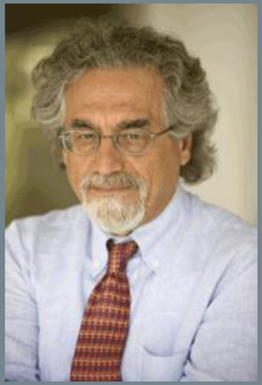
UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Catalytic and Electrochemical Processes

Dimitris I. Kondarides

Faculty Members

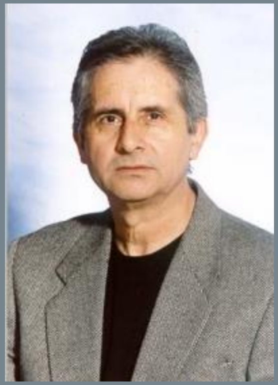
C.G. Vayenas, Professor
Electrochemistry
Electrocatalysis



X.E. Verykios, Professor
Heterogeneous Catalysis
Photocatalysis

S. Ladas, Professor
Surface Science

S. Boghosian, Professor
HT Raman Spectroscopy
Heterogeneous Catalysis



P. Lianos. Professor
Photo(electro)catalysis
Photo-Fuel cells

S. Bebelis, Assoc. Professor
Electrocatalysis
Fuel cells, Electrolyzers

D.I. Kondarides, Assoc. Professor
Heterogeneous Catalysis
Photo(electro)catalysis

A. Katsaounis, As. Professor
Electrochemistry
Electrocatalysis

General description of the Research Area

- **Heterogeneous Catalysis**
- **Electrochemistry**
- **Electrocatalysis**
- **Photocatalysis**

Environmental and energy-related applications

Production/purification of H_2

Fuel cells, solar cells

CO_2 utilization, biomass valorization

Catalytic destruction of VOCs

Wastewater treatment

Fundamental Research

(Electro)chemical promotion

Metal-support interactions

Catalytic materials

Synthesis, characterization, evaluation, optimization

Reaction engineering

Kinetic and mechanistic studies

New reactor concepts

Novel reactor configurations

Laboratory of Chemical and Electrochemical Processes (LCEP)

Prof. C.G. Vayenas, Assist. Prof. A. Katsaounis

Researchers

2 Faculty members

Prof. Constntinos G. Vayenas

As. Prof. Alexandros Katsaounis

1 Senior Scientist

Dr. Susanne Brosda

7 Graduate students

Mr. Andreas Gousev

Mr. Dimitris Theleritis

Ms. Ioanna Kalaitzidou

Ms. Marialena Makri

Ms. Eftychia Martino

Mr. Alexandros Simillidis

Mr. Evangelos Kalamaras

6 Undergraduate Students

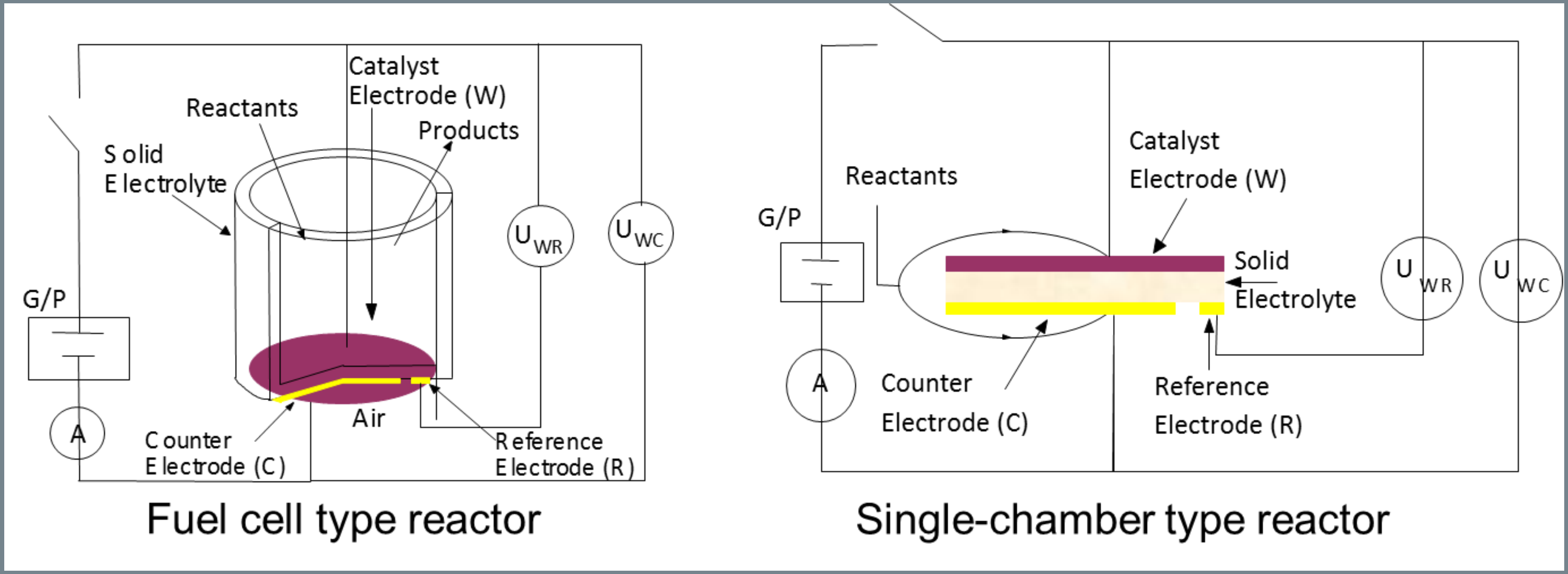
Research Activities

Catalytic and Electrocatalytic Processes

- Electrochemical promotion of Catalysis (EPOC)
- Development of fuel cells fed with alternative fuels for simultaneously generation of electrical power and useful chemicals (chemical cogeneration).
- Triode fuel cells where a third auxiliary electrode is used to enhance the anodic or cathodic electrocatalysis.
- Development of the monolithic electropromoted reactor (MEPR) which significantly facilitates the practical utilization of electrochemical promotion of catalysis

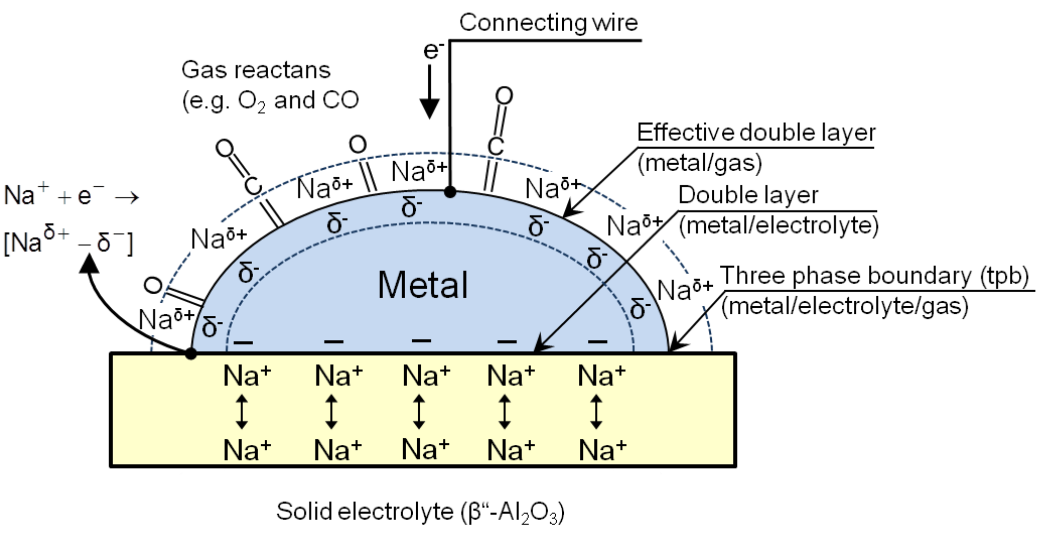
Electrochemical Promotion of Catalysis (EPOC) or NEMCA or Electrochemical Promotion (EP)

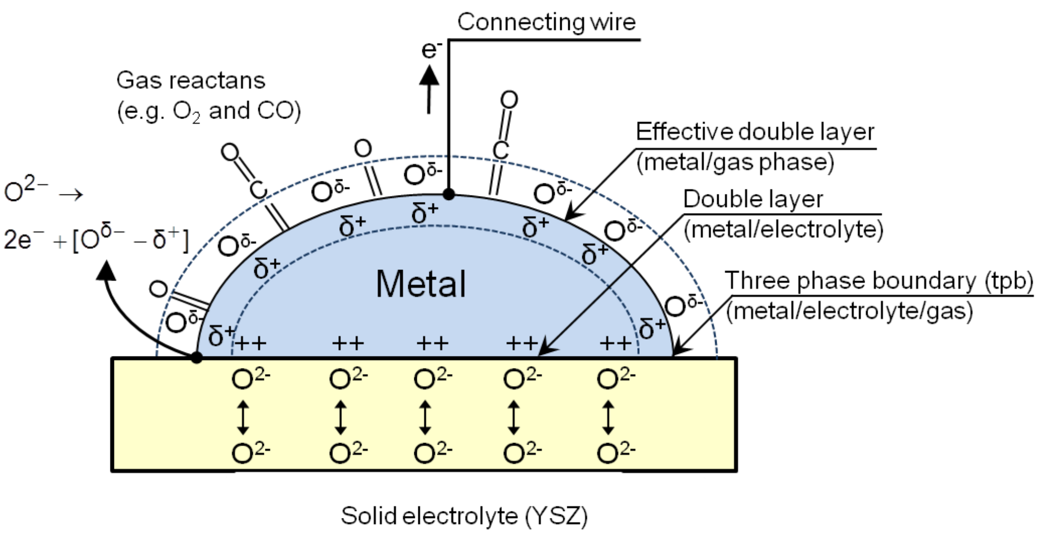
EPOC is a phenomenon where application of small currents or potentials on catalysts in contact with solid electrolytes leads to pronounced strongly non-Faradaic and reversible changes in catalytic activity and selectivity.



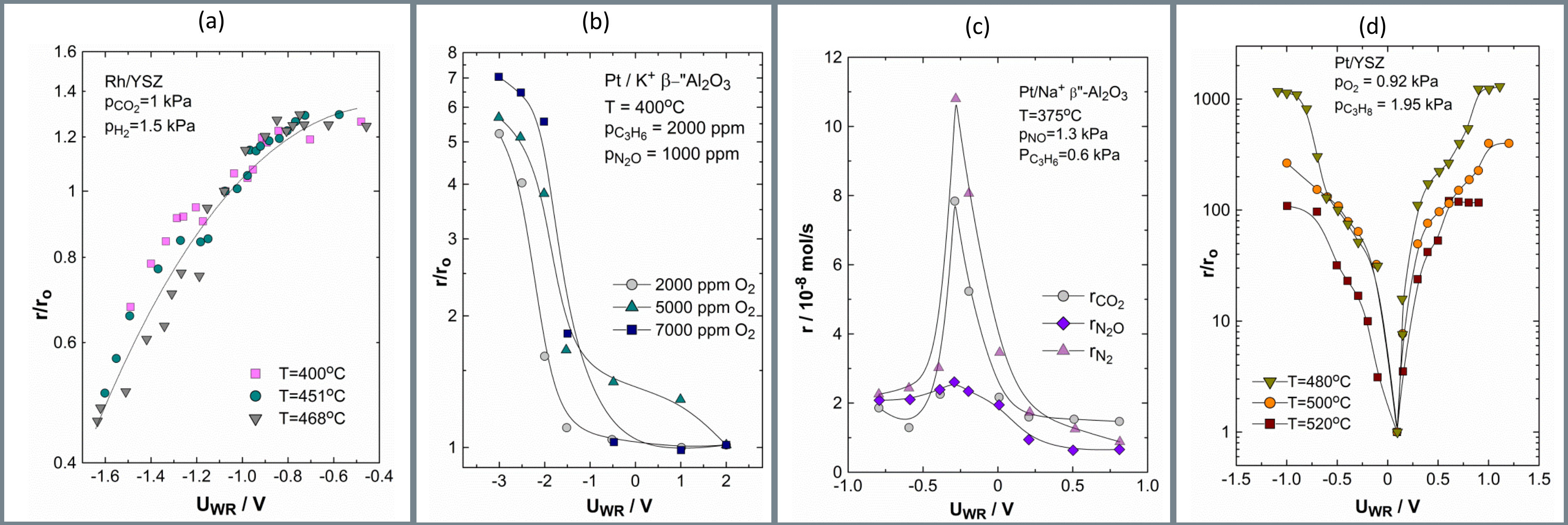
C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal Support Interactions, Kluwer Academic Publishers/Plenum Press, New York, 2001, and references therein

Electrochemical Promotion



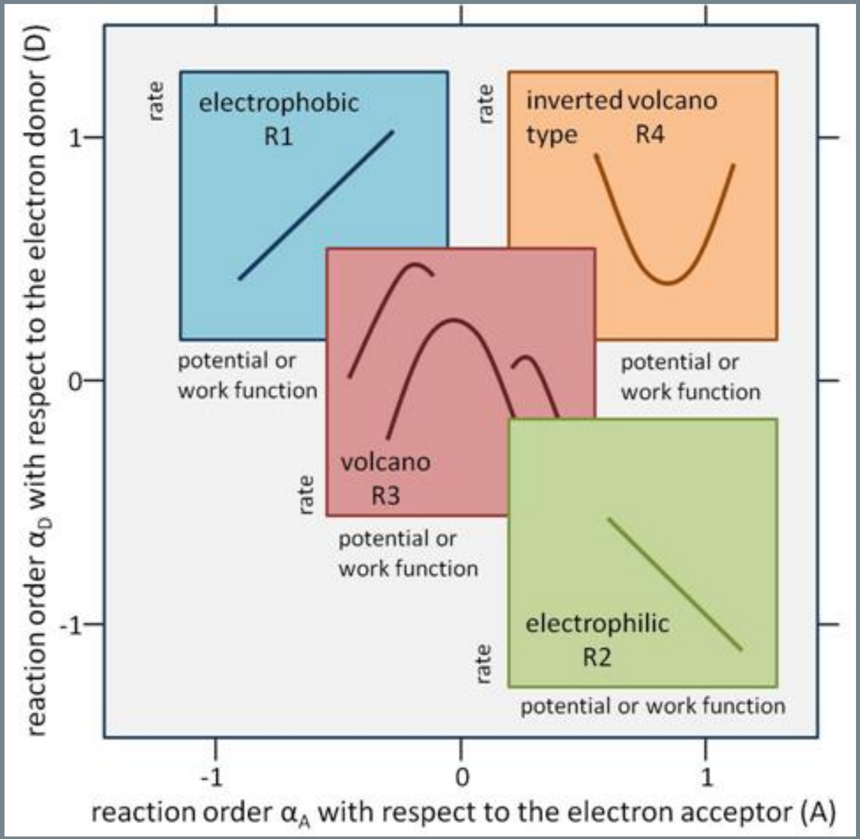


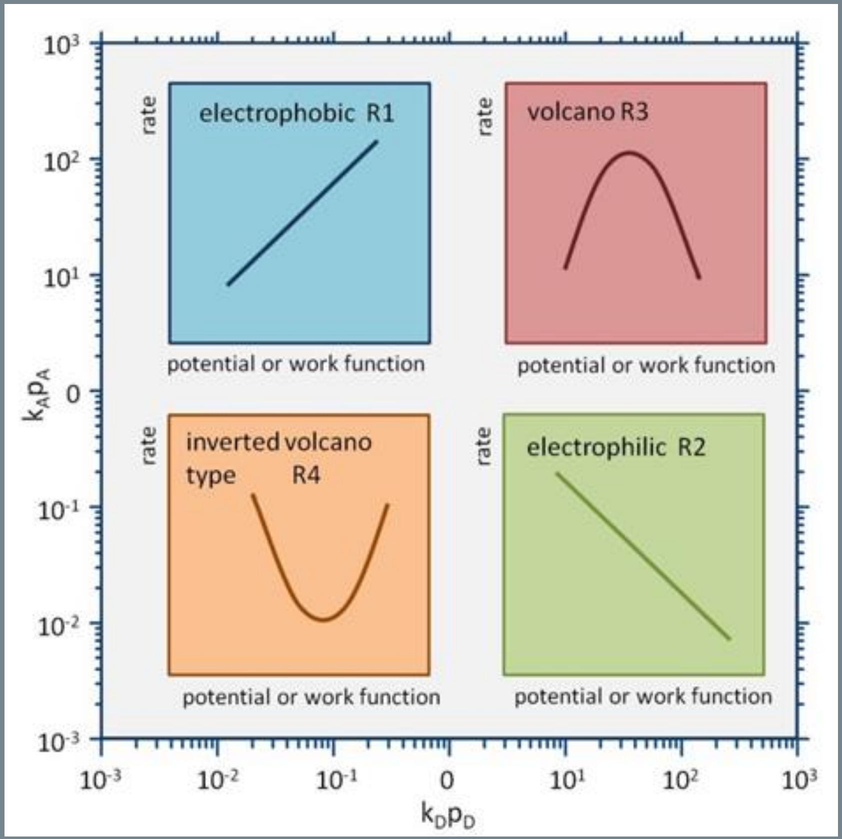
The four types of Electrochemical Promotion



