Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

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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.
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
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

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

\[
\begin{align*}
Q(\text{ads}) + 2e + 2H^+ & \rightarrow H_2Q(\text{ads}) \quad \text{reaction (I)} \\
H_2Q(\text{ads}) + O_2 & \xrightarrow{k} Q(\text{ads}) + H_2O_2 \quad \text{reaction (II)}
\end{align*}
\]

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.

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Previous work:

Work done with two-dimensional electrodes:
- Glassy carbon
- Edge plane pyrolytic graphite (EPPG)
- Basal plane pyrolytic graphite (BPPG)

Previous work:
B. Sljukic et al. Electroanalysis 2005, 17, 1025-1034
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

Present work:
Electrocatalysts analyzed

9,10-phenanthraquinone (PAQ)

anthraquinone

nitrobenzene
**Electrochemical synthesis of hydrogen peroxide assisted by ultrasound**

Electrodes to be used: Three-dimensional electrodes

Reticulated vitreous carbon 10 ppi

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression Strength</td>
<td>(0.28-1.20 MPa)</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>(0.17-1.02 MPa)</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>(31-62 MPa)</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>(30.3 MPa)</td>
</tr>
<tr>
<td>Hardness</td>
<td>6-7 Mohs</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>(1.26 J·g⁻¹·°C⁻¹)</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion:</td>
<td></td>
</tr>
<tr>
<td>· 0 - 100°C</td>
<td>(2.2 · 10⁻⁶·m·m⁻¹·°C⁻¹)</td>
</tr>
<tr>
<td>· 100 - 1000°C</td>
<td>(3.2 · 10⁻⁶·m·m⁻¹·°C⁻¹)</td>
</tr>
<tr>
<td>Bulk Resistivity</td>
<td>(5 · 10⁻²· ohm·cm)</td>
</tr>
<tr>
<td>Sublimation Point</td>
<td>(3500°C)</td>
</tr>
<tr>
<td>Temperature Limitations:</td>
<td></td>
</tr>
<tr>
<td>· in air</td>
<td>(315°C)</td>
</tr>
<tr>
<td>· in non-oxidizing environment</td>
<td>(3500°C)</td>
</tr>
</tbody>
</table>
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 H₂SO₄ 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)
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
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
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Procedure

\[ \text{electrochemical modification} \]

\[ \text{+2H} + 2e \]

![Chemical structures](image)
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Characterization of the coverage of the modification

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

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.
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
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Characterization of the coverage of the modification
The surface concentration of the electrocatalyst adsorbed on the reticulated vitreous carbon electrode, $\Gamma$, can be calculated from the following equation

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

$\Gamma$: 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
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results for PAQ and physical modification:

<table>
<thead>
<tr>
<th>( \nu ) / mV/s</th>
<th>( I_{\text{peak}} )/A</th>
<th>Charge/C</th>
<th>( \Gamma )/mol cm(^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>(-0.170 \times 10^{-3})</td>
<td>(0.890 \times 10^{-3})</td>
<td>(3.30 \times 10^{-10})</td>
</tr>
<tr>
<td>10</td>
<td>(-0.279 \times 10^{-2})</td>
<td>(0.818 \times 10^{-3})</td>
<td>(3.03 \times 10^{-10})</td>
</tr>
<tr>
<td>15</td>
<td>(-0.414 \times 10^{-2})</td>
<td>(0.875 \times 10^{-3})</td>
<td>(3.24 \times 10^{-10})</td>
</tr>
<tr>
<td>20</td>
<td>(-0.555 \times 10^{-2})</td>
<td>(0.850 \times 10^{-3})</td>
<td>(3.14 \times 10^{-10})</td>
</tr>
<tr>
<td>25</td>
<td>(-0.700 \times 10^{-2})</td>
<td>(0.988 \times 10^{-3})</td>
<td>(3.66 \times 10^{-10})</td>
</tr>
<tr>
<td>30</td>
<td>(-0.870 \times 10^{-2})</td>
<td>(1.153 \times 10^{-3})</td>
<td>(4.26 \times 10^{-10})</td>
</tr>
</tbody>
</table>

18th March
RVC (2x1x1) modified without O\(_2\)

\(j \)/mA cm\(^{-2}\)

18th March
RVC (2x1x1)
modified without O\(_2\)

\( \nu \)/ mV/s

\( I_{\text{peak}} \)/A

Charge/C

\( \Gamma \)/mol cm\(^{-2}\)
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Voltammetry in absence and presence of oxygen
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 \( \nu^{1/2} \) 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 \( k\Gamma \), with the following equation:

\[ x = \log \left[ \frac{k\Gamma}{D^{1/2} (F\nu/RT)^{1/2}} \right] \rightarrow k \]
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results for PAQ and physical modification:

<table>
<thead>
<tr>
<th>v/ mV/s</th>
<th>I_{\text{peak}}/A</th>
<th>Charge/C</th>
<th>Γ/mol cm^{-2}</th>
<th>I_{\text{peak}}/A</th>
<th>Γ_{\text{peak}}/A</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>-0.170 \times 10^{-3}</td>
<td>0.890 \times 10^{-3}</td>
<td>3.30 \times 10^{-10}</td>
<td>-0.211 \times 10^{-2}</td>
<td>-0.194 \times 10^{-2}</td>
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<tr>
<td>10</td>
<td>-0.279 \times 10^{-2}</td>
<td>0.818 \times 10^{-3}</td>
<td>3.03 \times 10^{-10}</td>
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<td>-0.226 \times 10^{-2}</td>
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<td>15</td>
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<td>3.24 \times 10^{-10}</td>
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<tr>
<td>25</td>
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<td>3.66 \times 10^{-10}</td>
<td>-0.328 \times 10^{-2}</td>
<td>-0.269 \times 10^{-2}</td>
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<tr>
<td>30</td>
<td>-0.870 \times 10^{-2}</td>
<td>1.153 \times 10^{-3}</td>
<td>4.26 \times 10^{-10}</td>
<td>-0.361 \times 10^{-2}</td>
<td>-0.285 \times 10^{-2}</td>
</tr>
</tbody>
</table>

