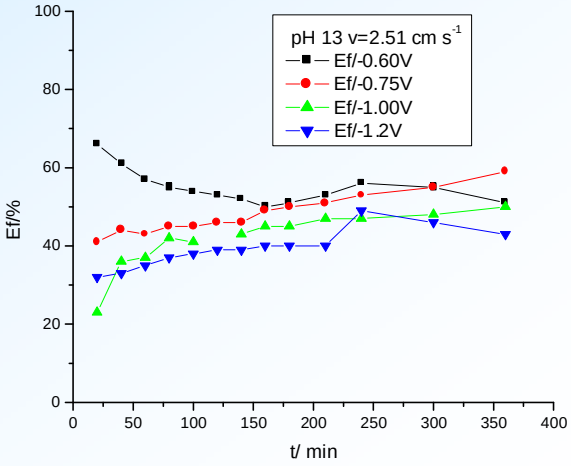
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Silent conditions

Influence of the electrode potential. pH 13









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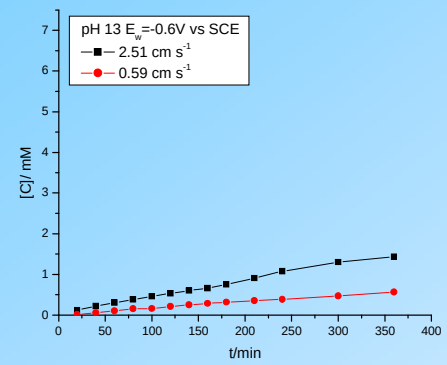
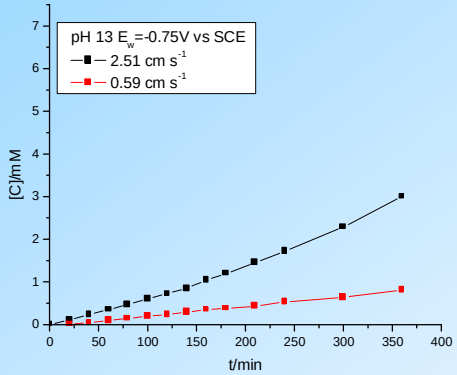
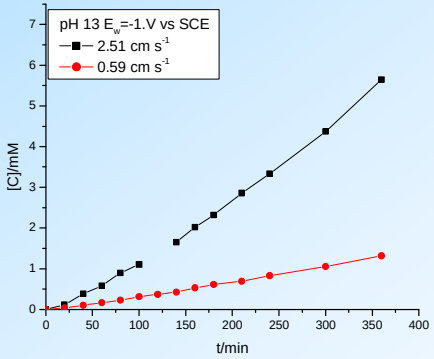
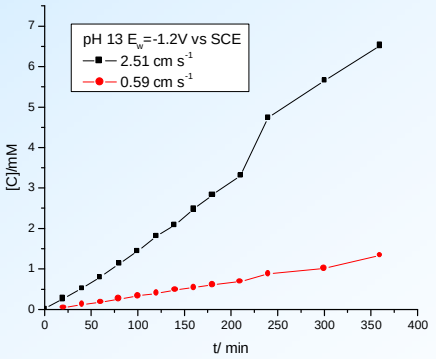
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound Silent conditions