Nucleophilic | **Electrophilic** | **Volcano** | **Inverted volcano**

The rules of Chemical and Electrochemical Promotion





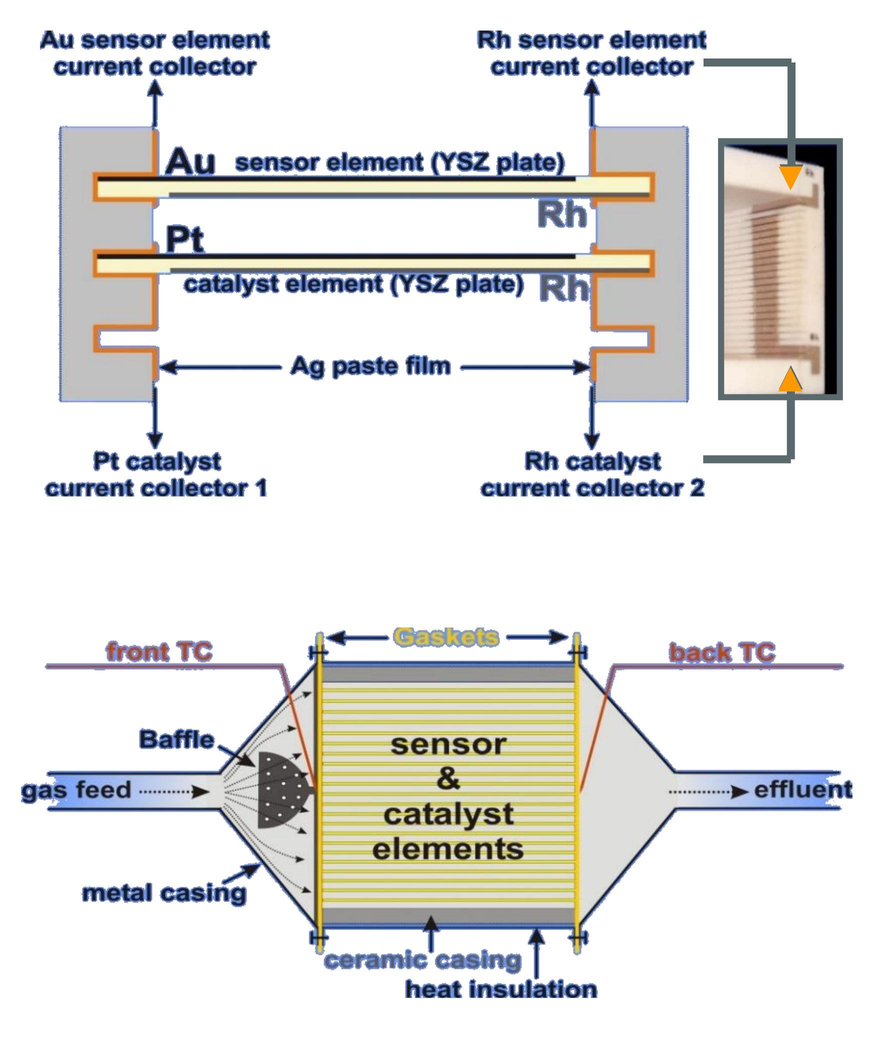
Brosda S, Vayenas CG, Wei J (2006) Rules of chemical promotion. Applied Catalysis B: Environmental 68 (3–4):109-124.

Vayenas CG (2011) Bridging electrochemistry and heterogeneous catalysis. J Solid State Electrochem 15:1425-1435

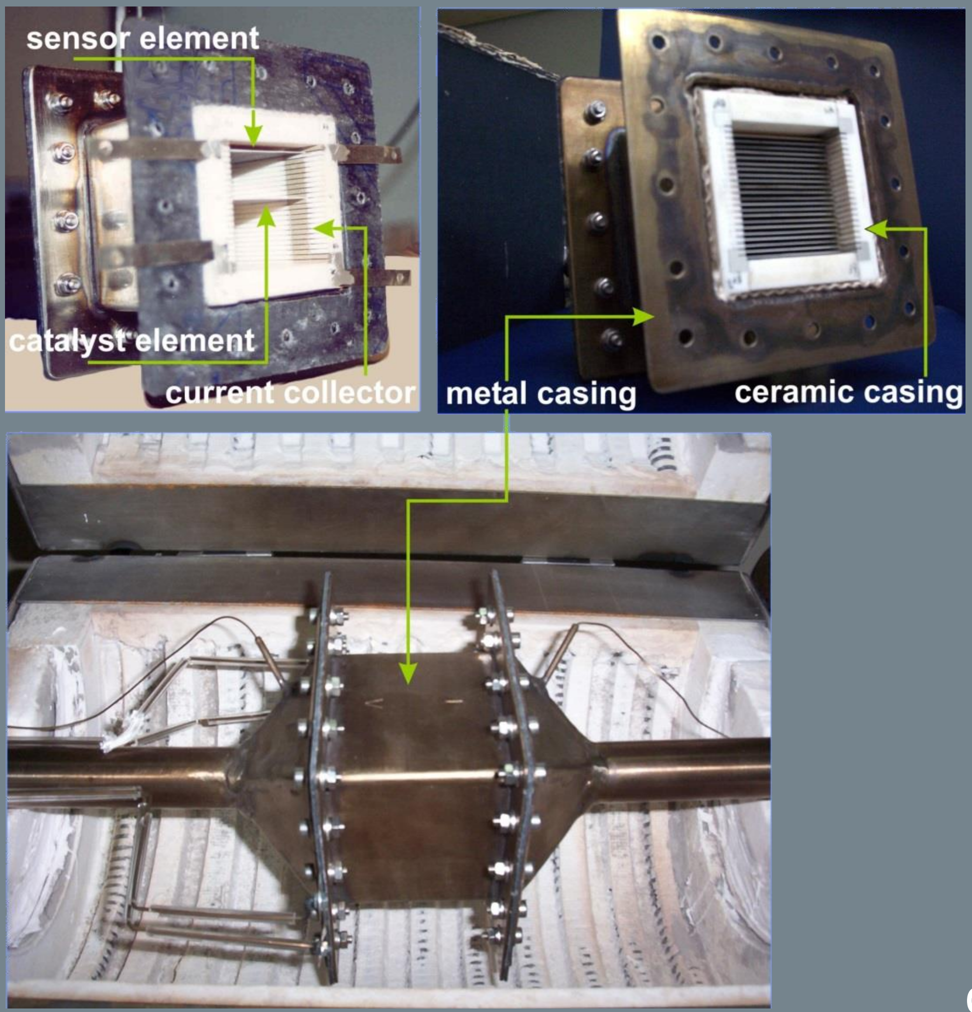
Monolithic Electropromoted Reactor (MEPR)

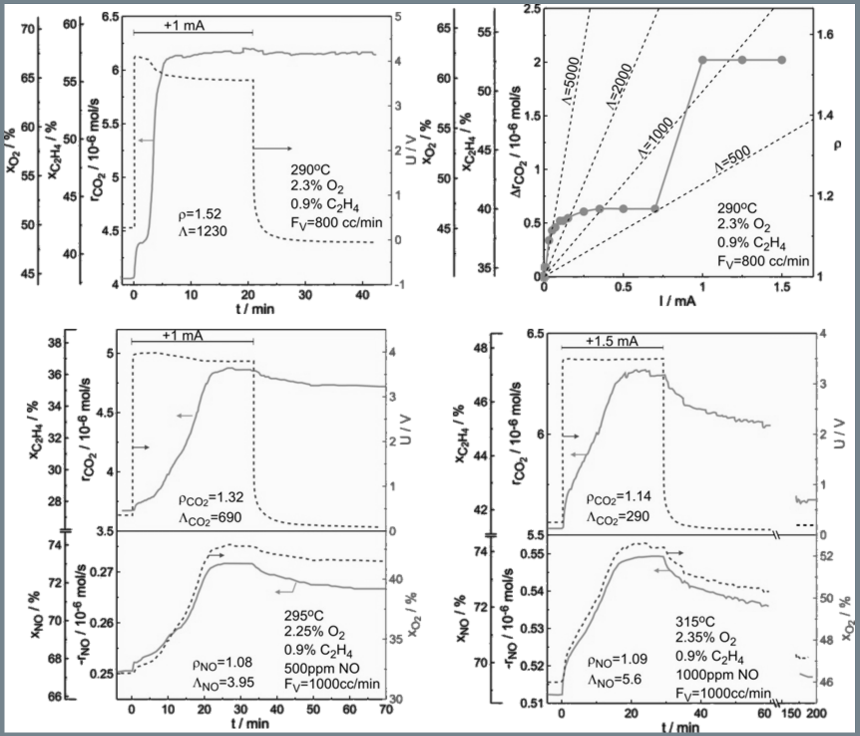
The practical utilization of EPOC requires the development of a new generation of hybrid catalytic reactors which combine several aspects of a classical monolithic reactor and of a flat plate fuel cell.

Such a reactor is the monolithic electropromoted reactor (MEPR), recently designed and operated with 21 parallel catalyst plates and one sensor plate, all covered with thin (40nm) metal electrodes.



Monolithic Electropromoted Reactor (MEPR)



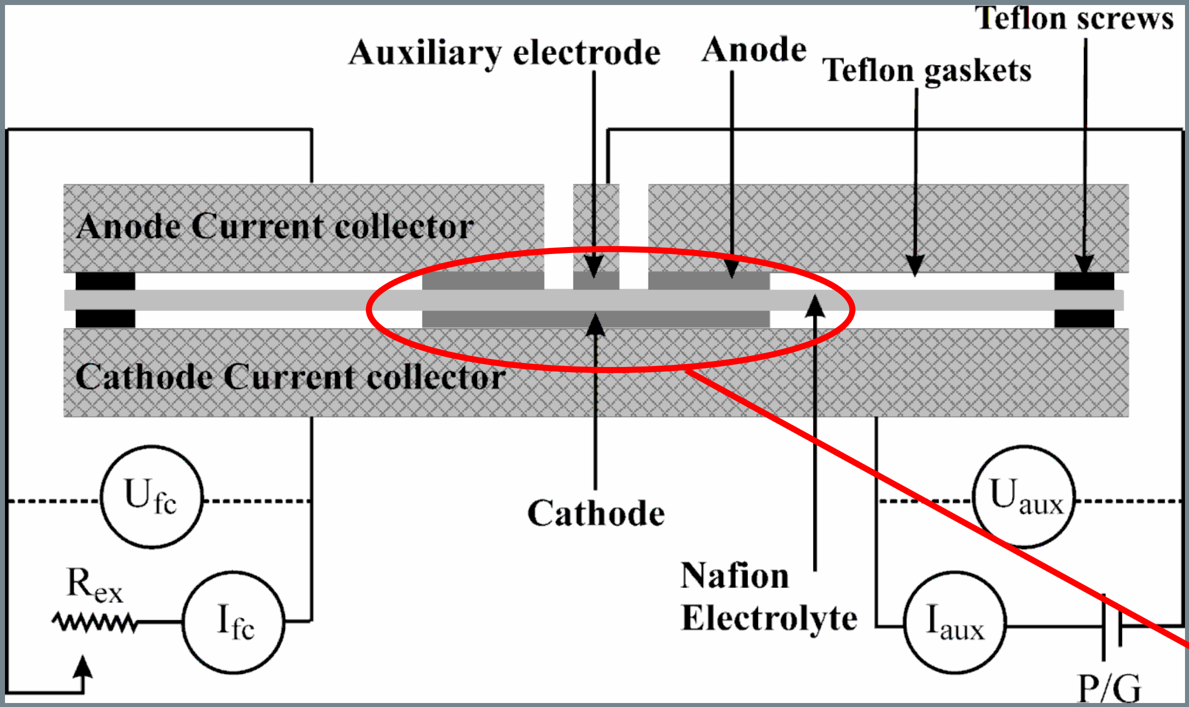


Electrochemical promotion of ethylene oxidation on thick Rh and Pt films deposited on a YSZ plate in a MEP reactor

Electrochemical Promotion of Catalysis: Recent Invited Reviews

- Vayenas CG, Koutsodontis CG (2008) Non-Faradaic electrochemical activation of catalysis. Journal of Chemical Physics 128 (18).
- Tsiplakides D, Balomenou S (2009) Milestones and perspectives in electrochemically promoted catalysis. Catalysis Today 146 (3–4):312-318.
- Katsaounis A (2010) Recent developments and trends in the electrochemical promotion of catalysis (EPOC). Journal of Applied Electrochemistry 40 (5):885-902.
- Vayenas CG (2011) Bridging electrochemistry and heterogeneous catalysis. J Solid State Electrochem 15:1425-1435.
- Vayenas C (2013) Perspectives paper: Promotion, Electrochemical Promotion and Metal–Support Interactions: Their Common Features. Catalysis Letters 143 (11):1085-1097.
- Vernoux P, Lizarraga L, Tsampas MN, Sapountzi FM, De Lucas-Consuegra A, Valverde J-L, Souentie S, Vayenas CG, Tsiplakides D, Balomenou S, Baranova EA (2013) Ionically Conducting Ceramics as Active Catalyst Supports. Chemical Reviews 113 (10):8192-8260.