(Γ=3.03 \times 10^{-10} \text{ mol cm}^{-2}) \text{ the chemical rate constant: } 2.34 \times 10^{3} \text{ M}^{-1} \text{ s}^{-1}
Γk=7.09 \times 10^{-4} \text{ cm s}^{-1}
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results: PAQ physical adsorption

<table>
<thead>
<tr>
<th>υ/mV/s</th>
<th>I_{peak}/A</th>
<th>Charge/C</th>
<th>Γ/mol cm^{-2}</th>
<th>I_{peak}/A</th>
<th>Γ_{peak}/A</th>
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<tbody>
<tr>
<td>5</td>
<td>-0.178 10^{-3}</td>
<td>2.501 10^{-3}</td>
<td>1.85 10^{-9}</td>
<td>-0.078 10^{-2}</td>
<td>-0.603 10^{-3}</td>
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<td>10</td>
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<td>1.693 10^{-3}</td>
<td>1.25 10^{-9}</td>
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</tr>
<tr>
<td>15</td>
<td>-0.321 10^{-3}</td>
<td>1.337 10^{-3}</td>
<td>9.90 10^{-10}</td>
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<td>-0.840 10^{-3}</td>
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<tr>
<td>20</td>
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<td>1.026 10^{-3}</td>
<td>7.60 10^{-10}</td>
<td>-0.124 10^{-2}</td>
<td>-0.893 10^{-3}</td>
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<tr>
<td>25</td>
<td>-0.436 10^{-3}</td>
<td>0.889 10^{-3}</td>
<td>6.58 10^{-10}</td>
<td>-0.139 10^{-2}</td>
<td>-0.990 10^{-2}</td>
</tr>
<tr>
<td>30</td>
<td>-0.475 10^{-3}</td>
<td>0.623 10^{-3}</td>
<td>4.61 10^{-10}</td>
<td>-0.155 10^{-2}</td>
<td>-1.100 10^{-2}</td>
</tr>
</tbody>
</table>

k = 6.05 10^2 M^{-1} s^{-1}
Γk = 7.56 10^{-4} cm s^{-1}
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results: Anthraquinone (Fast Red AL) Chemical modification

\[ k = 1.05 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \]
\[ \Gamma k = 3.97 \times 10^{-4} \text{ cm s}^{-1} \]
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results: Nitrobenzene (Fast Red GG) Chemical modification

\[ k = 8.02 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \]

\[ \Gamma k = 4.35 \times 10^{-4} \text{ cm s}^{-1} \]
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results: Anthraquinone (Fast Red AL) Electrochemical modification

\[ k = 8.22 \times 10^2 \text{ M}^{-1} \text{s}^{-1} \]
\[ \Gamma = 5.07 \times 10^{-4} \text{ cm s}^{-1} \]
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Results: Nitrobenzene (Fast Red GG) Electrochemical modification

\[ k = 3.87 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \]
\[ \Gamma k = 6.31 \times 10^{-4} \text{ s}^{-1} \text{ cm}^{-1} \]
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Identification of electrocatalysts

Final results

Voltammetry in presence of oxygen
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
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

**State of the art**

Cathodic reaction: \( \text{O}_2 + 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \)

Anodic reaction: \( 2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e \)

Global reaction: \( \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 \)

Drawbacks of the synthesis
- Slow kinetics
- Current efficiency not higher than 40%
- High alcalinity

Parasitic reactions:
- Cathodic reduction of hydrogen peroxide: \( 2\text{H}_2\text{O}_2 + 4e \rightarrow 4\text{OH}^- \)

Anodic oxidation of hydrogen peroxide \( \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2e \)
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Silent conditions

Influence of the electrode potential. pH 13
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Silent conditions

Influence of the volumetric flow. pH 13
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Silent conditions

Influence of the electrode potential. pH 10
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Silent conditions

Influence of the volumetric flow. pH 10
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

Ultrasonic conditions

Voltammetric study

RVC (10 x 10 x 10 mm) pH 10
(a) Silent conditions. Solution saturated in N₂
(b) Silent conditions. Solution saturated in O₂
(c) Ultrasonic conditions. Solution saturated in O₂

RVC (60 x 50 x10 mm) pH 10
(a) Silent conditions. Solution saturated in N₂
(b) Silent conditions. Solution saturated in O₂
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound

Ultrasonic conditions. Preliminary results

Influence of the ultrasonic intensity
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Ultrasonic conditions. Preliminary results

Influence of the volumetric flow. pH 13. Under ultrasound
Electrochemical synthesis of hydrogen peroxide assisted by ultrasound
Ultrasonic conditions. Preliminary results

Influence of the volumetric flow. pH 10. Under ultrasound
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 transport to the electrode surface but it seems that there are other effects, (probably related to the activation of the surface (OH radicals?)) but there is not any direct evidence for this.