

Universitat d'Alacant Universidad de Alicante







# NIVERSITÉ DE FRANCHE-CO

# **ELECTROCHEMISTRY WITH ULTRASOUND**

University of Coventry. UK
University of Oxford. UK

Département de Chimie. Ecole Normale Supérieur<mark>e.Paris.</mark> France • Academy of Sciences of the Cze<mark>ch Rep</mark>ublic. Czech Republic

•University of Franché-Comté. France

•University of Alicante. Spain









## **ELECTROCHEMISTRY WITH ULTRASOUND** Environmental applications

\*Improved strategies for waste minimisation:

obviation of environmentall-unfriendly systems in synthesis

sonoelectrochemical reactor design

\*Degradation of pollutants and enhanced environmental clean-up using sonoelectrochemistry

## New systems

\*Novel electrosynthesis reactions with applications in organic and biochemistry

\*Novel functional materials and their practical applications, including nanoparticles and conducting polymers.

\*Development of new electrode materials and the understanding of surface processes in these processes

## **Technological applications**

\*Improved methods for electrodeposition, electrodissolution, including effects on morphology, hardness, microestructure...

\*Scale-up form micro-scale to pilot-plant scale

## Electroanalysis

\*Development of enhanced elecroanalytical procedures that are effective in real media, leading to imporved sensors and biosensors

\* Sensitive electroanalyses for metal ions and other deleterious electroactive species in the environment



## WORK PROGRAMME FOR THIS TERM

#### **Events**

Kick off COST D-32 Meeting, held in Alicante, July 2004.

Kick off Working Group Meeting, held in Alicante, December 2004.

Annual Working Group Meeting, held in Prague, November 2005.

#### **Tasks**

General task: Finding and development of common research interests by means of: **Research** interactions Short term scientific missions

#### **Specific tasks**:

Sonoelectrochemical reactor design Degradation of pollutants using sonoelectrochemistry Development of new electrode materials Sensitive electroanalyses for metal ions



# **ELECTROCHEMISTRY WITH ULTRASOUND**

#### \*University of Alicante: Grupo de Electroquímica Aplicada y Electrocatálisis. Departamento de Química Física e Instituto de Electroquímica. Spain

Modified electrodes for Environmental Clean up and Remediation. Scale-up

- \*University of Oxford: Physical and Theoretical Chemistry Laboratory. UK Sonoelectrochemical mechanisms and analyses, fundamental studies, polyphasic systems
- \*University of Coventry: School of Science and the Environment. UK Electroorganic synthesis, Functional Materials, conducting polymers, bioelectrochemistry

#### \*University of Franche-Comté: Laboratoire de Chimie des Matériaux et des Interfaces. Site de l'IUT. Département Chimie. France

Sonoelectrochemistry, corrosion, electroplating, electrode surface studies, scale-up

## \*Ecole Normale Supérieure: Département de Chimie. Paris. France

High-speed studies, kinetics and mechanistic elucidation

#### \*Academy of Sciences of the Czech Republic: J. Heyrovsky Institute of Physical Chemistry. Czech **Republic**

Physical aspect of sonoelectrochemistry, molecular electrochemistry



#### Working group meetings

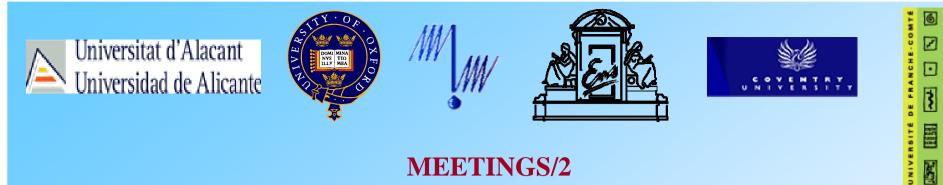
Kick off COST D-32 Meeting, held in Alicante, July 2004.

Kick off Working Group Meeting, held in Alicante, December 2004.

Annual Working Group Meeting, held in Prague, November 2005.

#### **Participations in anothers WG Meetings**

"Physical aspects of Sono(electro)chemistry: Distribution of intensity of ultrasound" J. Klíma, A. Frias-Ferrer, J. González-García, J. Ludvík, V. Sáez, J. Iniesta COST WG 2+WG7 Workshop 9-10 June 2005, Oxford, UK



#### **General Meetings (WG labs met up)**

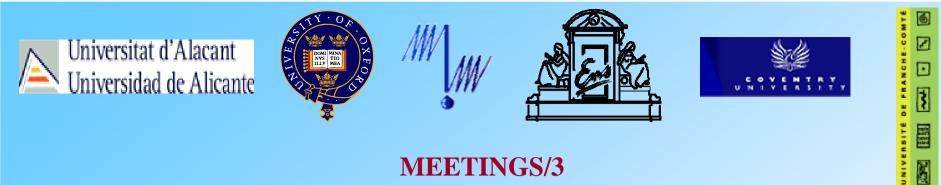
#### **Talks**

**1**."Contribution of electrochemistry to the study of power ultrasound applied to surfaces" J.Y. Hihn (WG4) ESS9th Conference April 2004. Badajoz. Spain

2."Effects of ultrasonic irradiation on electroless coating and electroplating" F. Touyeras, J.Y. Hihn, X. Bourgoin, B. Jacques, L. Hallez (WG4) ESS9th Conference April 2004. Badajoz. Spain

3."New reactor design for sonochemical applications" R. Viennet, J.Y. Hihn, M. Jeannot, R. Berriet (WG4) ESS9th Conference April 2004. Badajoz. Spain

4."Characterization of a 20 kHz Sonoreactor. Part I: Analysis of Machanical effects by classical and numerical methods" V. Sáez, A. Frías-Ferrer, J. Iniesta, J. González-García, A. Aldaz, E. Riera (WG4+WG11) ESS9th Conference April 2004. Badajoz. Spain



#### General Meetings (WG labs met up)

5."The Effect of Ultrasound on the voltammetry of Copper in strong alkali" D. J. Walton, M. Plattes, T. J. Mason, J. P. Lorimer (WG4+WG2) ESS9th Conference April 2004. Badajoz. Spain

#### **Posters**

**1**. "Visualisation of the actives zones near the transducer in an ultrasonic reactor using 40 kHz frequency"

A. Mandroyan, R. Viennet, Y. Bailly, L. Girardot, M. L. Douche, J.Y. Hihn, P. Nika (WG4) ESS9th Conference April 2004. Badajoz. Spain