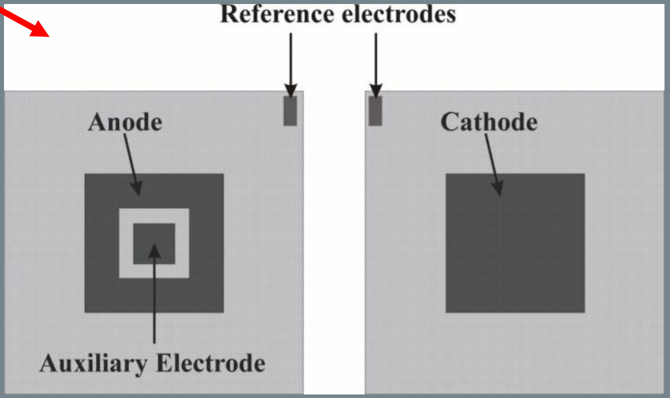
Triode SOFC and PEM fuel cells



Triode PEMFC geometry

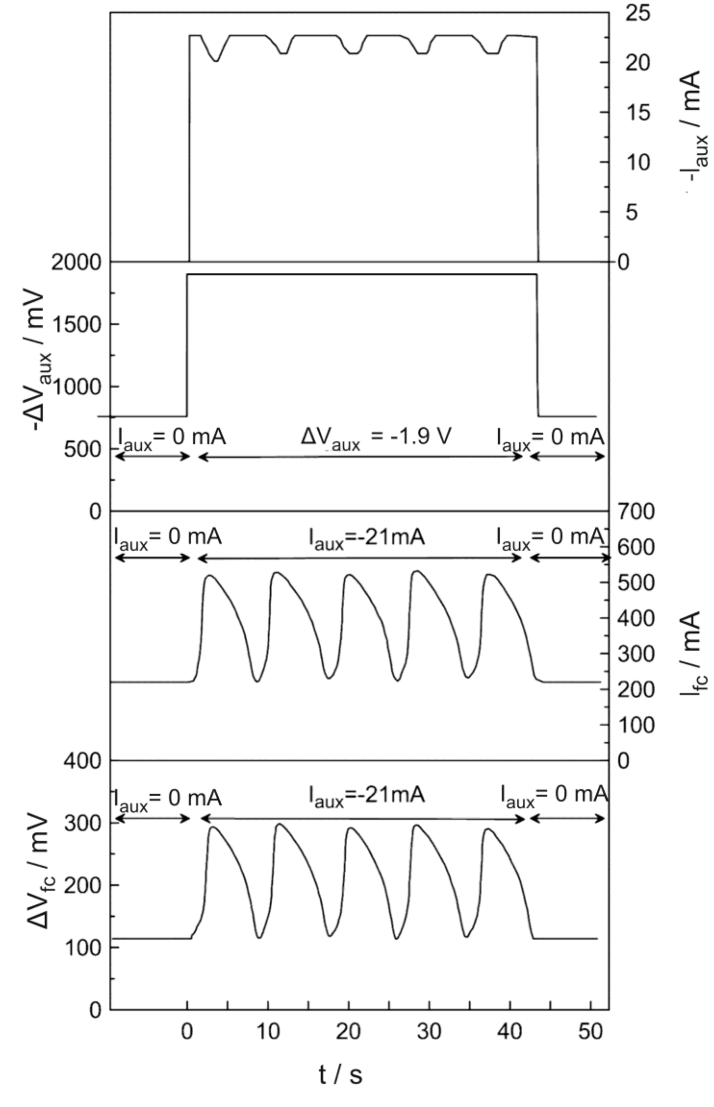
Alexandros Katsaounis,
Constantinos G. Vayenas

Membrane Electrode Assembly



Electrolyte: Nafion 117, Dupont
Anode: PtRu-Carbon cloth, ETEK, 3.85 cm^2
Auxiliary electrode: PtRu-Carbon cloth, ETEK, 0.49 cm^2
Cathode: Pt-Carbon cloth, ETEK, 5.29 cm^2

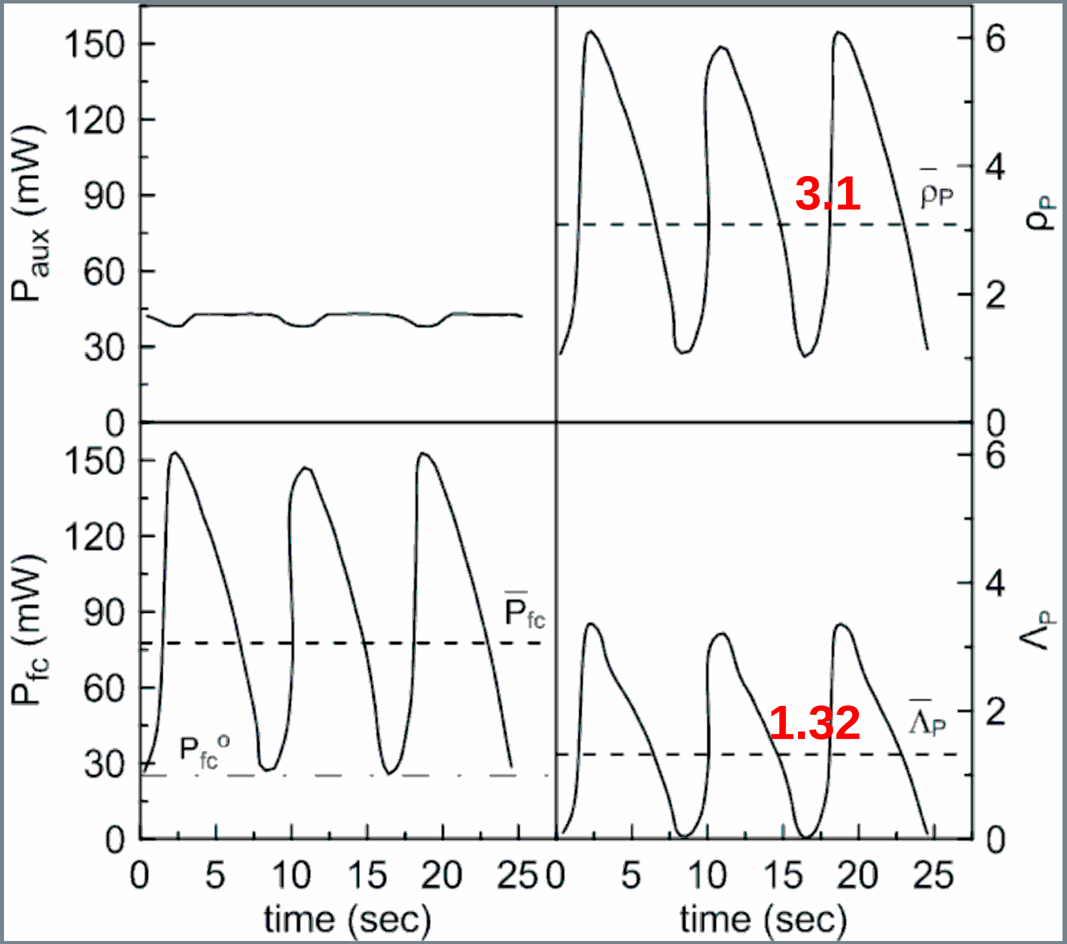
Triode PEMFC operation under R_{ext}=0.5 Ohm



Imposition of a constant electrolytic potential (-1.9 V) and current (-21 mA) in the auxiliary circuit causes the ***induction of self-sustained high amplitude oscillations*** in the fuel cell current and potential.

The induction of this oscillatory behavior is ***reversible*** as oscillations disappear when the cell operation returns to the conventional mode.

Triode PEMFC operation under R_{ext}=0.5 Ohm



F. Sapountzi, S. Divane, M. Tsampas and C.G. Vayenas, Electrochim. Acta, 56 (2011) 6966.

Power enhancement ratio:

$\rho_p = P_{fc}/P_{fc}^o$

Power gain ratio:

$\Lambda_p = \Delta P_{fc} / P_{aux}$

$$\bar{\rho}_p = \frac{1}{T}\int_0^T \frac{P_{fc}}{P_{fc}^o} dt$$

$$\bar{\Lambda}_p = \frac{1}{T}\frac{\int_0^T \left(P_{fc} - P_{fc}^o\right) dt}{\int_0^T \mathrm{P_{aux}}\, dt}$$

When Λ>1, the increase in the power output of the PEMFC is higher than the power sacrificed in the electrolytic circuit

Research Projects

- "Electrochemically promoted CO_2 hydrogenation for the production of clean fuels" (2010-2013).
- "Nano-structured electrodes for water electrolysis in high temperature Polymer Electrolyte Membrane electrolyzers" (2010-2013).
- "Triode fuel Cells" (2013-2015).

Funding by the Industry

EPOC	**Triode Fuel Cells**
BASF	Prototech (Norway)
TOYOTA	SOFC Power (Italy)
Du Pont	Saint Gobain (France)

Patents – 1/2

Electrochemical Promotion of Catalysis

- U.S. Patent 4,643,806 "Electrocatalytic Energy Conversion and Chemicals Production", L.L. Hegedus, C.G. Vayenas and J.N. Michaels (1987).
- European Patent Appl. 90600021.1 "Metal-Solid Electrolyte Catalysts" C.G. Vayenas, S. Bebelis, I.V. Yentekakis and P. Tsiakaras (1990); European Patent 0480116; 24.7.1996; **purchased by BASF**.
- PCT Patent Appl. GR94/00001 "Method and Apparatus for Forming Ethylene from Methane" C.G. Vayenas, I.V. Yentekakis and Y. Jiang (1994).
- European Patent Appl. 94600002.3 "New monolithic three-way catalysts with optimized distribution of precious metals within three separate washcoat layers" C.G. Vayenas, X.E. Verykios, V.G. Papadakis, I.V. Yentekakis, C. Pliangos (1994).

Patents – 2/2

Electrochemical Promotion of Catalysis

- U.S. Patent 6,194,623 B1 “Hydrogenation of organic compounds with the use of the NEMCA effect” A. Frenzel, C.G. Vayenas, A. Giannikos, P. Petrolekas, C. Pliangos (2001).
- PCT/GR2004/000006 “Method and Apparatus for carrying out electrochemically promoted reactions” C.G. Vayenas, S. Balomenou, D. Tsiplakides, A. Katsaounis, S. Brosda, G. Foti, C. Comninellis, S. Thieman-Handler, B. Cramer, (2004).
- U.S. Patent 7,267,807 B2 “Method and Device for Treating Automotive Exhaust” Leo B. Kriksunov and C.G. Vayenas, (2007).

Triode Fuel Cells

- PCT/GR03/00032 “Triode FC and battery and method for conducting exothermic chemical reactions” C. G. Vayenas, S. Balomenou (2003).

Research Group of Assoc. Prof. Symeon Bebelis

Prof. S. Bebelis

Researchers

1 Faculty member

Assos. Prof. S. Bebelis

1 Graduate student

Mr. Alexandros Safakas

Research activities

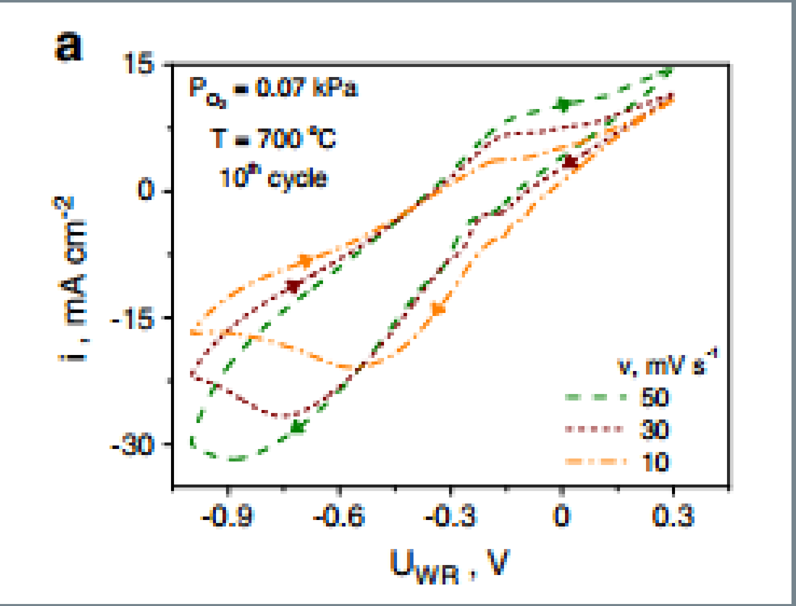
- Conventional and non-conventional fuel cells
- Heterogeneous Catalysis and Electrochemical Promotion

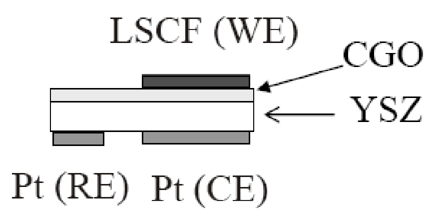
Solid oxide fuel cells (SOFCs)

Development and characterization of new catalyst-electrodes and electrolytes for intermediate temperature (600-800 °C) SOFCs.

- Mixed ion-electron conducting perovskitic cathodes with high activity for oxygen reduction, mainly La-Sr-Co-Fe perovskites.

- Cermet anodes for SOFCs operating under internal reforming (IR-SOFC) or chemical cogeneration conditions using carbon-based fuels.

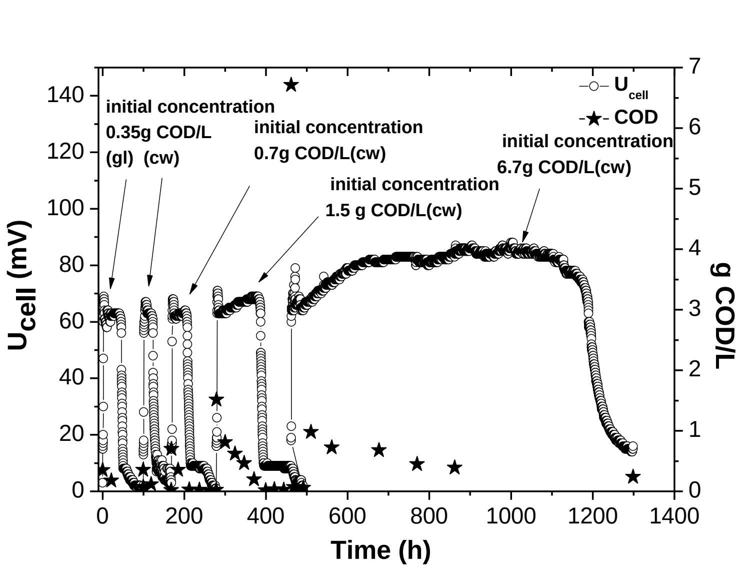




Non-conventional Fuel Cells

- Microbial fuel cells (**MFCs**)

  Development MFCs fed with by-products or wastes from food industries, such as cheese whey, focusing on the study of the factors affecting their performance and on scale up (in collaboration with Prof. G. Lyberatos, NTUA).