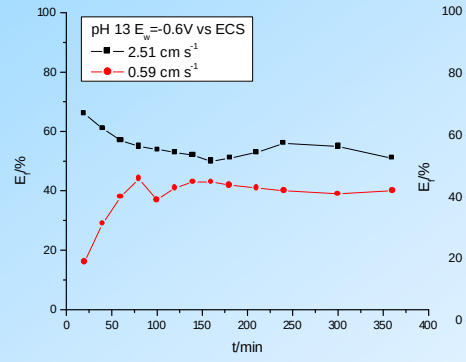
Influence of the volumetric flow. pH 13

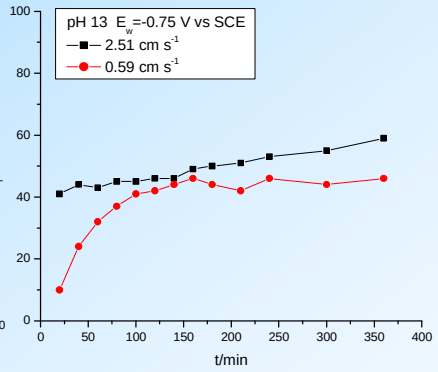


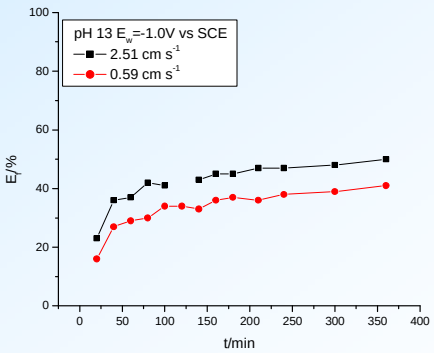


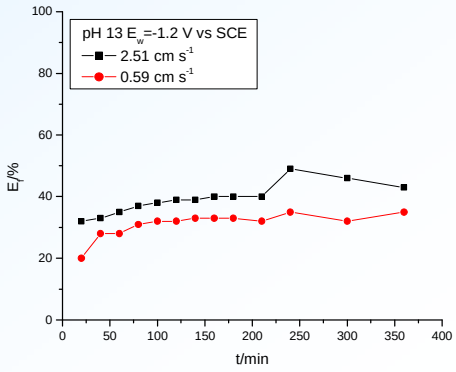












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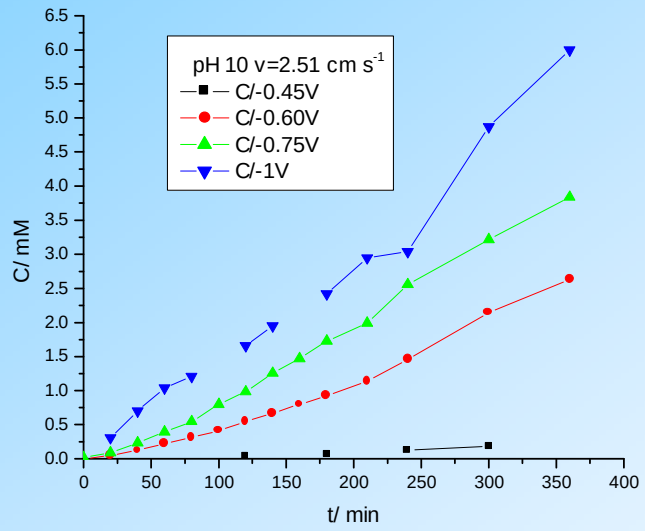
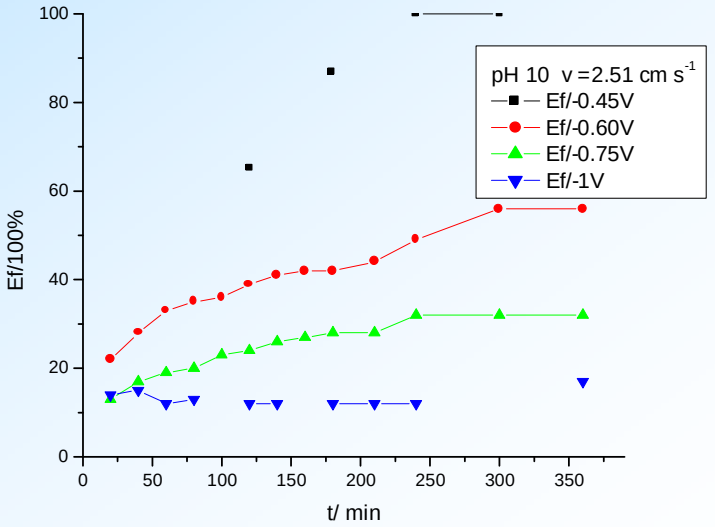
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound Silent conditions