2."Hydrodynamic and mass transfer measurements close to an ultrasonic horn vibrating at two frequencies" A. Mandroyan, M.-L. Doche, J.Y. Hihn, R. Viennet (WG4) ESS9th Conference April 2004. Badajoz. Spain

3." Characterization of a 20 kHz Sonoreactor. Part II: Analysis of chemical effects by classical and electrochemical methods"

V. Sáez, A. Frías-Ferrer, J. Iniesta, J. González-García, A. Aldaz, E. Riera (WG4+WG11) ESS9th Conference April 2004. Badajoz. Spain



#### **General Meetings (WG labs met up)**

4."Ultrasound effects on the kinetics reaction step in the silver thiosulphate reduction on platinum electrodes" B. Pullet, J. P. Lorimer, J.Y. Hihn, F. Touyeras, T. J. Mason (WG4+WG2) ESS9th Conference April 2004. Badajoz. Spain



#### **General Meetings-internal WG contributions**

**1**."Aplicación del método de salto de temperaturas inducido mediante irradiación con láser. Electrodos monocristalinos de oro y platino"

V. Climent, R. G. Compton, J. M. Feliu (Alicante+Oxford)

VII Iberic Meeting of Electrochemistry and XXVI Reunión del grupo de Electroquímica de la RSEQ. 2004. Córdoba. Spain

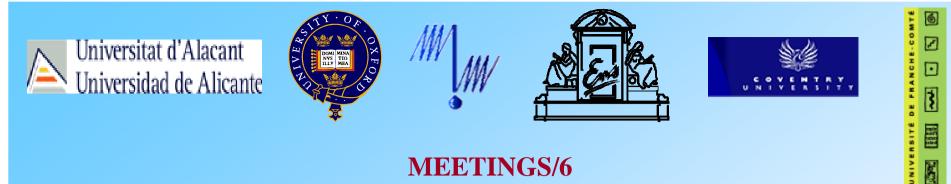
**2**. "Laser-Induced Temperature Jump Studies on Platinum Single-Crystal Electrodes. Potential of Maximum Entropy"

V. Climent, R. G. Compton, J. M. Feliu, A. Aldaz (Alicante+Oxford) 10th International Conference on Electrified Interfaces. 2004. Spa. Belgium

**3**. "Sonoelectrochemical degradation of perchloroethylene at 850 kHz" V. Sáez, J. Iniesta, A. Frías-Ferrer, J. González-García and D. J. Walton (**Alicante+Coventry**) Electrochem 2005, Newcastle, UK

**4**. "Structure function studies on Electrosynthetically-modified Proteins-Nitration of tyrosine" J. Iniesta, J. Heptinstall, D. J. Walton, I. R. Peterson, S. Mercer, H. J. Cooper, P. J. Derrick, F. Marhuenda-Egea, A. Donaire. (**Alicante+Coventry**)

XVIIIth International Sympsium on Bioelectrochemistry and Bioenergetics. 3rd Spring Meeting. Bioelectrochemistry 2005 Coimbra. Portugal



#### **General Meetings-internal and external WG contributions**

5."Comparison of the chemistry of tetracyclones and tetraarylthiophenes-S-oxides" A. Miura, F. Matasaka, J. Iniesta, D. Walton. S. Mataka, T. Thiemann Annual Japanese Chemical Society. 2005. Tokyo. Japan (WG4(2)+WG6)

6. "The chemistry of thiophene-S-oxides and related compounds" T. Thiemann, D. J. Walton, A. Oliveira Brett, J. Iniesta, F. Marken, Y.Q. Li. (WG4(2)+WG5+WG6) Kyushu International Symposium on Physical Organic Chemistry, KISPOC-XI. 2005, Fukuoka, Japan



## **RESEARCH INTERACTIONS /1**

#### Internal research interactions/1

#### Financed by COST via STSM

\*Short term scientific mission STSM (financed by COST) one month. **1016 euros** Verónica Sáez (University of Alicante) in Coventry University Topic: Sono(electro)chemical degradation of PCE at 850 kHz. Identification of final products. Comparison with 20 kHz results from Alicante

\*Short term scientific mission STSM (financed by COST) two weeks Jiri Klima (J. Heyrovsky Institute of Physical Chemistry) in University of Alicante Topic: Numerical simulation of the US intensity distribution Optimized geometry. First results to be used as basis for further studies

**1200 euros** 

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## **RESEARCH INTERACTIONS /2**

#### Internal research interactions/2

#### **External financial support**

- \*Mobility grant (financed by Ministerio Educación y Ciencia (Spain)) one year. 28400 euros José González-García (University of Alicante) in University of Oxford Topic: Electrochemical synthesis of hydrogen peroxide assisted by ultrasound Fundamental aspects and scale up to a 1000 W sonoelectrochemical reactor
- \* Mobility grant (financed by Generalidad Valenciana) two months. **2500 euros** Victor Climent (University of Alicante) in Ecole Normale Supérieure (Paris) Topic: Fabrication of platinum and gold ultramicroelectrodes with well-defined surface structures. Gold and platinum ultramicroelectrodes with (111) surface orientation were fabricated and applied to study the kinetics of fast electron transfer reactions
  - \*Research visit(financed by Université de Franché-Comté, Besançon) two weeks 500 euros A. Mandroyan (Université de Franché-Comté, Besançon) in Ecole Normale Supérieure (Paris) Topic: High speed voltammetry on Ultramicroelectrodes. Comparison of results with the ultrasonic generators form Besançon at 3 frequencies (20, 40 and 60 kHz). Better comprehension of asymmetric cavitation







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1720 euros

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## **RESEARCH INTERACTIONS /3**

#### External (with other D32 labs) research interactions/1

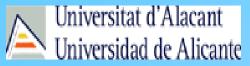
#### **Financed by COST via STSM**

\*Short term scientific mission **STSM** (financed by COST) two weeks D. Bogdal (Politechnika Krakowska, Poland) (**WG10**) in University of Coventry Topic: Sonoelectrochemical studies on polycarbazoles Polycarbazole films on indium-tin oxide coated (ITO) glass

#### **External financial support**

Research visit (financed by EPSRC (UK)). six months.7500 eurosD. Walton (University of Coventry) in University of Kyushu7500 eurosTopic: Synthesis of new dibenzothiophene derivatives7500 eurosObtention of initial products1500 euros