MFC voltage U_{cell} and COD consumption versus time using glucose (gl) and cheese whey (cw) as substrates at different initial concentrations. R_{ext} = 100 Ω

- Photoelectrochemical cells (**PECs**)

  Development of photoelectrocatalysts for PECs responding efficiently to the visible light (in collaboration with Prof. D.I. Kondarides)

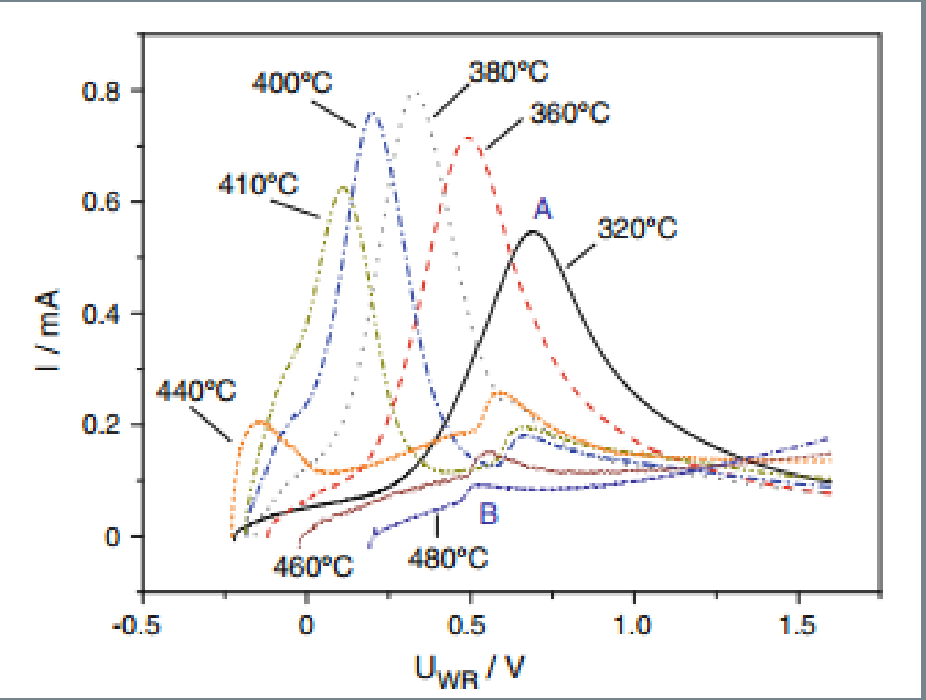
Heterogeneous Catalysis and Electrochemical Promotion

Research interest mainly focuses on potential novel applications of EPOC or NEMCA effect in reactions of industrial and environmental importance as well as on the electrochemical characterization of the catalyst-solid electrolyte system under EPOC conditions, in particular in the case of alkali-ion conductors.

Electrochemical characterization of the Pt/β"-Al_2O_3 system under EPOC conditions (propane combustion):

Linear sweep voltammograms obtained at different T after previous application of -50 μA for 8 min

P_{O_2} = 1 kPa, $P_{C_3H_8}$ = 0.2 kPa, v= 20 mV s^{-1}



Recent Publications

- “Cyclic voltammetry characterization of a $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ electrode interfaced to CGO/YSZ”, V. Ch. Kournoutis, F. Tietz, S.Bebelis, Solid State Ionics 197(1) (2011) 13-17
- “Study of the synergistic interaction between nickel, gold and molybdenum in novel modified NiO/GDC cermets, possible anode materials for CH_4 fuelled SOFCs”, D.K. Niakolas, M. Athanasiou, V. Dracopoulos, I. Tsiaoussis, S. Bebelis, S.G. Neophytides, , Appl. Catal. A: General 456 (2013) 223-232
- “Operation and characterization of a microbial fuel cell fed with pretreated cheese whey at different organic loads”, A. Tremouli, G. Antonopoulou, S. Bebelis, G. Lyberatos, Biores. Technol. 131 (2013) 380.
- “Electrochemical characterization of the Pt/β"-alumina system under conditions of electrochemical promotion of propane combustion”, N. Kotsionopoulos, S.Bebelis, J. Appl. Electrochem. 40(10) (2010) 1883.

Research Projects

- ROBANODE PROJECT (2010-2012)
  Understanding and minimizing anode degradation in hydrogen and natural gas fueled SOFCs

  Partners: FORTH/ICE-HT, T. U. Clausthal, NTUA, EPFL, CSIC (Spain), CNRS, MIRTEC S.A. (Greece), Saint Gobain C.R.E.E.)

  Total funding: ~1600 k€, ICE-HT & DCE funding: ~310 k€





Laboratory of Heterogeneous Catalysis (LHC)

Prof. X.E. Verykios, Assoc. Prof. D.I. Kondarides

Researchers

2 Faculty members

Prof. Xenophon E. Verykios
Assoc. Prof. Dimitris I. Kondarides

2 Post doctoral fellows

Dr. Paraskevi Panagiotopoulou
Dr. Nikolaos Hourdakis

1 Researcher

Mr. Ioannis Sionakides

7 Graduate students

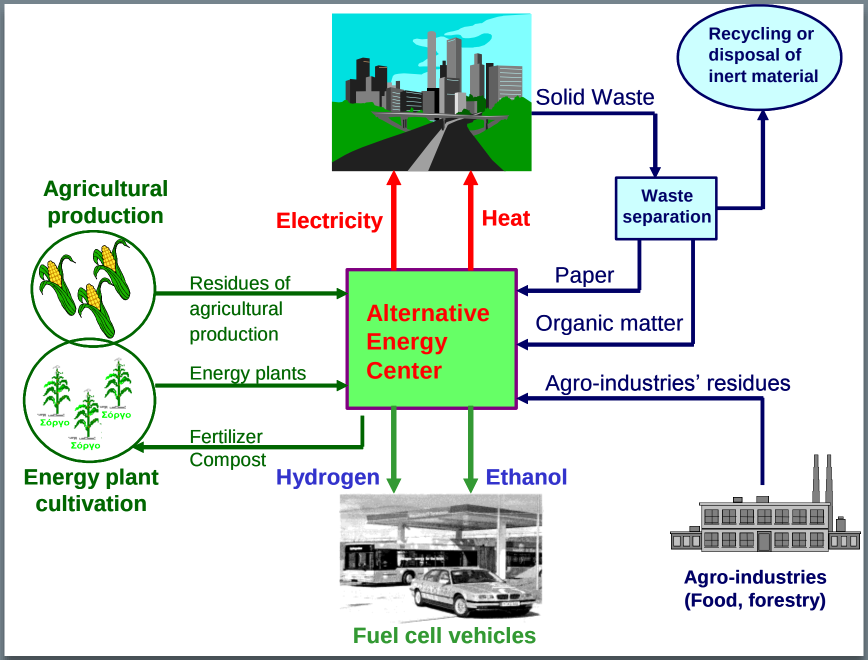
Ms. Siranush Akarmazyan
Ms. Elina Ioannidou
Mr. Marios Kourtelesis
Ms. Natassa Petala
Mr. Andreas Kouroumlidis
Mr. Georgios Bambos
Ms. Kelly Kousi

4 Undergraduate Students

Research Activities

LHC is conducting fundamental and applied research, with particular emphasis on the

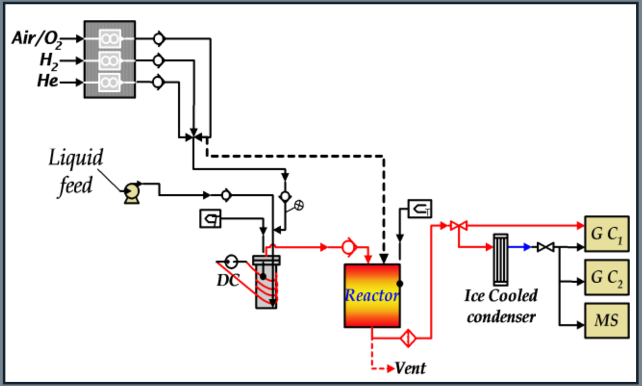
- synthesis, characterization and evaluation of catalytic materials
- reactor analysis and design
- development of novel environmental and energy-related processes.



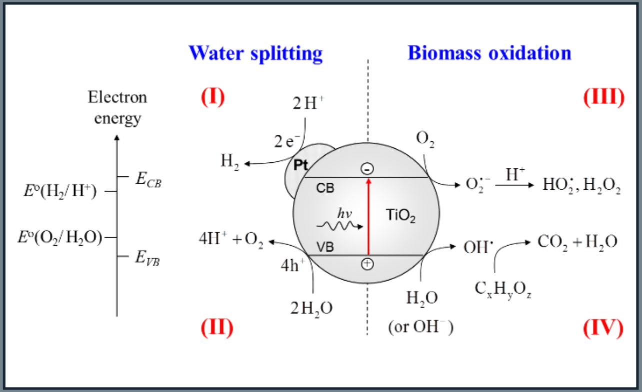
Research Activities

Over the last years, the Laboratory of Heterogeneous Catalysis has initiated, in a global scale, two areas of scientific and technological research, which have proven to be attractive to a large number of scientists:

(a) **Heterogeneous catalytic reformation of biofuels**, such as bioethanol, biogas and bio-oil, for the production of H_2 for fuel cell applications or synthesis gas for the production of chemicals.



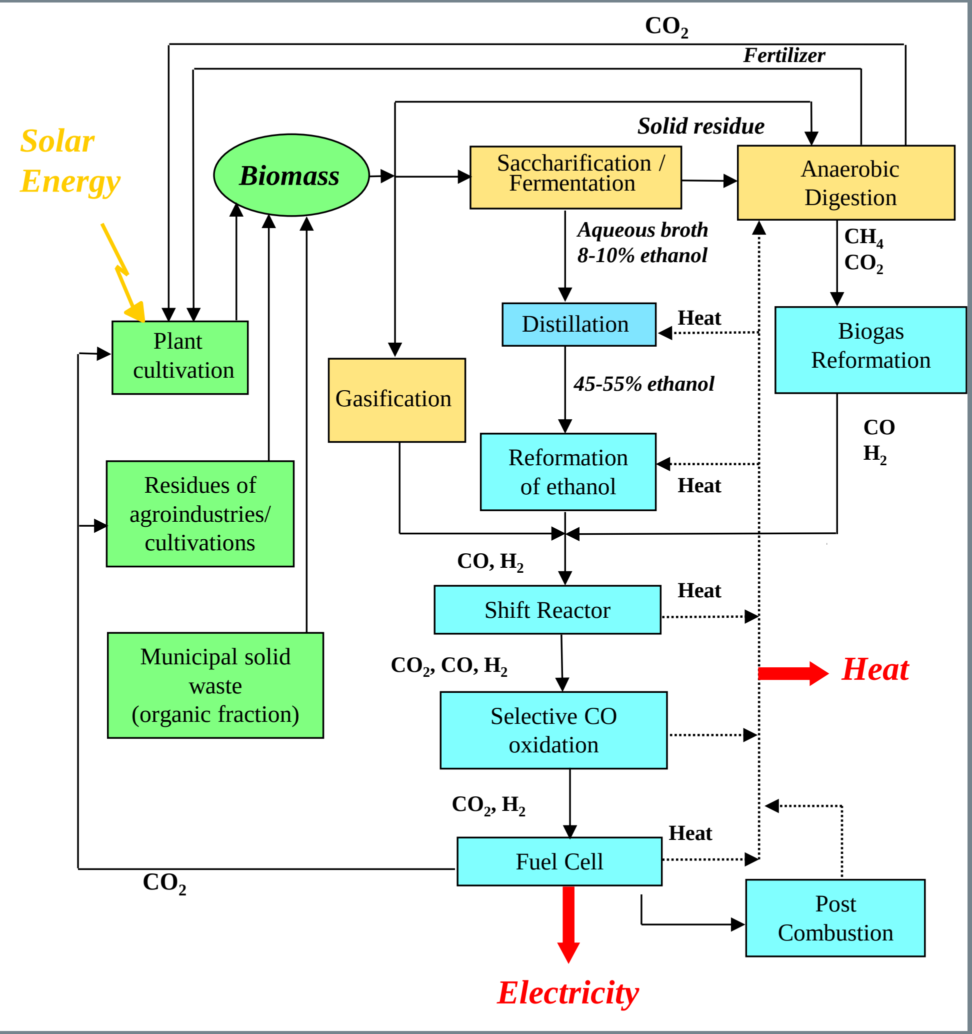
(b) **Photocatalytic reformation of biomass** components and biomass derivatives at ambient conditions for the production of hydrogen.



Catalytic Reforming of Biofuels

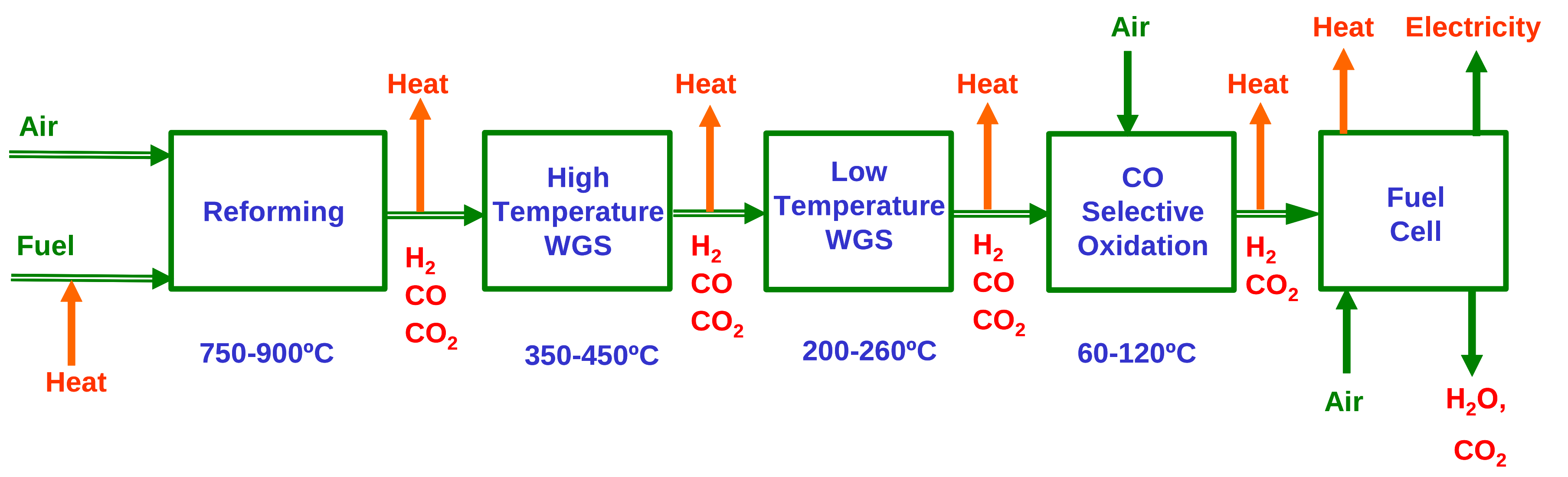
A complete process was proposed, which includes utilization of waste biomaterials, cultivations of energy crops and agricultural residues for the production of bio-ethanol, biogas and bio-H_2.

Such process was described in international patents and has attracted significant interest.