Influence of the electrode potential. pH 10





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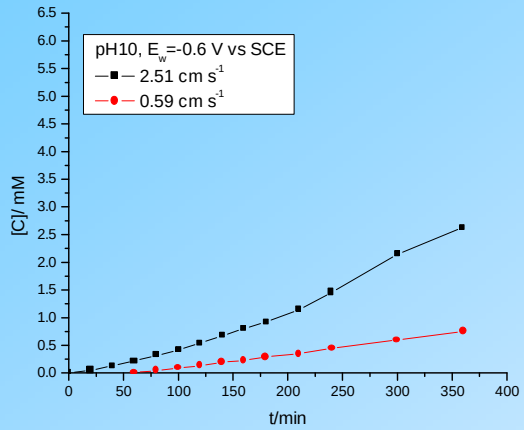
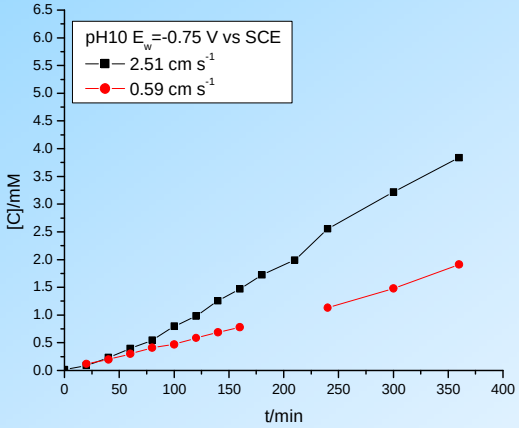
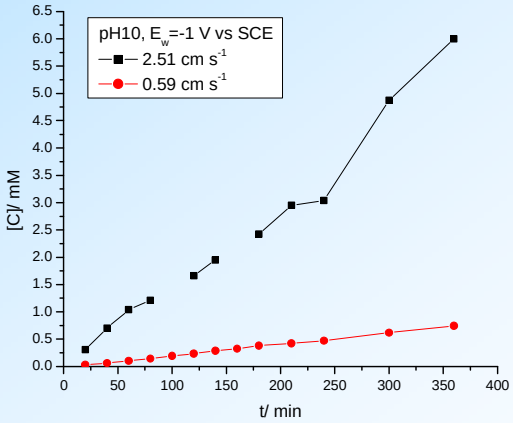
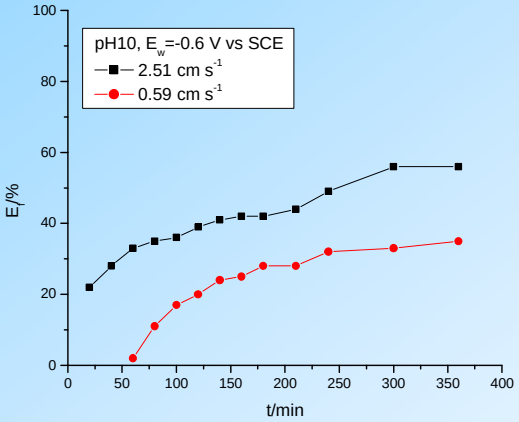
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Silent conditions