Research visit (financed by Ministerio Educación y Ciencia (Spain)). One month.1500eurosJesús Iniesta Valcárcel (University of Alicante) in University of KyushuTopic: Synthesis of new dibenzothiophene derivativesObtention of initial products









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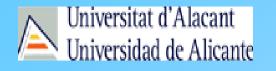
**EXTERNAL FINANCIAL SUPPPORT** 

## **Recently completed projects**

 1. School of Science and the Environment. University of Coventry. United Kingdom "Electrochemical and photochemical reactions of thiophene-S-oxides". D. J. Walton (one year: 1.1.2004-31.12.2004)
 82500 euros
 Financed by EPSRC Postdoctoral Assistantship. Dr. J. Iniesta

2.Department of Physical Chemistry. University of Alicante
 "Sonoelectrochemical degradation of chlorinated organocompounds". J. González-García
 (one year: 01.1.2003-30.09.2004).
 16200 euros
 financed by University of Alicante. Spain

 3. School of Science and the Environment. University of Coventry. United Kingdom "The electrosynthetic modification of bioactive species". Professor D. J. Walton (two years: 01.09.2001-31.08.2003)
 120000 euros
 Financed by EU. Marie Curie Fellowship: Dr. J. Iniesta









**EXTERNAL FINANCIAL SUPPPORT** 

#### **Individual WG004 members ongoing research projects**

1.Laboratory of Molecular Electrochemistry, Department of Electrochemisty.Prague
 "Sonoelectrochemistry-physical mechanism and application in molecular electrochemistry".
 (four years: 1.1.2005-31.12.2008).
 47000 euros
 Ministry of Education, Youth and Sports of the Czech Republic

2.Laboratory of Molecular Electrochemistry, Department of Electrochemisty.Prague
 "Sonoelectrochemistry-physical mechanism and application in molecular electrochemistry".
 (four years: 1.1.2005-31.12.2008).
 88000 euros
 J. Heyrovsky Institute of Physical Chemistry. Czech Republic

3.Department of Physical Chemistry. University of Alicante
 "Design and characterization of sonoelectrochemical reactors".
 (two years: 01.01.2005-31.12.2006).
 33539 euros
 Ministry of Industry, University and Science. Comunidad Valenciana. Spain

4. School of Science and the Environment. University of Coventry "Grant support for COST D32 Working Group 004".
(three years: 01.11.2005-31.10.2008).
EPSRC. United Kingdom

22500 euros

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## **EXTERNAL FINANCIAL SUPPPORT**

#### **Individual WG004 members ongoing research projects**

5.Department of Physical Chemistry. University of Alicante "Structural and functional effects of the electrochemical modification of proteins on diamond electrodes: nitration of tyrosine". Dr. J. Iniesta (one year: 1.1.2006-31.12.2006). 14224 euros Financed by University of Alicante.

6.Department of Physical Chemistry. University of Alicante "Developments of novel materials, processes and decives for the photochemical, photoelectrochemical and sonochemical desulphurisation of organosulphur compounds in fuels and wastes". Dr. J. Iniesta (five years: 01.03.2005-28.02.2010). 12000 euros Financed by Ministry of Education and Science. Spain

7.Department of Physical Chemistry. University of Alicante "Surface Electrochemistry" Dr. V. Climent (five years: 01.01.2004-31.12.2008). Financed by Ministry of Education and Science. Spain

6000 euros



## **EXTERNAL FINANCIAL SUPPPORT**

#### Joint ongoing research projects

- **1.** School of Science and the Environment. University of Coventry
- "Framework 6 STREP Network "Selectnano" coordinated by University Israel (with other D32 labs)

(From September 2005) 150000 euros. European Union

**2.** School of Science and the Environment. University of Coventry "Marie Curie Transfer of Knowledge "Sopholides" coordinated by National Hellenic Institute, Athens, Greece. (with others D32 labs) (From May 2005 date) 30000 euros. European Union



#### **Publications jointed between WG laboratories/1**

**1.** Coulostatic potential transients induced by laser heating of platinum stepped electrodes: influence of steps on the entropy of double layer formation" V. Climent, B. A. Coles, R. G. Compton, J. M. Feliu (Alicante+Oxford) J. Electroanal. Chem. 561 (2004) 157-165

2."Ultrasound effects on the kinetic reaction step in the silver thiosulphate reduction on platinum electrodes" B. G. Pollet, J. P. Lorimer, J. Y Hihn, F. Touyeras, T. J. Mason, D. J. Walton (Besançon+Coventry) Ultrasonics Sonochemistry 12 (2005) 7-11

3."Optimisation of 20 kHz sonoreactor geometry on the basis of numerical simulation of local ultrasonic intensity and qualitative comparison with experimental results" J. Klíma, A. Frias-Ferrer, J. González-García, J. Ludvík, V. Sáez, J. Iniesta (Alicante+Prague) Ultrasonics Sonochemistry (accepted)

4."At point of use Sono-electrochemical generation of Hydrogen Peroxide for Chemical synthesis: The Green Oxidation of Benzonitrile to Benzamide" J. González-García, L. Drouin, C. E. Banks, B. Šljukić, R. G. Compton (Alicante+Oxford) Ultrasonics Sonochemistry (accepted)



#### Publications jointed between WG laboratories/2

5."Effect of deposited bismuth on the potential of maximum entropy of Pt(111) single crystal electrode"

V. Climent, N. García-Aráez, R. G. Compton, J. M. Feliu (Alicante+Oxford)

J. Phys. Chem. B (2006) (submitted)

6."Energetic balance in an ultrasonic reactor using focused or plan high frequency transducers" L. Hallez, F. Touyeras, J. Y. Hihn, J. Klima (Besançon+Prague) Ultrasonics Sonochemistry (submitted)

7."Electrosynthesis of hydrogen peroxide via reduction of oxygen assisted by power ultrasound" J. González-García, C. E. Banks, B. Šljukić, R. G. Compton (Alicante+Oxford) Ultrasonics Sonochemistry (submitted)



#### Publications jointed with laboratories from others D32 WG labs/1

**1.** "The photochemistry of thiophene-S-oxides" K. Arima, D. Ohira, M. Watanabe, A. Miura, S. Mataka, T. Thiemann, J.Iniesta, D. J. Walton Journal of Photochem. Photobiol.Sci. 4 (2005) 808-816 (WG4(2)+WG6)

2."Characterization of a 20 kHz sonoreactor: Part I: Analyisis of mechanical effects by classical and numerical methods" V. Sáez, A. Frías-Ferrer, J. Iniesta, J. González-García, A. Aldaz, E. Riera (WG4+WG11) Ultrasonics Sonochemistry 12 (2005) 59-65