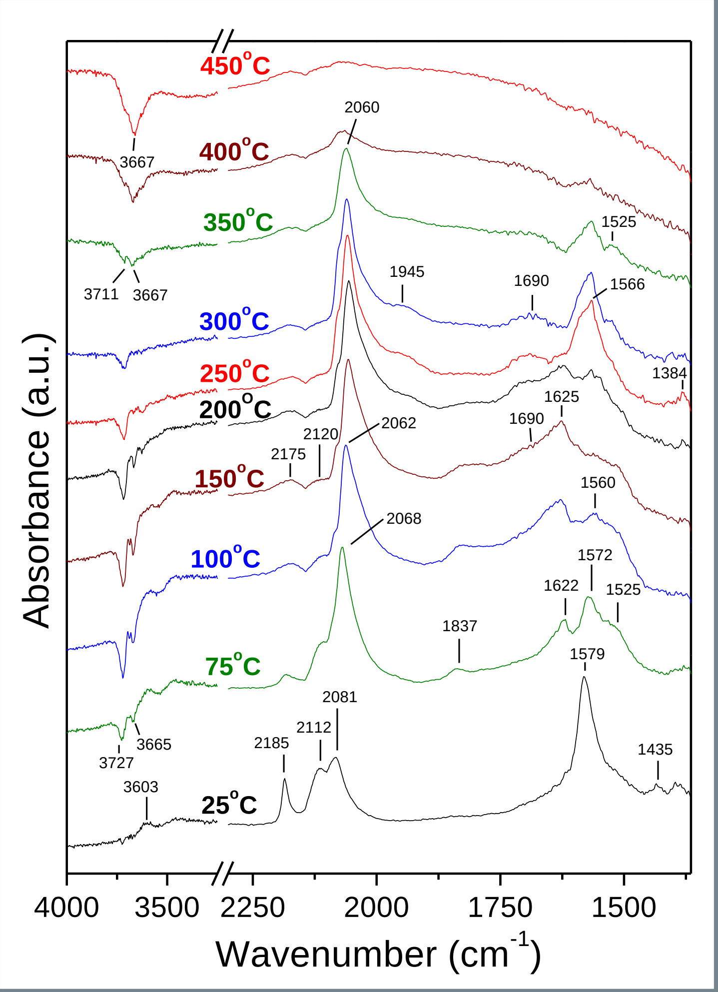


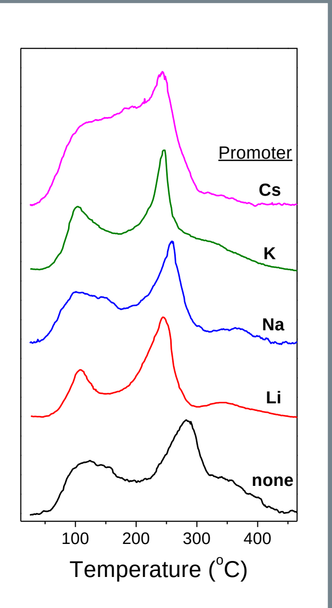
Catalytic Reforming of Biofuels
Catalyst development

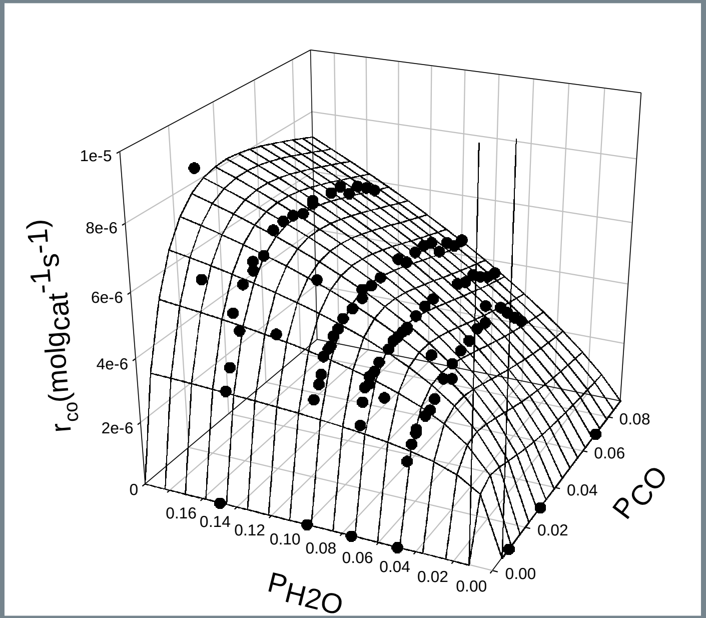
In addition to the process, optimal catalytic materials were developed for the various conversion steps, namely reformation, water-gas shift reaction and selective oxidation or methanation reaction.

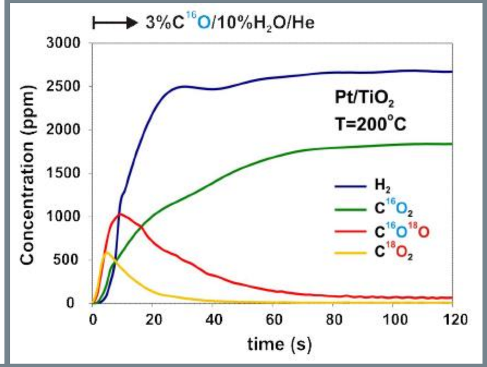


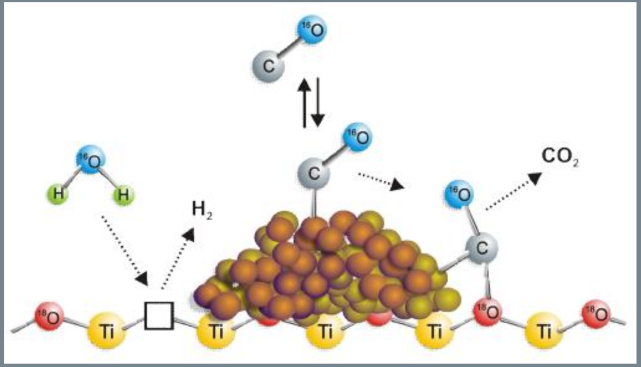
Catalytic Reforming of Biofuels
Kinetic and mechanistic studies









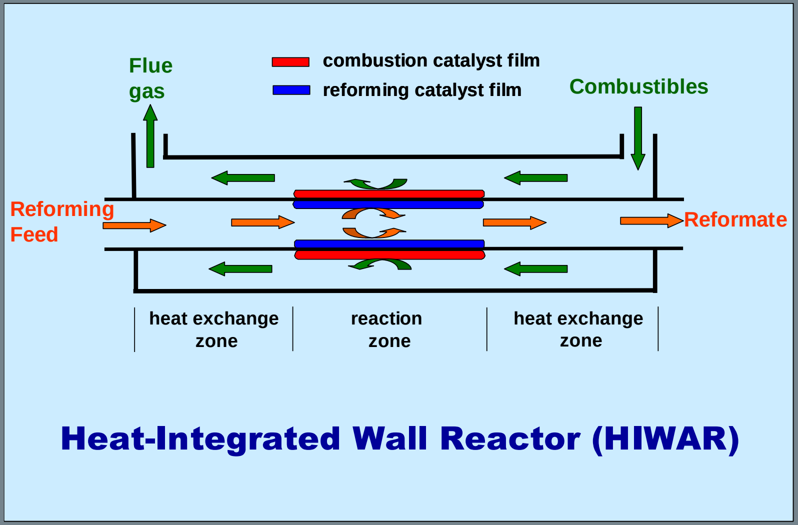


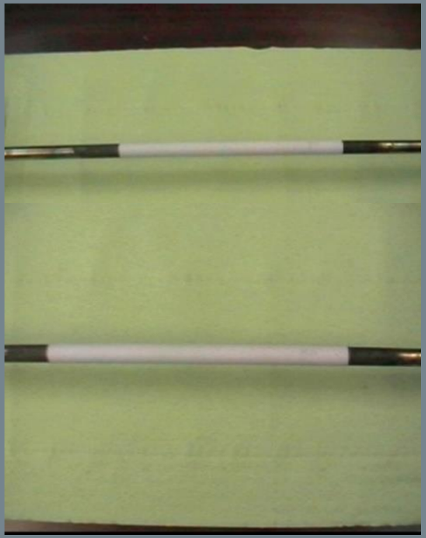
The Water-Gas Shift (WGS) reaction over 0.5 wt% Pt/TiO_2 catalyst

Catalytic Reforming of Biofuels
Advanced reactor configurations

Development of novel reactor configurations, integrating the catalytic materials with advanced heat transport mechanisms.

Ceramic monolith reactor





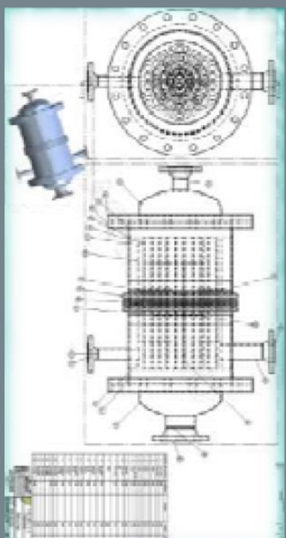
In this way, highly compact and very efficient reactors have been developed.

Catalytic Reforming of Biofuels
Pilot plant demonstration

10kW ethanol reforming pilot plant

Catalytic Reforming of Biofuels Spin-off Company

HELBIO S.A. was established in November 2001 as a spin-off from the University of Patras to commercialize fuel processing technology developed at the University.



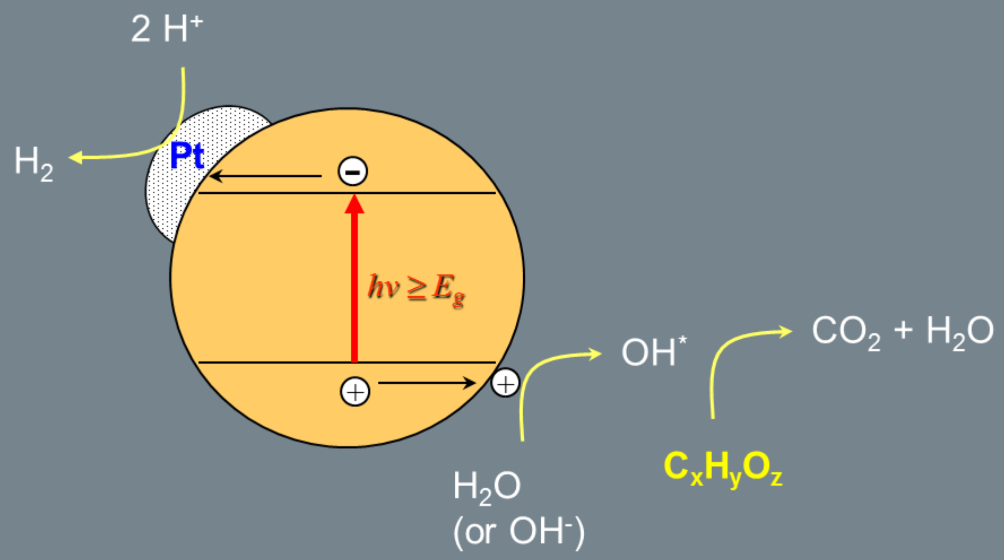
HELBIO develops and markets hydrogen fuel processors for energy applications and has established a leading position worldwide in hydrogen production from bio-fuels.

The fuel processors are delivered either fully integrated with fuel cells or as stand alone units.

Photocatalytic Reformation of Biomass Components and Derivatives for H_2 Production

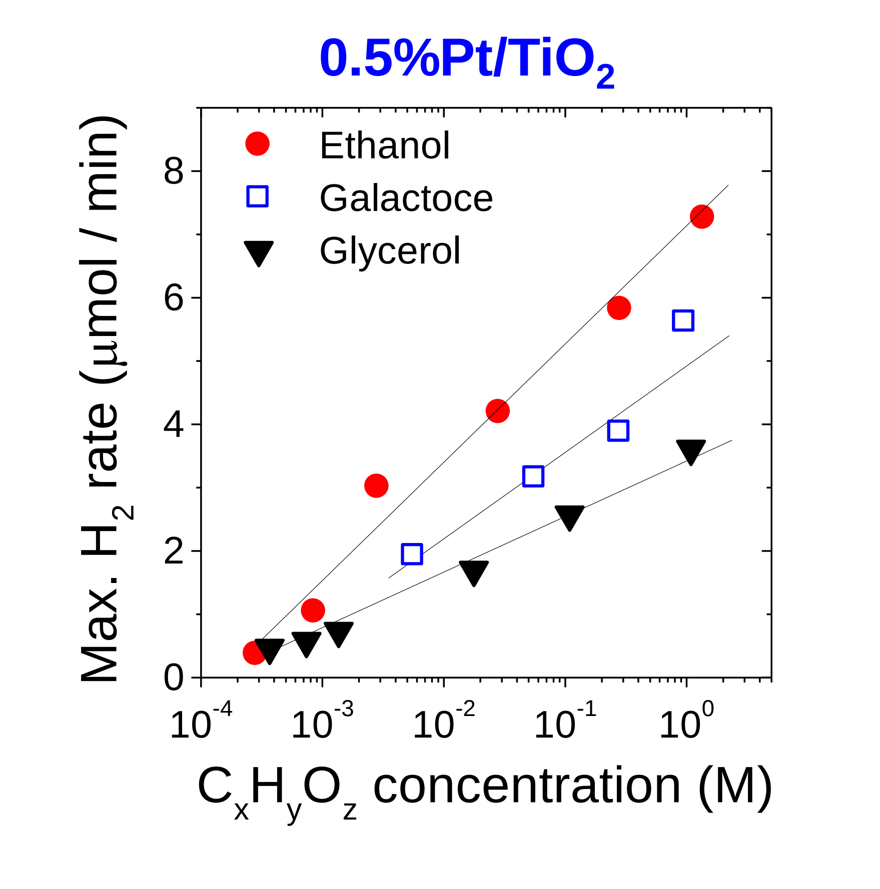
It was shown that three abundant and renewable sources (**solar light**, **biomass** and **water**) can be used in an effective way to produce power via hydrogen and fuel cells.

It was established that biomass components and derivatives, mostly waste biomass, can be reformed at ambient conditions to produce hydrogen via solar light and a photocatalyst.



$$C_xH_yO_z + (2x - z)H_2O \xrightarrow[h\nu \geq E_{bg}]{Pt/TiO2} xCO_2 + (2x - z + y/2)H_2$$

Photocatalytic Reformation of Biomass Components and Derivatives for H_2 Production



Effect of substrate concentration on the maximum rate of hydrogen evolution

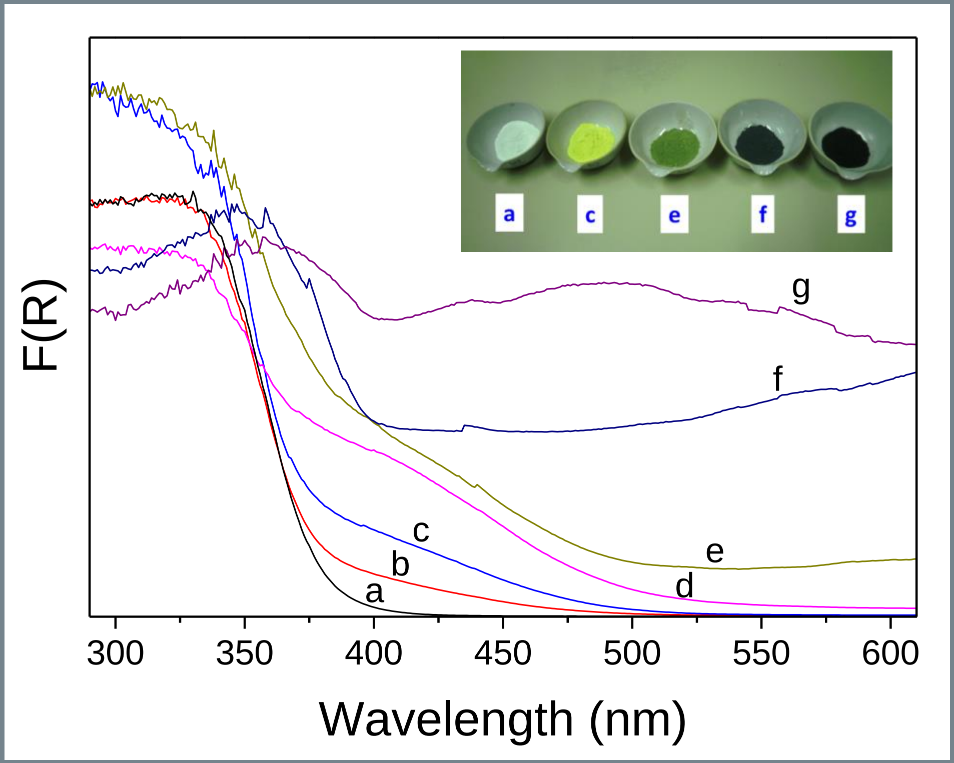
The rate maximum increases by more than 2 orders of magnitude in the presence of biomass components (1M) in solution.