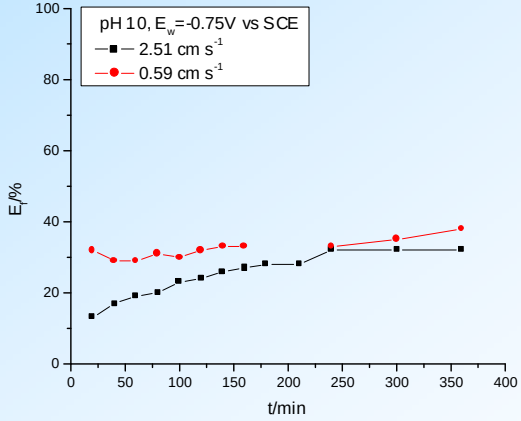
Influence of the volumetric flow. pH 10

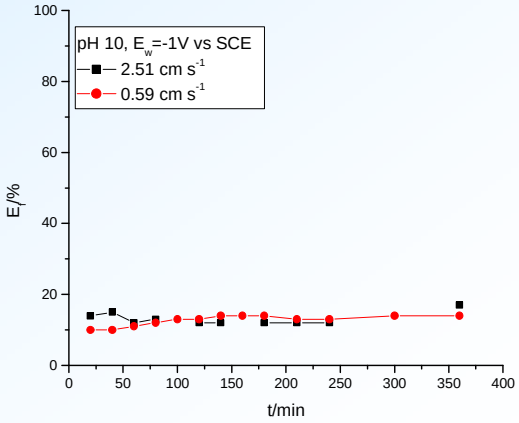












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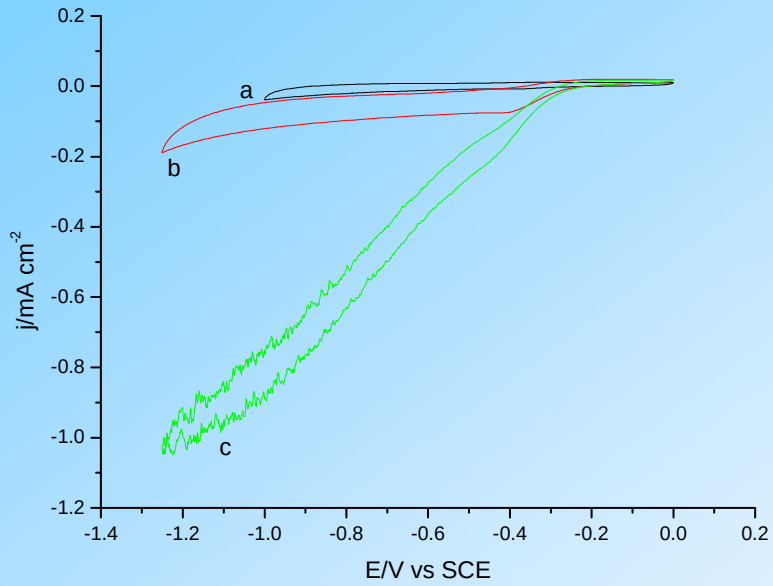
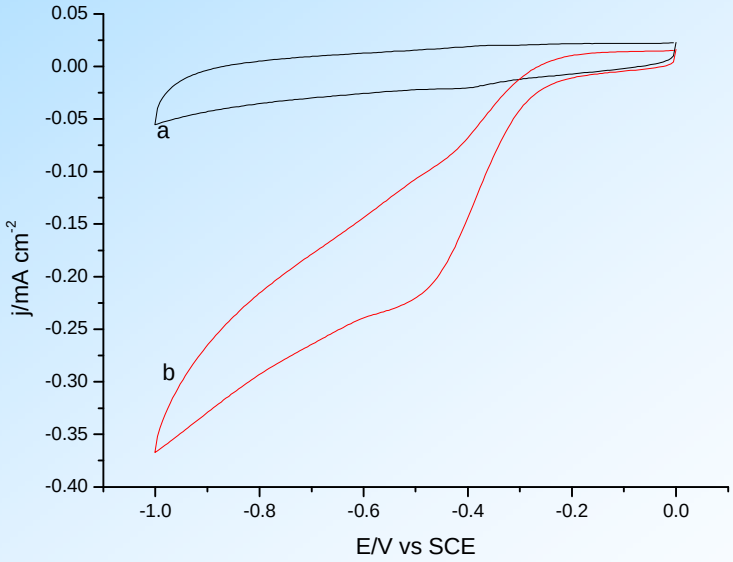
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Ultrasonic conditions