3." Characterization of a 20 kHz sonoreactor: Part II: Analyisis of chemical effects by classical and electrochemical methods" V. Sáez, A. Frías-Ferrer, J. Iniesta, J. González-García, A. Aldaz, E. Riera (WG4+WG11) Ultrasonics Sonochemistry 12 (2005) 67-72

4."Microwave-enhanced electrochemical processes in micellar surfactant media" M. A. Ghanem, F. Marken, B. A. Coles, R. G. Compton (WG4+WG5) Journal of Solid State Electrochemistry 12 (2005) 809-815



#### Publications jointed with laboratories from others D32 WG labs/2

5."Microwave activation of the electro-oxidation of glucose in alkaline media" M. A. Ghanem, R. G. Compton, B. A Coles, A. Canals, A. Vourema, P. John, F. Marken (WG4+WG5)

Physical Chemistry Chemical Physics 7 (2005) 3552-3559

**6.** Microwave enhanced electroanalysis of formulations: processes in micelar media at glassy carbon and at platinum electrodes" M. A. Ghanem, R. G. Compton B. A. Coles, A. Canals, F. Marken (WG4+WG5) Analyst 130 (2005) 1425-1431

7."Microwave activation of electrochemical processes at glassy carbon and boron-doped diamond electrodes"

U. K. Sur, F. Marken, R. Seager, J. S. Foord, A. Chatterjee, B. A. Coles, R. G. Compton (WG4+WG5) Electroanalysis 17 (2005) 385-391

**8.** Microwave activation of processes in mesopores: the thiourea electrooxidation at mesoporous platinum" M. A. Ghanem, B. A Coles, R. G. Compton, F. Marken (WG4+WG5) Electroanalysis 18 (2006) 793-800



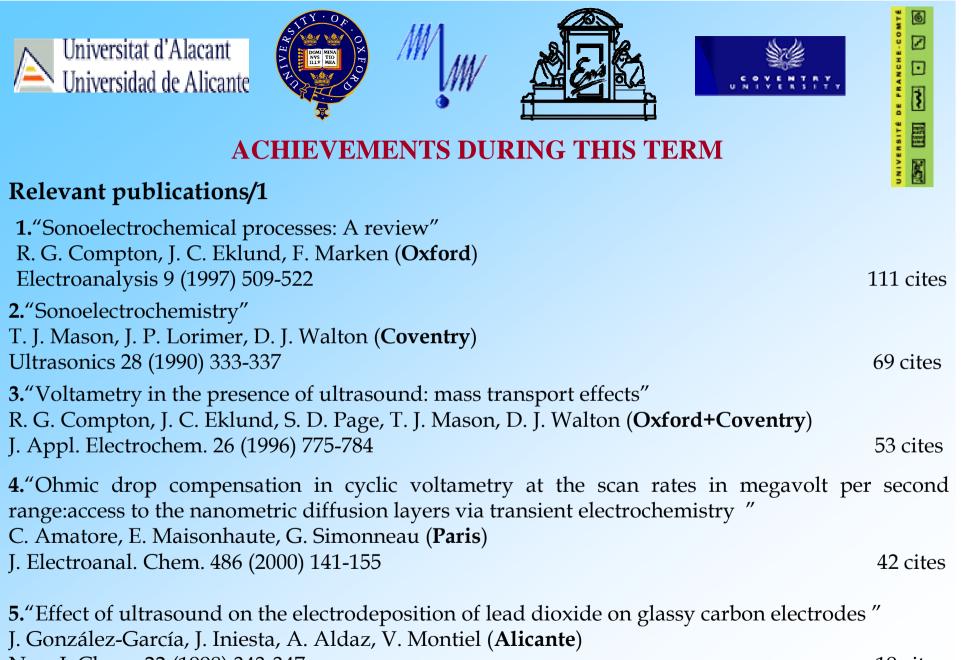
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#### Publications jointed with laboratories from others D32 WG labs/3

9."Focused microwaves in electrochemical processes" F. Marken, U. K. Sur, B. A. Coles, R. G. Compton (WG4+WG5) Electrochim. Acta 51 (2006) 2195-2203

**10.** "Electrochemical oxidation of tetracyclones and Tetraphenylthiophene-S-oxide" J. Iniesta, H. Alcock, D. J. Walton, M. Watanabe, S. Mataka, T. Thiemann (WG4(2)+WG6) Electrochim. Acta (2006) (accepted)



New J. Chem. 22 (1998) 343-347

19 cites



#### **Relevant publications/2**

6."Electrochemical behaviour of zinc in 20 kHz sonicated NaOH electrolytes" M. -L. Doche, J.-Y. Hihn, F. Touyeras, J. P. Lorimer, T. J. Mason, M. Plattes (Besançon+Coventry) Ultrason. Sonochem. 8 (2001) 291-298 11 cites

7."Sonoassisted electrooxidation polymerisation of salicylic acid: role of acoustic streaming and microjetting " J. Klima, C. Bernard (**Prague**) 6 cites

J. Electroanal. Chem. 462 (1999) 181-186

#### **Relevant** awards

1. Richard Compton (Oxford University) awared Tilden Medal (Royal Society of Chemistry) 2006 Professor Compton was awarded the medal for his innovative, quantitative investigations of the kinetics and mechanisms of reactions at solid and liquid interfaces.

2. J. González-García (Universidad de Alicante) awared Carl Wagner Award 2005 (Working Party on Electrochemical Engineering of the European Federation of Chemical Engineering) Dr. González-García was awarded the medal for his well-recognised scientific contribution in Europe in various areas of the Electrochemical Engineering.