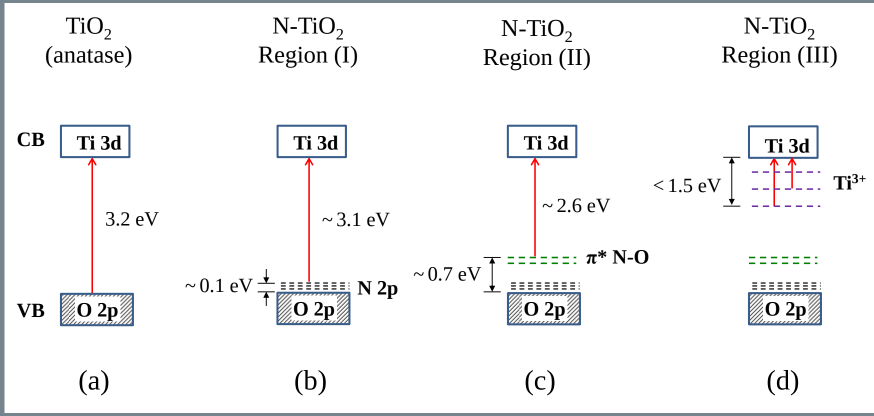
The photo-reforming process is very efficient, compared to, for example, photocatalytic splitting of water.

However, the rate achievable at the moment is low enough not to permit practical applications.

Photocatalysts with tunable response to vis. light N-doped TiO_2

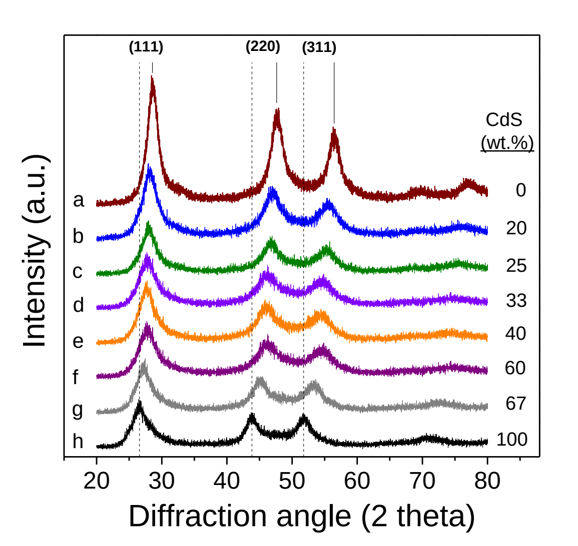
Current research efforts are directed toward the development and optimization of photocatalytic materials characterized by enhanced performance in the solar spectral region.

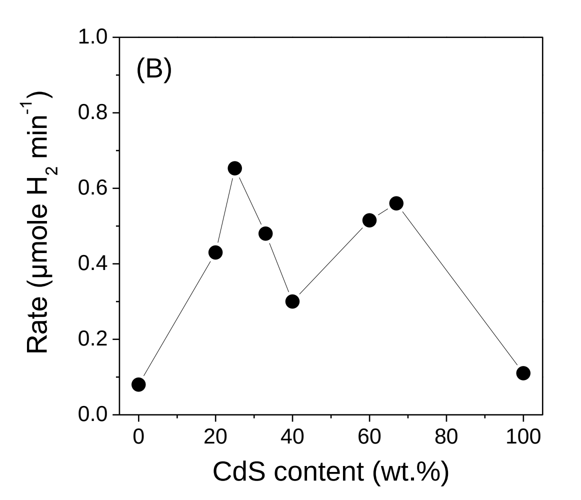


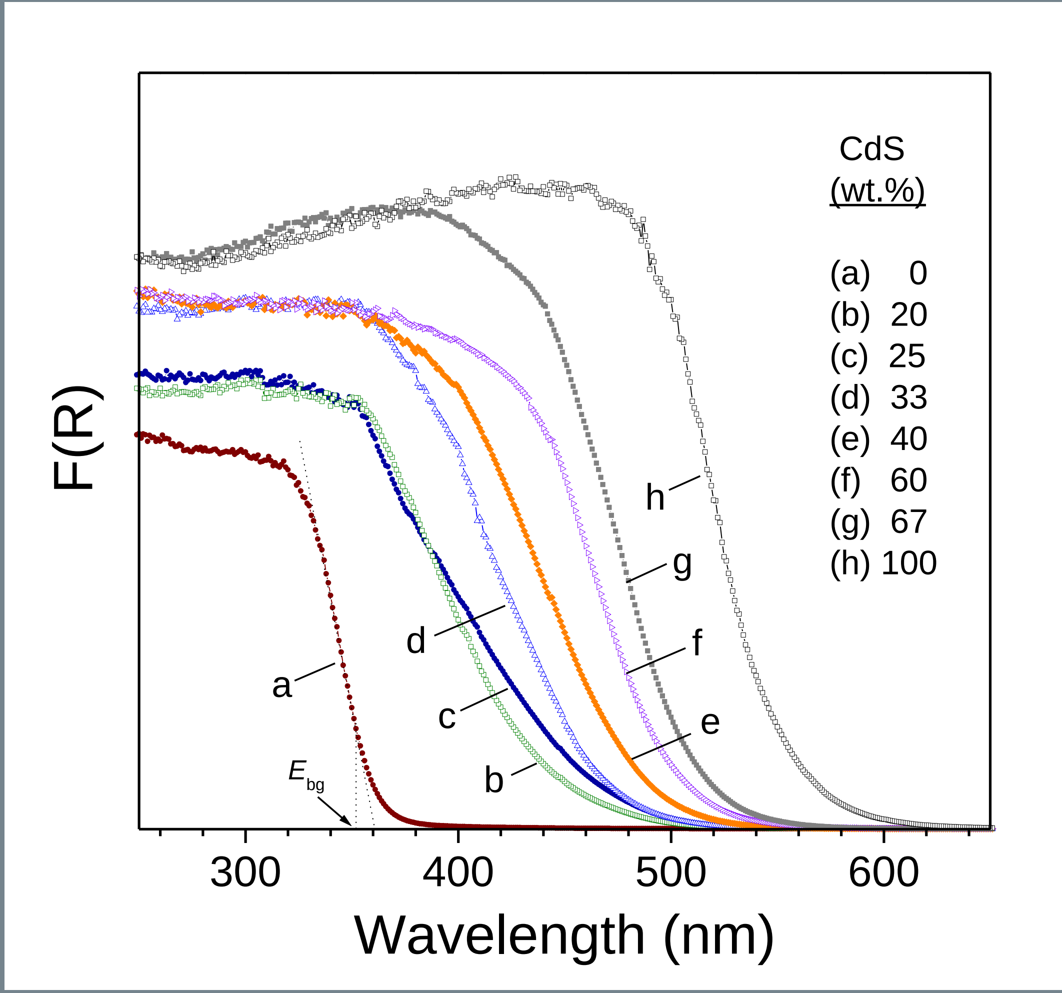


UV-vis diffuse reflectance spectra of N-doped TiO_2 photocatalysts with enhanced absorption to visible light.

Photocatalysts with tunable response to vis. light CdS-ZnS solid solutions







Appl. Catal. B 107 (2011) 188– 196

Selected Publications

- “Deluga, G.A., J.R. Salge, L.D. Schmidt, X.E. Verykios, "Renewable Hydrogen from Ethanol by Autothermal Reforming", SCIENCE, 993,303 (2004).
- Fatsikostas, A.N. and X.E. Verykios, “Reaction Network of Steam – Reforming of Ethanol over Ni-based Catalysts”, J. Catal., 225, 439 (2004).
- Patsoura, A., D.I. Kondarides, X.E. Verykios, “Photocatalytic Degradation of Organic pollutants with Simultaneous Production of Hydrogen”, Catal. Today, 124, 94 (2006).
- Basayiannis,A.C., X.E. Verykios, “Influence of the Carrier on steam reforming of Acetic Acid over Ru-based Catalysts”, Appl. Catal. B, 82, 77 (2008).
- Panagiotopoulou,P., D.I. Kondarides, X.E. Verykios, “Selective Methanation of CO over Supported Ru Catalysts”, Appl. Catal. B, 88, 470 (2009).
- P. Panagiotopoulou, X.E. Verykios “Mechanistic aspects of the Low Temperature Steam Reforming of Ethanol Over Supported Pt Catalysts”, Int. J. Hydrogen Energy, 37, 16333 (2012).

Research Projects – 1/2

- “Development and pilot plant demonstration of hydrogen production from solar energy and biomass (waste) compounds and derivatives at ambient conditions mediated by nanostructured photocatalysts”. 2008 E.ON International Research Initiative Call "Application of Nanotechnology in the Energy Business(Contract No: 2008/24_DCE-UoPatras). Budget (LHC): 376 k€. Duration: 36 months (2009-2012).
- “Development of novel Photo-Fuel Cells for the production of hydrogen and electricity via oxidation of organic compounds with the use of solar radiation” (PhotoFuelCell). Program: THALES, Ministry of Education Lifelong Learning and Religious Affairs (MIS 379320). Budget (LHC): 183 k€. Duration: 48 months (2011-2015).
- “Production of energy carriers from biomass by-products” (Glycerol2Energy). Program: THALES, Ministry of Education Lifelong Learning and Religious Affairs (MIS 379333). Budget (LHC): 153 k€. Duration: 48 months (2011-2015).

Research Projects – 2/2

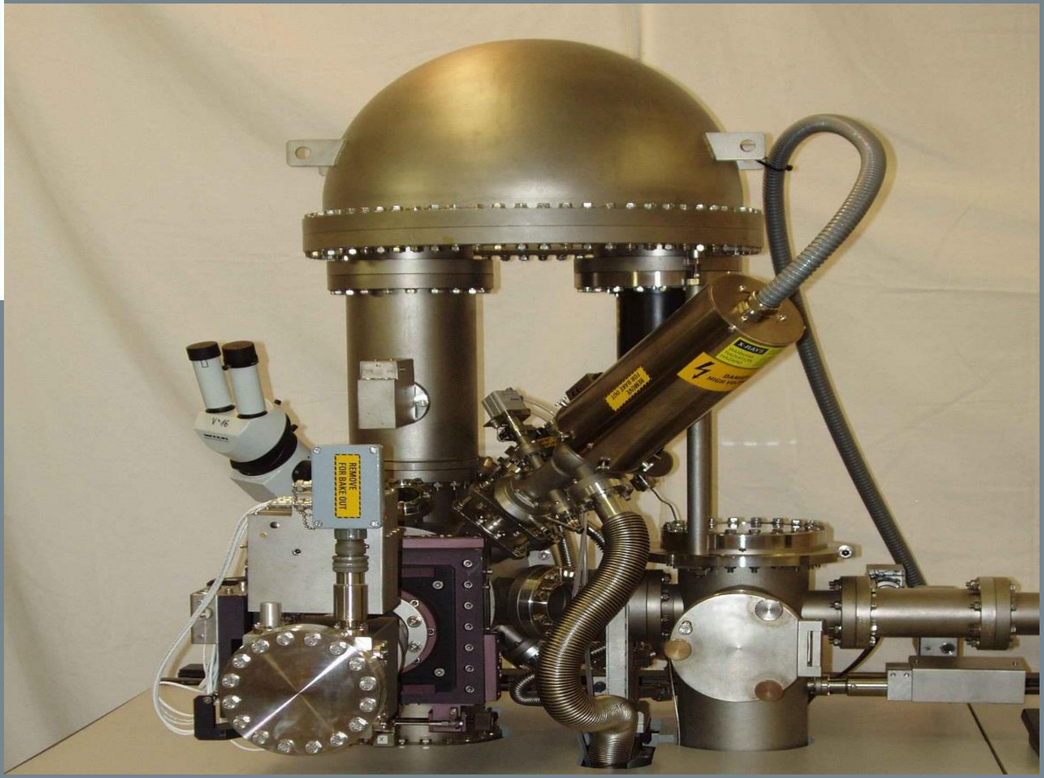
- "New catalytic processes for the production of second generation biofuels" (CAT-BIOFUEL). Program: THALES, Ministry of Education Lifelong Learning and Religious Affairs, (MIS 380405). Budget (LHC): 170 k€. Duration: 48 months (2011-2015)
- "Development of low cost PEM fuel cells based on novel low and non-Pt electrocatalysts (NonPt-PEM). Programme: Greece-China Cooperation 2012-2014» (EPAN-II) (12CHN269). Budget (LHC): 55 k€. Duration: 36 months (2012-2015),
- "Development of an innovative, energy efficient and environmentally friendly power system, operating with hydrogen and fuel cell, for standalone refrigeration applications" (HyPEMRef). Programme: Cooperation (11ΣΥΝ_7_396). Budget (LHC): 160 k€. Duration: 30 months (2012-2015).

Patents – 1/2

- V.A. Durante, A. Macris, R. Pitchai and X.E. Verykios, "Process for Catalytically Reforming a Hydrocarbon Feed in the Gasoline Boiling Range", U.S. Patent No. 5,221,464, June 22, 1993.
- C.G. Vayenas, X.E. Verykios, E. Papadakis, I. Yentekakis, C. Pliangos, "New Monolithic three-way Catalysts with Optimal Distribution of Precious Metals within three Separate Washcoat Layers", European Patent 94600002.3/28.01.94.
- Z.L. Zhang and X.E. Verykios, "A Stable and Active Nickel Catalyst for Carbon Dioxide Reforming of Methane to Synthesis Gas", European Patent 94600005.6/13.07.94.
- P. Papaefthimiou, T. Ioannides and X.E. Verykios, "Catalysts for the Combustion of Volatile Organic Compounds", Greek Patent.

Patents – 2/2

- X.E. Verykios, "A Process for the Production of Hydrogen and Electricity via Bioethanol Reforming, using Fuel Cells, with Zero Pollutants Emission", International Patent 980100180/22.5.98.
- X.E. Verykios, "Process for the production of hydrogen and electrical energy from reforming bio-ethanol", U.S. Patent No. 6, 605 376 (Aug. 12, 2003).
- D.K. Liguras and X.E. Verykios, "Highly Heat Integrated Reformer for Hydrogen Production", International Patent (2006)
- D.K. Liguras and X.E.Verykios, "Highly Heat Integrated Fuel processor for Hydrogen Production", International Patent (2006)
- X.E. Verykios, "Devise for separation and purification of hydrogen from reformate gas and method of fabrication thereof", International patent Application (2008).