Voltametric study





RVC (10 x 10 x 10 mm) pH 10
(a) Silent conditions. Solution saturated in N_2
(b) Silent conditions. Solution saturated in O_2
(c) Ultrasonic conditions. Solution saturated in O_2

RVC (60 x 50 x10 mm) pH 10
(a) Silent conditions. Solution saturated in N_2
(b) Silent conditions. Solution saturated in O_2

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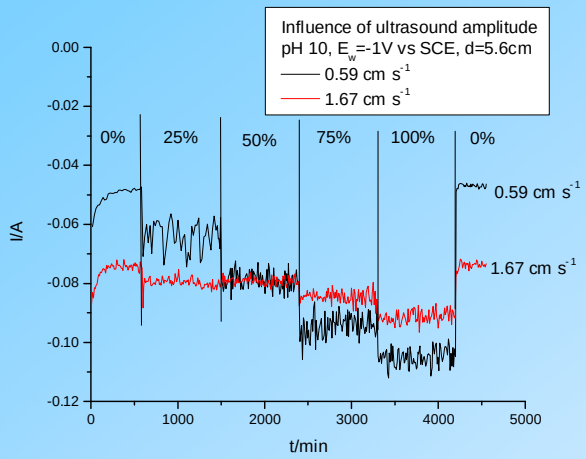
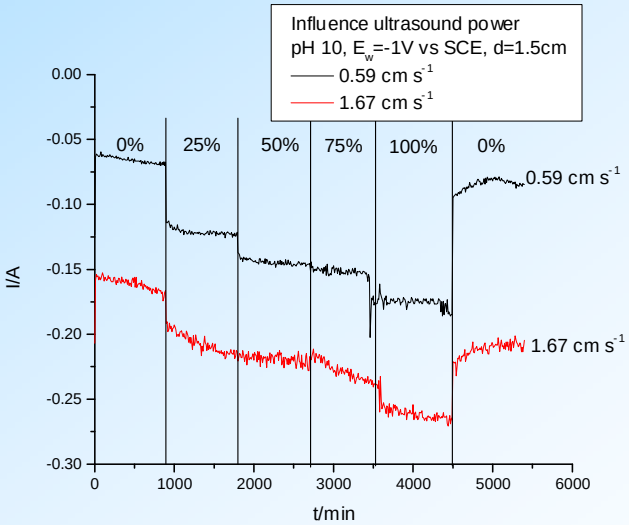
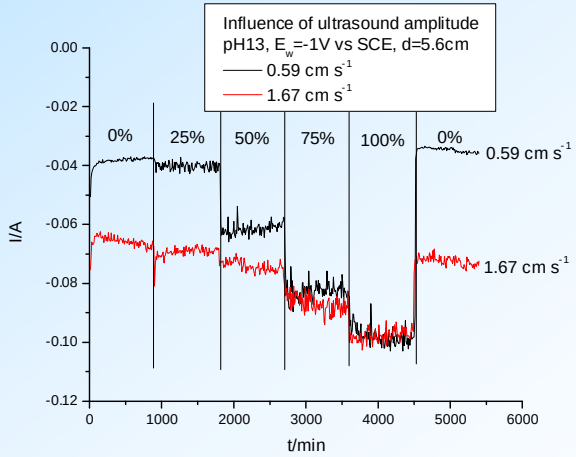
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound Ultrasonic conditions. Preliminary results