## **CONTRIBUTIONS TO ESS10 HAMBURG**

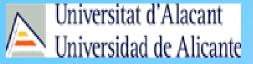
#### **Oral presentations**

1."Energetic balance in an ultrasonic reactor using focused or plan high frequency transducers" L. Hallez, F. Touveras, J. Y. Hihn, J. Klima (Besancon+Prague) ESS10th Conference June 2006. Hamburg. Germany

2."Characterization of bubble cavitation clouds by laser tomography" A. Mandroyan, R. Viennet, Y. Bailly, M.-L. Doche, J. Y. Hihn (Besançon) ESS10th Conference June 2006. Hamburg. Germany

3."Optimisation of Sonochemical and/or Sonoelectrochemical cell with the help of numerical simulation of ultrasonic intensity distribution" J. Klima, J. González-García, A. Frías-Ferrer, J. Ludvík, V. Sáez, J. Iniesta (Alicante+Prague) ESS10th Conference June 2006. Hamburg. Germany

4."Electrochemical synthesis of hydrogen peroxide assisted by ultrasound" J. González-García, C. E. Banks, B. Šljukić, R. G. Compton (Alicante+Oxford) ESS10th Conference June 2006. Hamburg. Germany









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## **CONTRIBUTIONS TO ESS10 HAMBURG**

#### **Poster presentations/1**

1."Electrochemical measurements of a flow induced by low frequencies ultrasound. Influence of horn diameter and cell design"
M. -L. Doche, A. Mandroyan, J. Y. Hihn, R. Viennet (Besançon)
ESS10th Conference June 2006. Hamburg. Germany

2."Effect of ultrasonic wave on the electropolymerization of conducting polymer films"F. Lallemand, J. Y. Hihn, L. Hallez, F. Touyeras (Besançon)ESS10th Conference June 2006. Hamburg. Germany

3. "Mass transfer measurements in small electrode-ultrasonic horn distances"
B. G. Pollet, J. Y. Hihn, M.-L. Doche, A. Mandroyan, J. P. Lorimer, T. J. Mason (WG4+WG2)
ESS10th Conference June 2006. Hamburg. Germany

**4**."Mapping flow velocities in an ultrasonic reactor working at 3 frequencies: 20, 40 and 60 kHz"

A. Mandroyan, R. Vinnet, Y. Bailly, L. Simonin, M.-L. Doche, J. Y. Hihn (**Besançon**) ESS10th Conference June 2006. Hamburg. Germany



## **CONTRIBUTIONS TO ESS10 HAMBURG**

#### **Poster presentations/2**

5."Effect of low frequency ultrasound irradiation on room temperature ionic liquid (RTIL's) dehydration" C. Costa, J. Y. Hihn, I. Bisel, P. Moisy, M. Rebetez, M. -L. Doche (Besançon) ESS10th Conference June 2006. Hamburg. Germany

6."500 kHz ultrasonic irradiation of a polymeric membrane during tangential filtration" L. Hallez, H. Abourabia, F. Touyeras, J. Y. Hihn, P. Fievet, A. Szymczyk (Besançon) ESS10th Conference June 2006. Hamburg. Germany

7."Effect of spatiotemporal characterization of cavitation bubbles collapse nearby ultramicroelectrodes by means of chronoamperometry" A. Mandroyan, M.-L. Doche, J. Y. Hihn, D. Chappe, J.M. Pothier (Besançon) ESS10th Conference June 2006. Hamburg. Germany

8. "Sonoelectrochemical degradation of perchloroethylene in aqueous solutions" V. Sáez, J. Iniesta, A. Frías-Ferrer, P. Bonete, J. González-García (Alicante) ESS10th Conference June 2006. Hamburg. Germany







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## **COST ACTION D32 MID TERM EVALUATION MEETING**

#### **Oral presentations**

1. "Electrochemistry with ultrasound: Report on WG4 activity"

J. González-García

COST Action D32 Mid Term Evaluation Meeting. June 2006. Hamburg. Germany

#### **Poster presentations**

**1**."Optimization of sonochemical and/or sonoelectrochemical cell with the help of numerical simulation of ultrasonic intensity distribution"

J. Klima, J. González-García, A. Frías-Ferrer, J. Ludvik, V. Sáez, J. Iniesta (Alicante+Prague) COST Action D32 Mid Term Evaluation Meeting. June 2006. Hamburg. Germany

2."Research in the group "New Technological Development in Electrochemistry: Sonoelectrochemistry and Bioelectrochemistry" Alicante University"
V. Sáez, A. Frías-Ferrer, P. Espí, M. D. Esclapez, P. Bonete, J. Iniesta, J. González-García COST Action D32 Mid Term Evaluation Meeting. June 2006. Hamburg. Germany

**3**."Selective modification at tyrosine residues by the electrochemical, sonoelectrochemical and sonochemical nitration of lysozyme"

D.J.Walton, J. Heptinstall, J. Iniesta (Alicante+Coventry)

COST Action D32 Mid Term Evaluation Meeting. June 2006. Hamburg. Germany



## **COST ACTION D32 MID TERM EVALUATION MEETING**

#### Poster presentations/2

4."Effect of low frequency ultrasound irradiation on room temperature ionic liquid (RTIL's) dehydration" C. Costa, J. Y. Hihn, I. Bisel, P. Moisy, M. Rebetez, M. -L. Doche (Besançon) COST Action D32 Mid Term Evaluation Meeting. June 2006. Hamburg. Germany

5."Electrochemical measurements of a flow induced by low frequencies ultrasound. Influence of horn diameter and cell design" M. -L. Doche, A. Mandroyan, J. Y. Hihn, R. Viennet (Besançon) COST Action D32 Mid Term Evaluation Meeting. June 2006. Hamburg. Germany



## **FURTHER ONGOING ACTIVITIES/1**

#### Individual WG004 members activities

1. Université de Franché-Comté. Besançon. France (three years): PhD. Grant in Besançon for Cedric Costa Title: Electrochemistry in RTIL's under ultrasound irradiation Financed by the Université de Franché-Comté

33000 euros

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2. Université de Franché-Comté.-IMASONIC-ITT industries (three years): Postdoctoral grant for Loic Hallez related to research project in Besançon Topic: ultrasonic irradiation of polymer film 180000 euros Financed by Frech Goverment



#### Further cooperations internal WG

Human mobility

**1.** Postdoctoral position A. Mandroyan (Besançon) in Coventry University (financed by \*\*\*\*\*\*\*) Topic: Electrochemical studies under ultrasound



## Further cooperations external WG

*Human mobility* 

**1.** Research visit V. Sáez (Alicante) in Bath University (WG4+WG5)**1980 euros**Topic: Electrochemical studies under ultrasoundFinanced by University of Alicante



#### Individual WG004 members activities

1. Universidad de Alicante. Spain.

September 2006: Collaboration between Spanish Ministry of Environment-University of Alicante Topic: Development of sonoelectrochemical reactors for the dry-cleaning waste treatment Financed by Spanish Ministry of Environment



## **FURTHER PLANNED ACTIVITIES/2**

#### Further planned cooperations internal WG

Human mobility Research visit D. J. Walton (Coventry) in Alicante University Topic: "Comparison of sonoelectrochemical and magnetoelectrochemical effects on a model electroorganic systems" finaced by University of Alicante

Joint research project proposal in Prospect via D32

University of Alicante-University of Coventry (D. J. Walton) Topic: Selective chlorination of proteins at tyrosine residues Spanish support

COST D32 WG004 and other labs from Action D32 Topic: "AERO" Advanced Elecrochemical Reactor operation" Framework European Network Grant



## **FURTHER PLANNED ACTIVITIES/3**

#### Further cooperations external WG

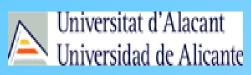
Human mobility

**1.** STSM (University of Coventry-Technical University Krakow, Poland) Topic: Sonoelectrochemical effect in conducting polymers financed by COST

Joint research project proposal in Prospect via D32

Université de Franché-Comté-University of Coventry (T. J. Mason) Topic: Nanoparticles synthesis by sonoelectrochemistry EGIDE programs

14000 euros









<u>ACTIVITY SUMMARY</u>	Inner WG	Jointed WGs (WG4lab +)	Subject/9 <sup>th</sup> ESS (labs met up)	General
Meetings	3 meetings	1 WG4 talk	4 lab talk 3 jointed WGs talk 2 lab posters 1 jointed WGs poster	6 jointed- inner talks
Research Interactions (STSM, visits)	3 funded by COST 3 extra funding	1 funded by COST 2 extra funding		
Research projects completed	1 lab project 2 WG project			
Research project ongoing	7 lab projects	2 jointed WGs		
Publications	7 papers	10 papers		
ESS10	1 lab talk 3 jointed-inner talk 7 lab posters 1 jointed-inner poster			
Mid-term COST Meeting	1 jointed-inner talk 3 lab posters 2 jointed-inner posters			



Financial support	COST/euros	EXTRA/euros	% COST
Human Mobility (STSM)	3936	40400	9
Research	-	402263	-



# **DETAILED EXPLANATION OF THE ACTIVITIES**



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**Kick off Working Group Meeting** 

Kick off Working Group Meeting , held in Alicante, 3er-4th December 2004.

#### **Participants and talks**

University of Alicante Welcome J. González-García "Sonoelectrochemistry: fundamental and applied studies" V. Sáez "Optimization of Hydrodynamics in Electrochemical Reactors: Use of numerical and experimental methods" A. J. Frías-Ferrer

University of Oxford "Sonoelectroanalysis" R. G. Compton "A hand held probe for the sonoelectroanalysis of arsenic". A. Simm "Materials for the sonoelectrosynthesis of hydrogen peroxide" C. Banks

University of Bath (Invited speaker)

"Microwave Effects and Applications in Electrochemsitry" F. Marken



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**Kick off Working Group Meeting (II)** 

## Participants and talks (II)

University of Coventry

"Electrooxidation and Photooxidation of Thiphene-s-Oxides" D. Walton

University of Franche-Comté "Electrochemistry under ultrasound at the interface" J.-Y. Hihn "Design of sonoreactors and application in surface treatment" M. L. Doche

J. Heyrovsky Institute of Physical Chemistry. Czech Republic "Intensity of ultrasound in sonochemical and sonoelectrochemical measurements" J. Klima

"Electrochemical reduction and dimerization of halogenated benzothiophenes and benzothiophene-2-oxazolines. Use of sonication" J. Ludvik

Université de Paris "Ultrafast sonoelectrochemistry" E. Masionhaute



**Kick off Working Group Meeting (III)** 

#### Other activities

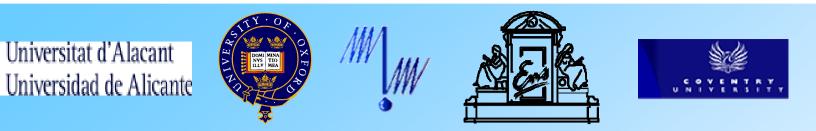
Visit to the pilot plant. The existence of this facility is an important aspect of the Operation at Alicante, which is not available at other laboratories in the network

#### Achievements and objectives

\*Talks reviewed the active research in the working group labs Alicante: Electrodeposition, pollutant degradation assited by ultrasound Design and Characterization of (sono)electrochemical reactors

Oxford: Sonoelectroanalysis in real practical applications Sonoelectrosynthesis, in particular hydrogen peroxide from oxygen

Coventry: Electroorganic and photoelectroorganic syntesis focused on the oxidation of thiophene-S-oxides



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**Kick off Working Group Meeting (IV)** 

#### **Objectives and achievements(II)**

Prague: Physical background in sonochemistry and sonoelectrochemistry Sonoelectrosynthesis in organic media. Mechanisims.

Besançon: Better modelling of sonoelectrochemical systems Electroplating assited by ultrasound Open to new emerging fields: Room temperature Ionic liquids polymer synthesis under US

Paris: Cavitation analysis with nanosecond time base equipment Fundamental approach to the cavitation event

\*Relevant points which can fit WG objectives

Definition of reproducibility and characterization of operating conditions Identification of problems in applications or phenomena needing theoretical understanding

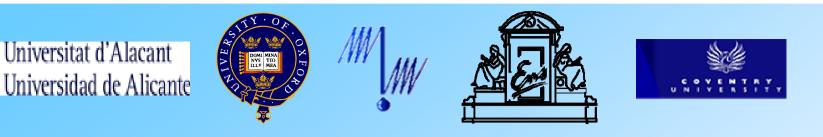
Sonoelctrochemical reactor design



#### **Objectives and achievements (III)**

\*As a first step, development of STSMs in order to establish bilateral collaborations for: Mutual exchange of expertise Mutual training Finding specific collaborating targets Definition of the tasks and contributions in a future research project

\*After, applications for the 7th European Framework will be considered looking at: Complementarity among laboratories Possibility to open the applicant list to other COST laboratories



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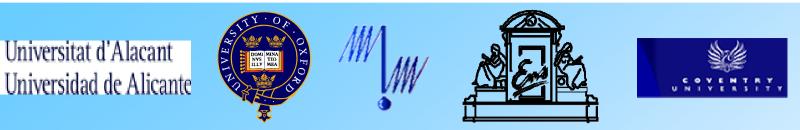
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## Short Term Scientific Mission: V. Sáez (Alicante) in Coventry

# **Degradation of pollutants and enhanced environmental clean-up using sonoelectrochemistry**

**Chlorinated hydrocarbons** are usually used as industrial degreasing agents:  $CCl_4$ ,  $CHCl_3$ ,  $C_2Cl_4$ ,  $C_2Cl_3$ , among others. Withspread chemical contaminants in the subsurface aquatic environment, which are difficult to treat by convenctional technologies.