Influence of the utrasonic intensity







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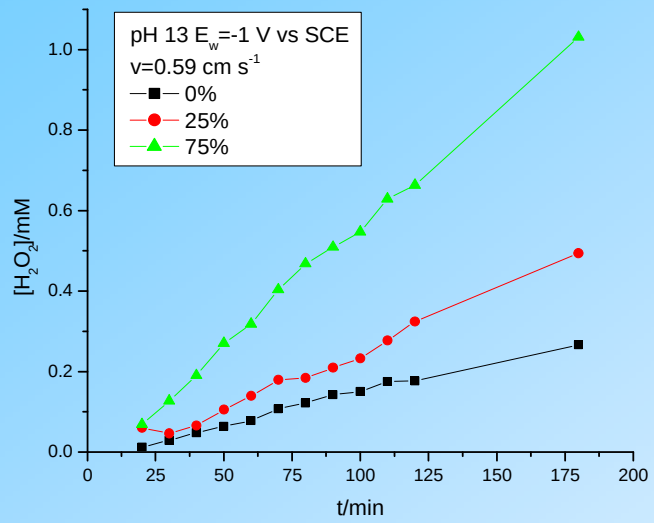
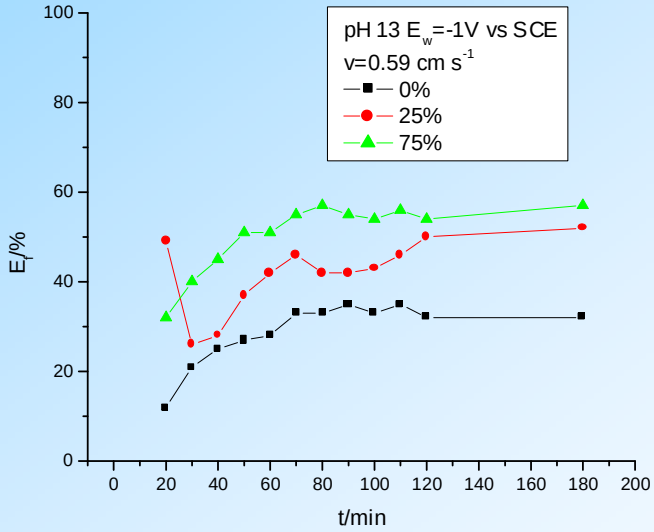
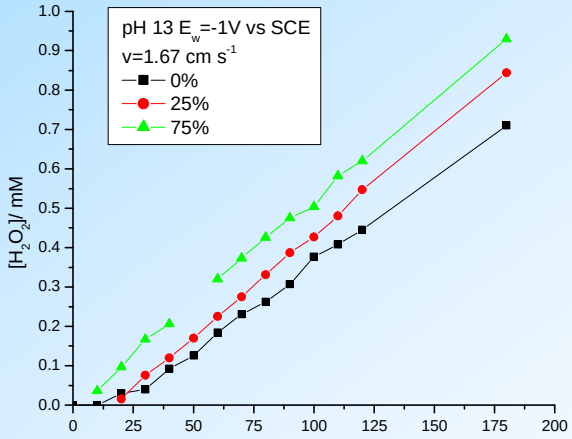
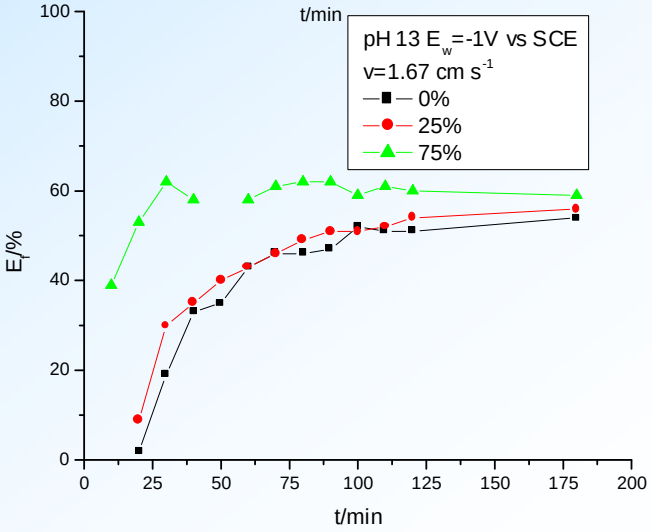
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Ultrasonic conditions. Preliminary results

Influence of the volumetric flow. pH 13. Under ultrasound









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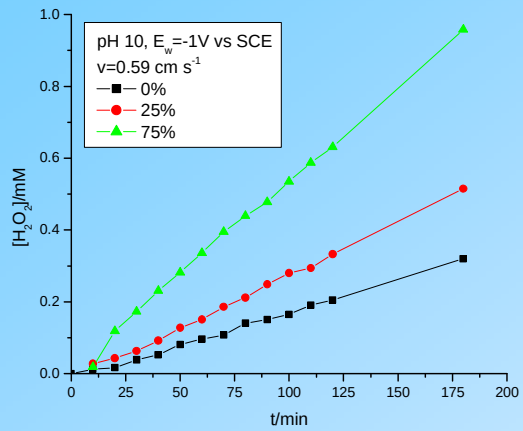
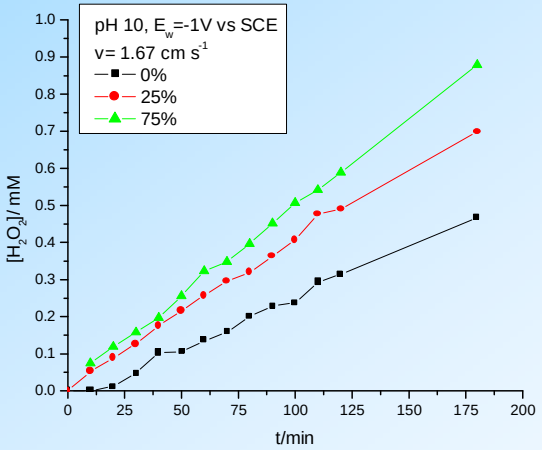
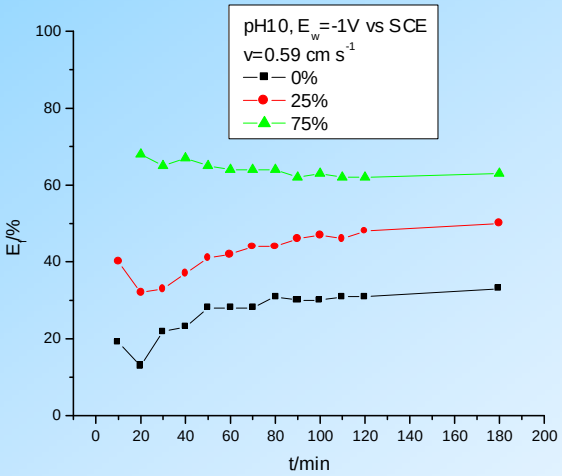
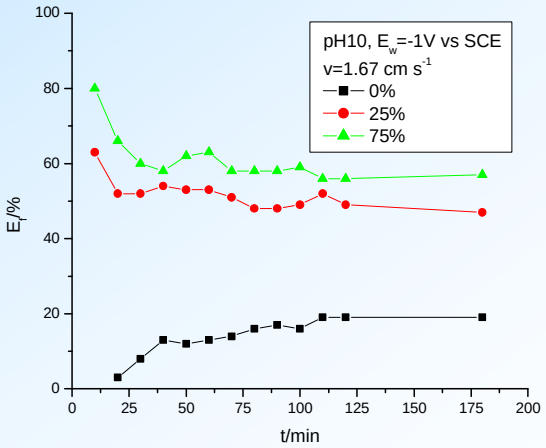
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Ultrasonic conditions. Preliminary results

Influence of the volumetric flow. pH 10. Under ultrasound









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Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Influence of an ultrasonic field

Conclusions

The electrochemical synthesis of hydrogen peroxide at pH 10 under ultrasound presents current efficiency higher than in silent conditions, close to competitive values.

The ultrasonic field increases the mass tranport to the electrode surface but it seems that there are other effects, (probably related to the activation of the surface ($OH^{\cdot}$ radicals?)) but there is not any direct evidence for this.