**Perchloroethylene** ( $C_2Cl_4$ ) is widely used as an industrial dry cleaning solvent and metal degreaser.



Short Term Scientific Mission: V. Sáez (Alicante) in Coventry

## Objectives

Study of the degradation of a chlorinated organic compound using sonochemical, electrochemical and finally the explotation of the combination of both metodologies at 850 kHz (equipment not available in UA)

Degradation of perchloroethylene as a model molecule in aqueous solution.

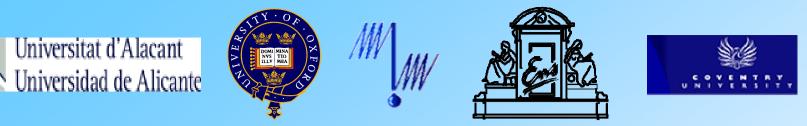
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Perchloroethylene

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## Short Term Scientific Mission: V. Sáez (Alicante) in Coventry

#### **Experimental set-up**



Sonoreactor 850 kHz/140 W by Meinhardt Ultraschalltechnik, K80-5

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#### Conclusions

-Sonochemical treatment: \*Higher yields with lower concentration of PCE \*Higher yields with higher frequencies \*Higher yields with higher ultrasonic intensities \*Radical mechanism \*After 5-hours treatment, no PCE, CF and CT were found

-Electrochemical treatment
 \*Yield not influenced by increasing current densities
 \*the mechanism does not seem to follow by radical soluble intermediates

Sonoelectrochemical treatment

\* Yield higher than electrochemical ones for the same current density

\*A maximum yield is obtained for ultrasonic intensities series (work in progress)



Short Term Scientific Mission: V. Sáez (Alicante) in Coventry

**Conclusions(II)** -Reaction products obtained by the three treatment are different: \*Sonochemical: PCE and saturated chlorinated compounds ( $C_1$  and  $C_2$ ) even higher than  $C_3$ 

\*Electrochemical: PCE, TCE and DCE (insaturated) No chlorinated compounds higher than C<sub>3</sub>

\*Sonoelectrochemical: PCE, TCE and DCE (insaturated) and only  $C_1$  saturated chlorinated compounds Compounds >  $C_3$  only at higher ultrasound intensities

#### Publications

"Sonoelectrochemical degradation of perchloroethylene at 850 kHz" V. Sáez, J. Iniesta, A. Frías-Ferrer, J. González-García and D. J. Walton Electrochem 2005, Newcastle, UK



Improved strategies for waste minimisation by sonoelectrochemical reactor design

Effects-events in sono(eletro)chemistry			
sonoluminescence	- hot spots		
sonolysis (thermolysis)	- hot spots		
mass transfer enhancement	- turbulence		
	- acoustic streaming		
	- microstreaming		
	- microjets		
surface activation	- microstreaming		
	- microjets		
surface destruction	- microjets		

# no sonochemical effect without cavitation !!!



#### **Objectives**

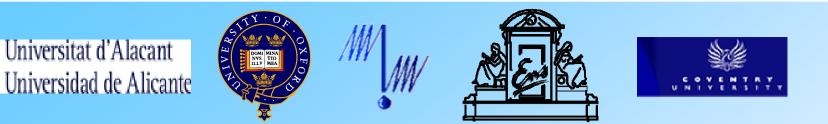
Knowledge of local distribution of ultrasonic intensity is necessary

measurement of intensity:

$$I = Wc = \frac{1}{2}\rho c \,\omega^2 A^2 = \frac{P_0^2}{2\rho c} \qquad \qquad I = \frac{P_{US}}{S}$$

only for progressive vawe

calculation



#### Procedure

resolution of wave equation using a FEM with Femlab Package:

$$\nabla \left(\frac{1}{\rho} \nabla P\right) - \frac{1}{\rho c^2} \frac{\delta^2 P}{\delta t^2} = 0$$

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$$P(r,t) = p(r)e^{i\omega t}$$

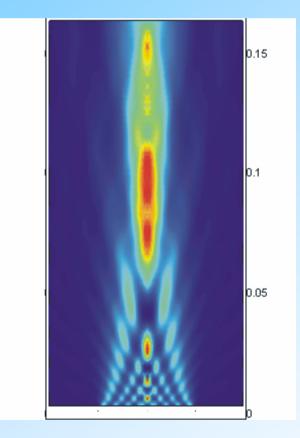
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$$\nabla \left(\frac{1}{\rho} \nabla p\right) - \frac{\omega^2}{\rho c^2} p = 0$$



#### **Procedure:** First with a well-known system with analytical resolution

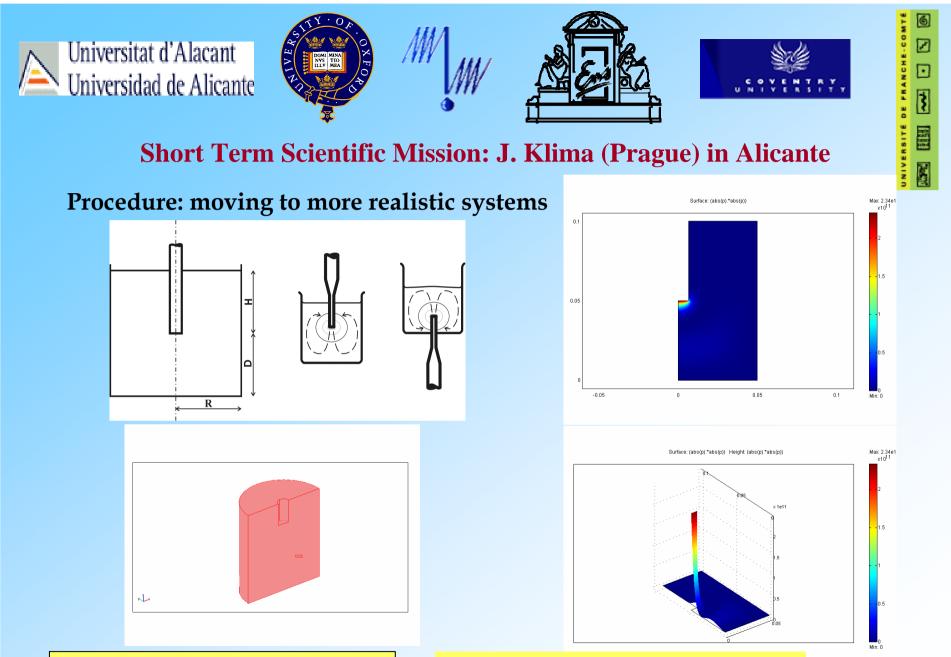


$$f = 1.1MH$$

$$z$$

$$r = 8mm$$

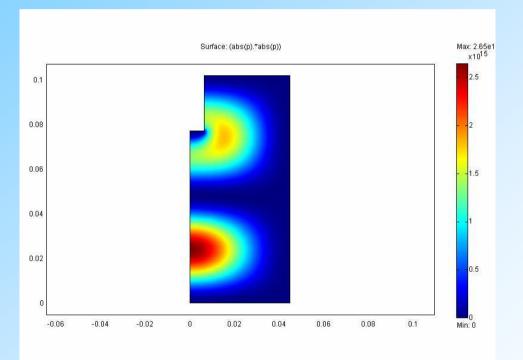
$$p_0 \approx \sin \frac{k}{2} \left( \sqrt{x^2 + r^2} - x \right)$$



 $x = 2r \rightarrow I_{US} < 3\% I_0 \quad V(I_{US} > 3\% I_0) < 1\%$ 



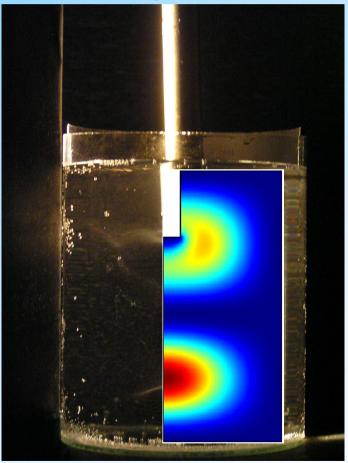
#### **Procedure: moving to more realistic systems**



R = 45, H = 25, D = 77 mm



**Procedure: moving to more realistic systems** 











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## Short Term Scientific Mission: J. Klima (Prague) in Alicante

## Conclusions

- numerical solution of the wave equation is in good agreement with experiment

- the optimal geometry of experimental arrangement can result in a strong increase of intensity in specific part of the cell

Advantages of optimised geometry:

- the cell is simple and cheap;
- whatever cell can be used;
- the ultrasonic power necessary for cavitation is low;
- low ultrasonic power results in weak heating of the solution

=> no cooling is necessary;

- the fraction of reactor volume where intensity is high is large. In sonoelectrochemistry :

- electrode does not need be placed in a small area near the horn surface

## Publications

"Physical aspects of Sono(electro)chemistry: Distribution of intensity of ultrasound" J. Klíma, A. Frias-Ferrer, J. González-García, J. Ludvík, V. Sáez, J. Iniesta COST WG 2 Workshop 9-10 June 2005, Oxford, UK



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## **One-year visit: J. González-García (Alicante) in Oxford**

## **Objectives**

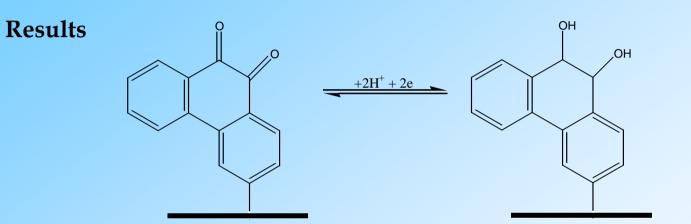
Identification of practical electrocatalysts capable of acting as electrode materials in a sonoelectrochemical reactor for the reduction of oxygen (air) to hydrogen peroxide

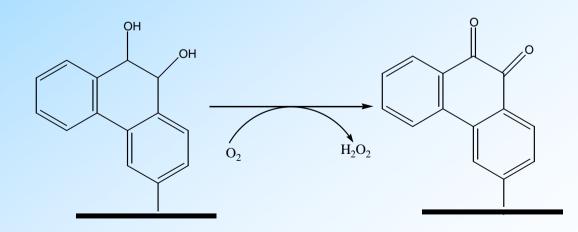
The determination of the stability of the electrocatalysts in respect of insonation to identify the optimal sonoelectrocatalysts for hydrogen peroxide formation

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



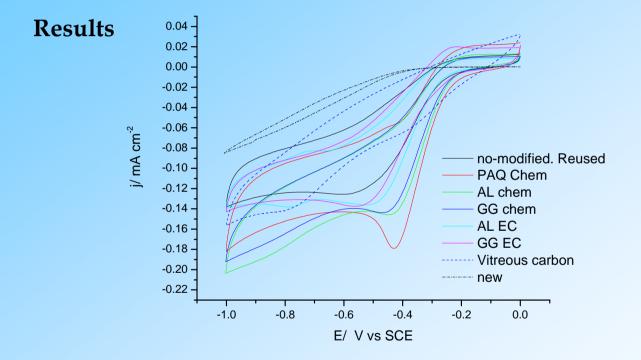
## **One-year visit: J. González-García (Alicante) in Oxford**







## One-year visit: J. González-García (Alicante) in Oxford





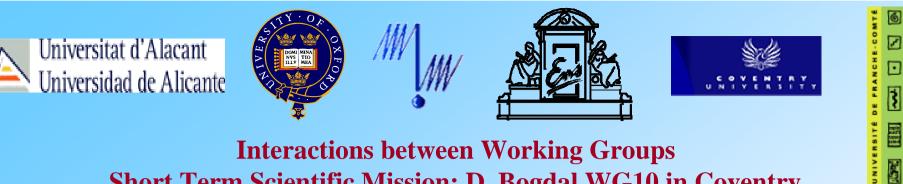
## **One-year visit: J. González-García (Alicante) in Oxford**

#### **Conclusions and further work**

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

Work in progress to analyze the stability as a electrode material in a sonoelectrochemical reactor

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



## **Interactions between Working Groups Short Term Scientific Mission: D. Bogdal WG10 in Coventry**

## **Objectives**

Carbazole electropolymerization in acentonitrile/ammonium system. Influence of the ultrasound and a magnetic field

#### **Results**

Polycarbazole films on indium-tin oxide coated (ITO) glass

## **Further work**

Characterization of the luminiscent properties in Politechnika Krakowska



**Further actions** 

#### Annual Working Group Meeting, to be held in Prague, November 2005.