Surface Science Laboratory (SSL)

Prof. S. Ladas, Prof. S. Kennou

Surface Science Laboratory (SSL)

2 Faculty members

Prof. Spyros Ladas
Prof. Stella Kennou

2 Graduate students

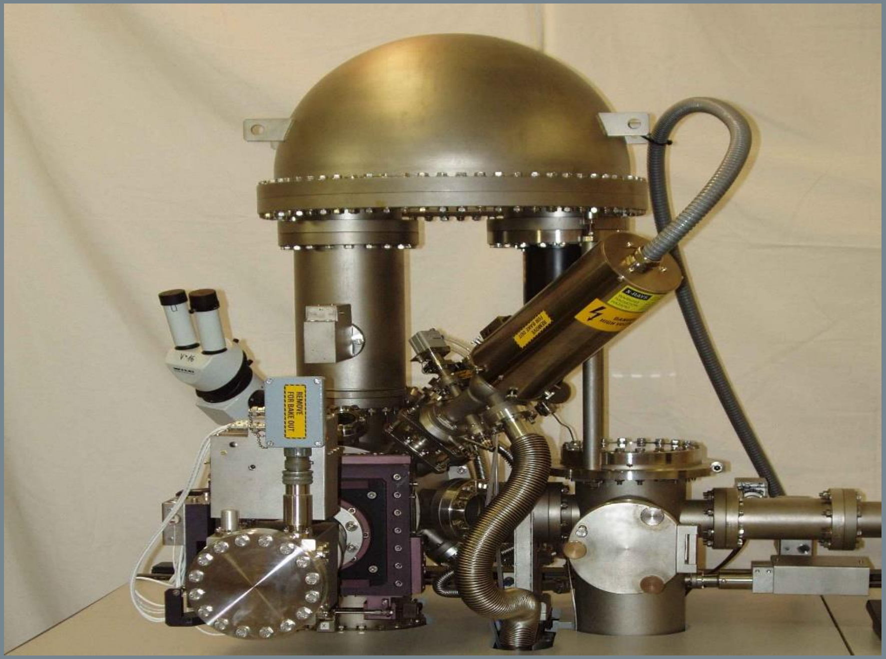
Mr Dimitris Tsikritzis
Mr. Giorgos Skoulatakis

SSL Projects and Publications are listed in the SSL Webpage:

http://athena4.chemeng.upatras.gr

and have been also included in the presentation of the research area

"Surfaces Interfaces and Thin Films"

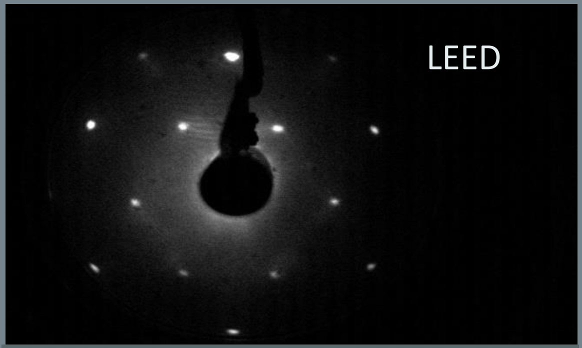


LH/SPECS MAX200 system

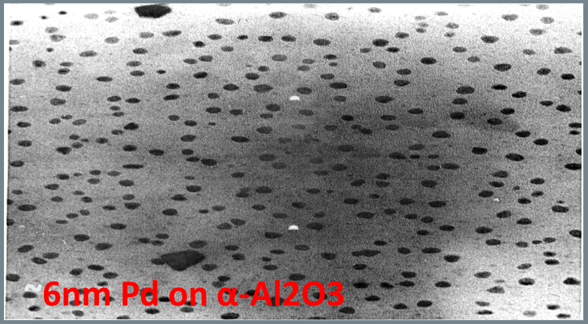
A fully automated Electron/Ion Spectrometer (currently fitted for XPS, ISS) for Surface

Analysis of specimens supplied by collaborating groups in Catalysis and other research areas both within and outside the Department

SSL Research Activities Related to Catalysis



(√3x√3)R30° Sn/Ni(111) alloy

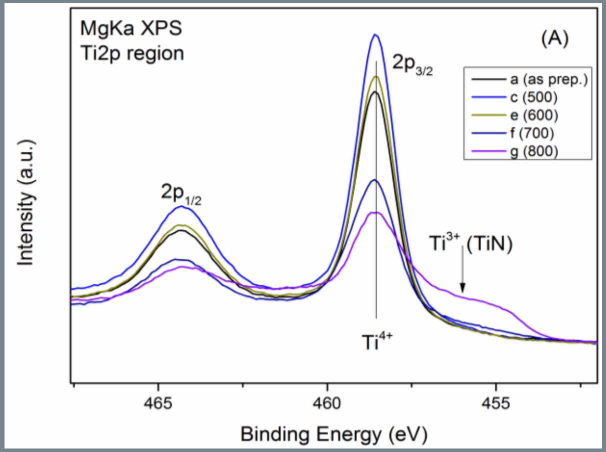


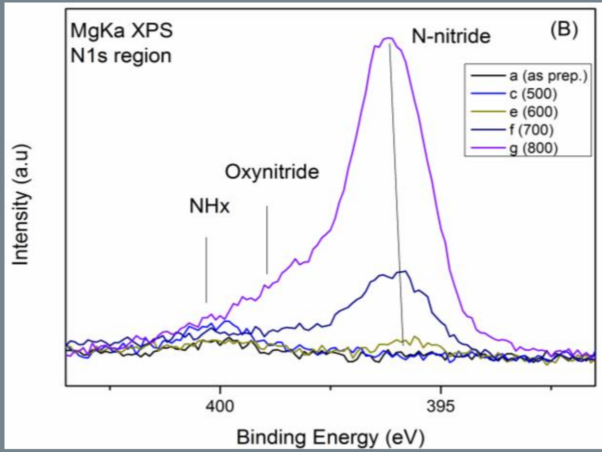
Surface Science aspects of Heterogeneous Catalysis :

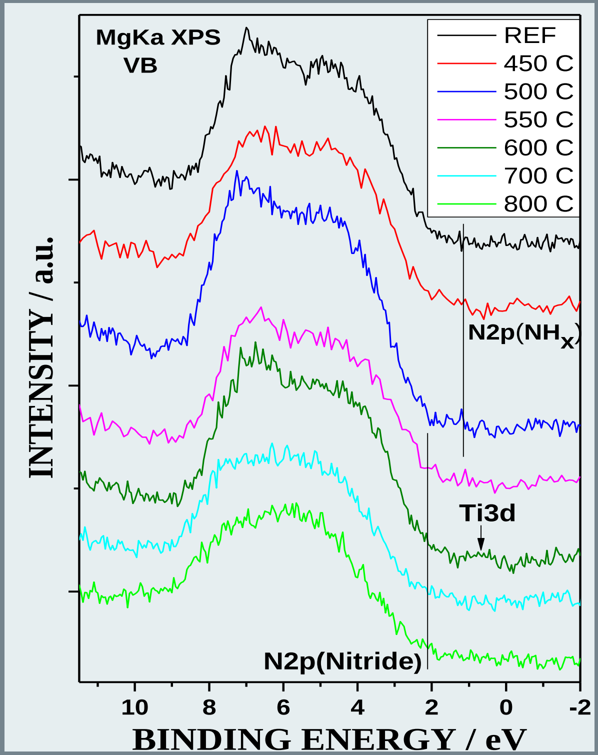
- ❖Experiments on single-crystal model catalysts
- ❖Study of realistic model catalysts

Ex-situ Spectroscopic Catalytic Materials Characterization for collaborating research groups:

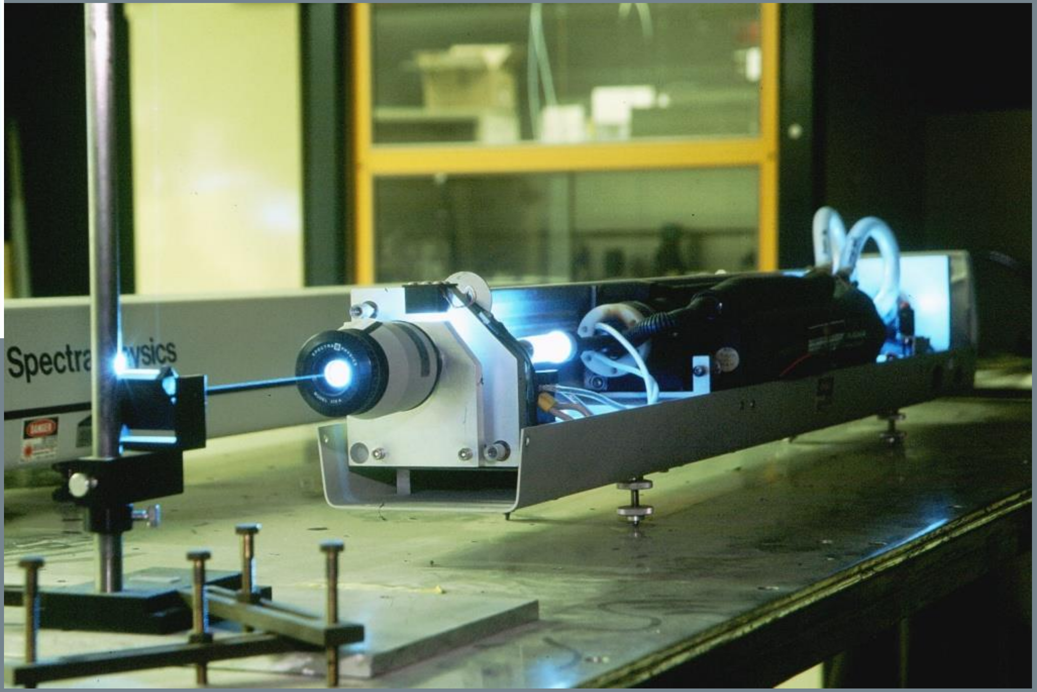
Characterization of N-doped TiO_2 Photocatalysts







Core-level and Valence Band XPS reveals partial nitridation of TiO_2



Laboratory of Physical Chemistry and Molecular Spectroscopy

Prof. Soghomon Boghosian

Researchers

1 Faculty member

Prof. Soghomon Boghosian

1 Researcher

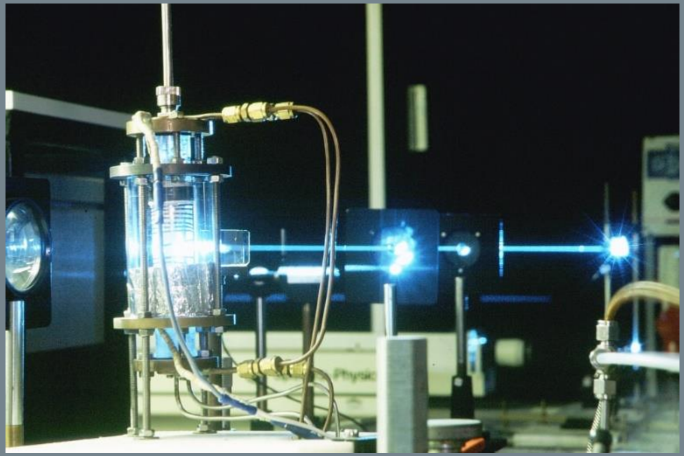
Dr. Angelos Kalampounias

1 Graduate student

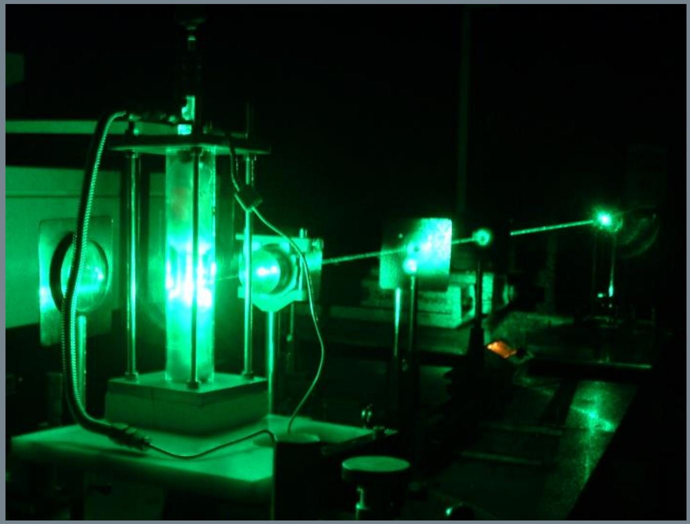
Mr. Antonis Tribalis

Research activities

The molecular structure and vibrational properties of supported metal oxide and mixed metal oxide catalyst systems are studied by in situ Raman spectroscopy combined with $^{18}O/^{16}O$ isotopic labeling and/or in situ FTIR.



The in situ optical Raman cell

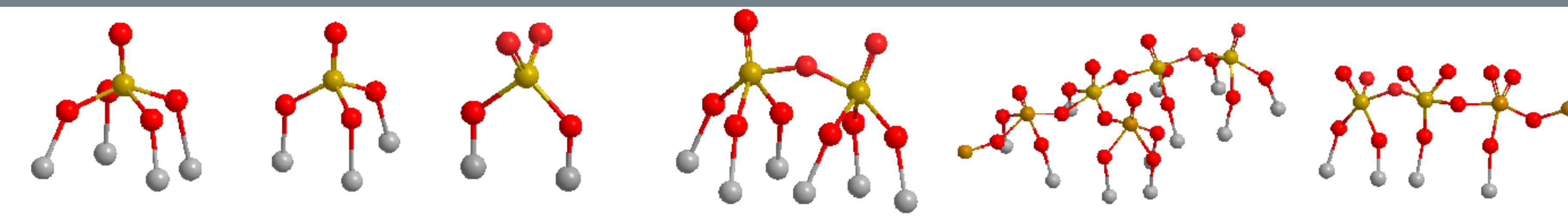


The operando optical Raman cell

Raman Spectroscopy of Catalysts under Operating Conditions

Particular goals pertain to:

- Determine the speciation and molecular structure of deposited oxometallic species (active components: V_2O_5, MoO_3, WO_3 etc. on oxide carriers: ZrO_2, TiO_2, Al_2O_3, SiO_2 etc)
- Monitor the temperature-dependent evolution of structural configurations for the deposited metal oxide species (active components: V_2O_5, MoO_3, WO_3 etc on TiO_2)

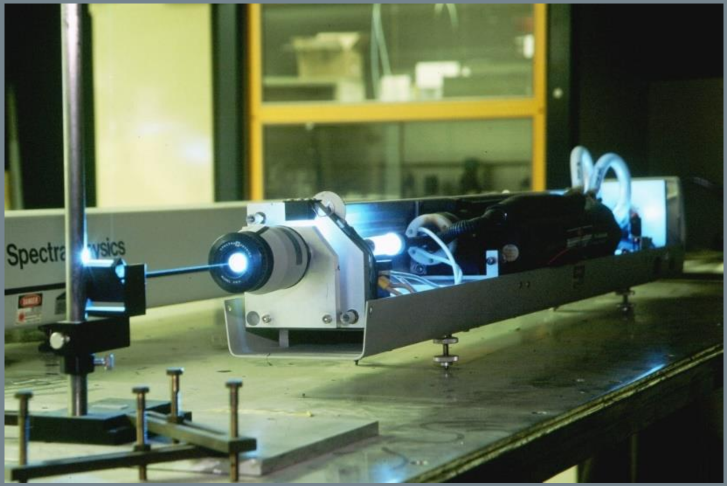


mono-oxo, monomer $CN_{Me} = 5$	mono-oxo, monomer $CN_{Me} = 4$	di-oxo, monomer $CN_{Me} = 4$	mono-oxo, dimer $CN_{Me} = 5$	mono-oxo, 2D polymer $CN_{Me} = 5$	di-oxo, polymer $CN_{Me} = 5$

Raman Spectroscopy of Catalysts under Operating Conditions

Particular goals pertain to:

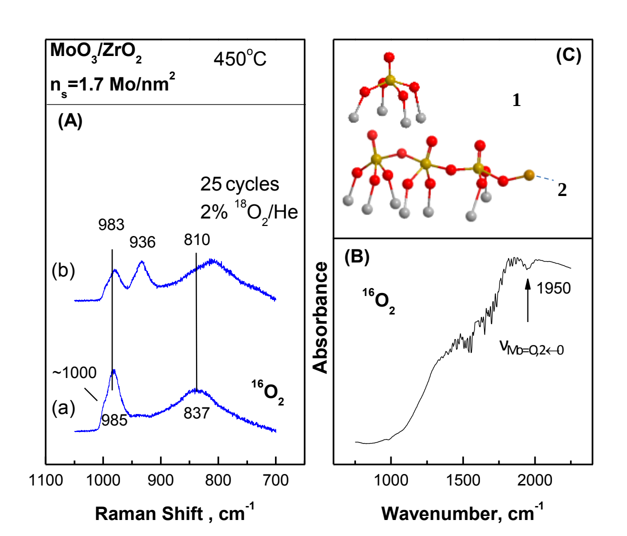
- Understanding/deriving structure-function relationships for catalytic materials at the molecular level
- Characterize the molecular structure, the defects and the crystallinity in ceria- and zirconia- based mixed metal oxide materials

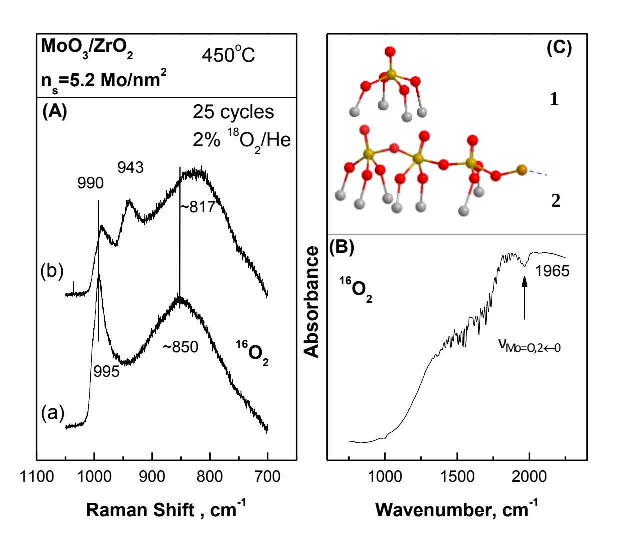


Molecular structure of supported molybdenum oxide catalyst materials

Strategy: In situ Raman combined with $^{18}O/^{16}O$ isotope exchange and in situ FTIR

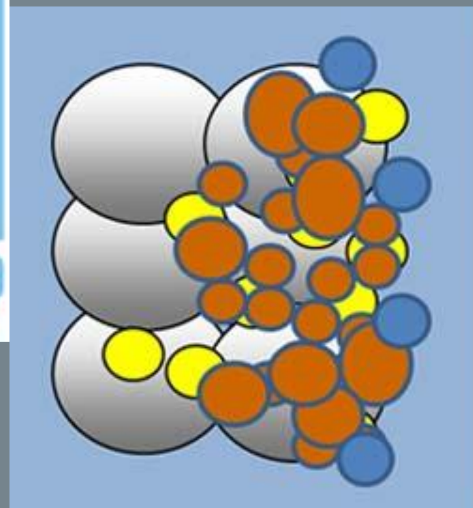
- The critical issue of differentiating between mono-oxo (Mo=O) and di-oxo $[Mo(=O)_2]$ configurations is addressed
- molecular structures for the oxo-molybdenum $[(MoO_x)_n]$ sites (including aspects related to coordination number of Mo and extent of polymerization) deposited on typical supports such as Al_2O_3, ZrO_2 and TiO_2 are unraveled

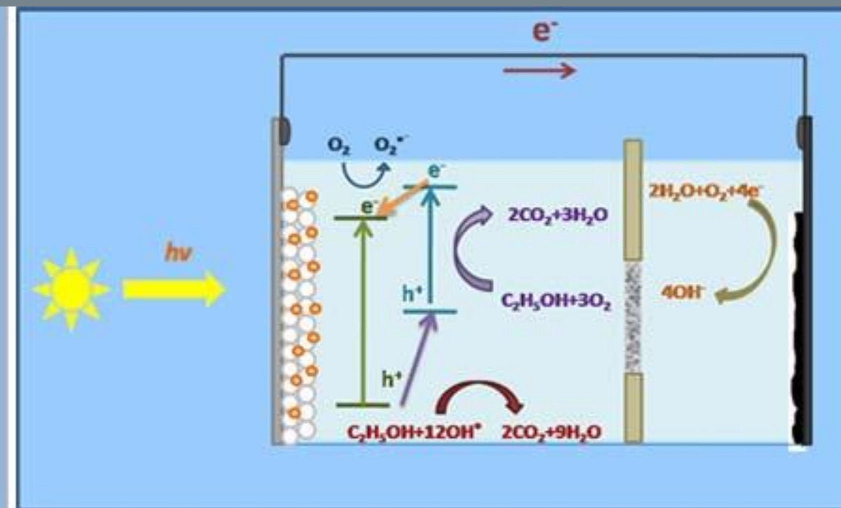




Representative Publications

- *In situ* Raman and FTIR spectroscopy of molybdenum(VI) oxide supported on titania combined with $^{18}O/^{16}O$ exchange: molecular structure, vibrational properties and vibrational isotope effects. G. Tsilomelekis, S. Boghosian, *J. Phys. Chem. C*, 2011, **115**, 2146-2155.
- An operando Raman study of molecular structure and reactivity of molybdenum(VI) oxide supported on anatase for the oxidative dehydrogenation of ethane. G. Tsilomelekis, S. Boghosian, *PCCP*, 2012, **14**, 2216.
- On the configuration of MoO_x sites on alumina, zirconia, titania and silica. Vibrational properties, molecular structure and vibrational isotope effects. G. Tsilomelekis, S. Boghosian, *Catal. Sci. Technol.*, 2013, **3**, 1869 – 1888.
- Interfacial impregnation chemistry in the synthesis of molybdenum catalysts supported on titania G.D. Panagiotou, Th. Petsi, K. Bourikas, A.G. Kalampounias, S. Boghosian, Ch. Kordulis, A. Lycourghiotis, *J. Phys. Chem. C*, 2010, **114**, 11868.
- Molecular structure and activity of molybdena catalysts supported on zirconia for ethane oxidative 4Bdehydrogenation studied by operando Raman spectroscopy. A. Christodoulakis and S. Boghosian, *J. Catal.*, 2008, **260**, 178-187.





Applied Photophysics & Photochemistry Laboratory (APPLA)

Prof. P. Lianos

Researchers

1 Faculty member

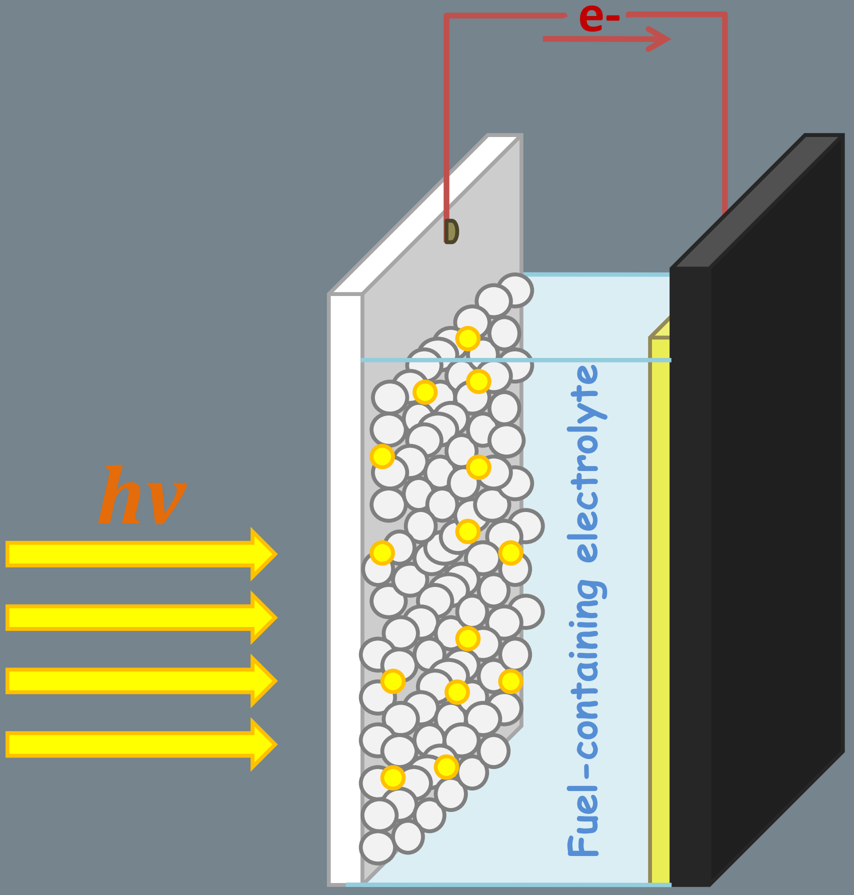
Prof. Panagiotis Lianos

1 Post doctoral fellow

Dr. Maria Antoniadou

3 Graduate students

Ms. Stavroula Sfaelou
Mr. Iosif Tantis
Ms. Archontoula Nikolakopoulou



Research Activities

- **Colloids and Surfaces**: Structure and dynamics of micelles, microemulsions and lipid vesicles. Self-organization of surfactants and lipids in solution and in thin films. Interaction of proteins with lipid bilayers. Growth of organic or inorganic particles in organized molecular assemblies. Water-soluble polymers. Hydrogels-Cross-linked hydrophilic polymers.

- **Photophysics**: Photophysical studies of aromatic molecules, semiconductors and conjugated polymers. Fluorescence probing of organized molecular assemblies, gels and macromolecules. Light emission and amplification. Lasers. Organic LEDs. Solar Cells.

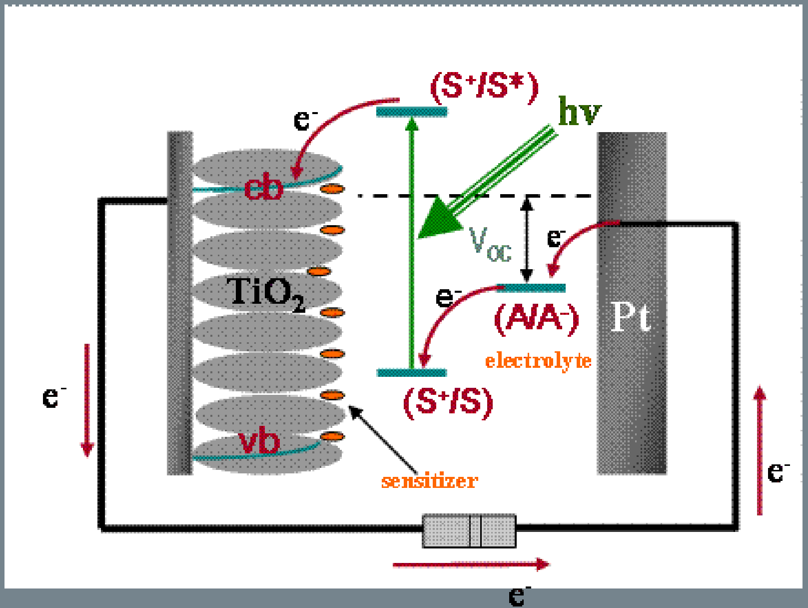
- **Materials and Devices**: Sol-gel chemistry. Semiconductor nanoparticles. Heterogeneous photocatalysis for water and air purification. Organic and Hybrid Organic-Inorganic Mesoscopic Solar Cells. Organic light-emitting diodes. New materials for light emission and amplification. Water purification materials. Photocatalytic hydrogen production. Photoelectro-catalytic hydrogen and electricity production.

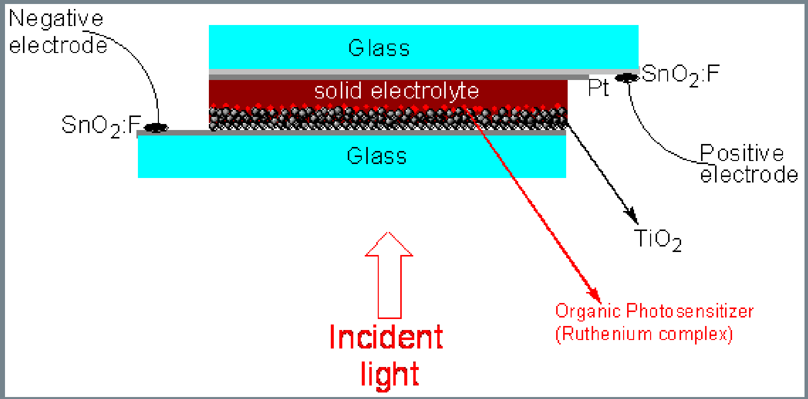
Quasi-solid state Dye-sensitized Solar Cells

- Development of quasi-solid state DSSCs where the liquid electrolyte is substituted by a gel, comprising functional redox species.

- A nanocomposite organic-inorganic gel synthesized by the sol-gel method, was used to construct efficient cells, which do not necessitate sealing and thus decrease fabrication cost.

- The above technology was the basis ***for setting up of the spin-off Brite Hellas***.



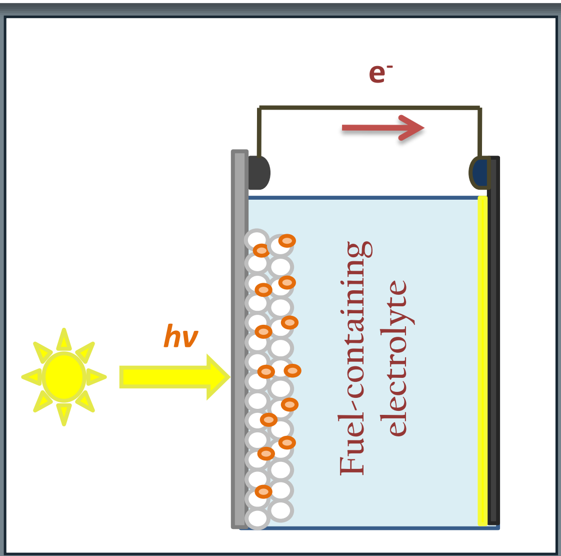


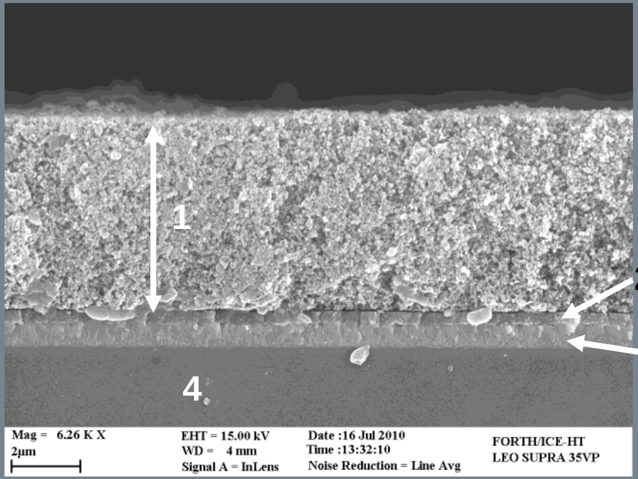
Heterogeneous photocatalysis using oxide semiconductors

- Nanoparticulate titania, in pure or doped form was used as photocatalyst for photodegradation of water-borne organic pollutants.

- Research was mainly focused on the synthesis of high quality pure or doped titania nanostructured thin films.

- The related data gave a lot of information, which is also useful for the amelioration of solar cells through optimized oxide semiconductor nanostructures.

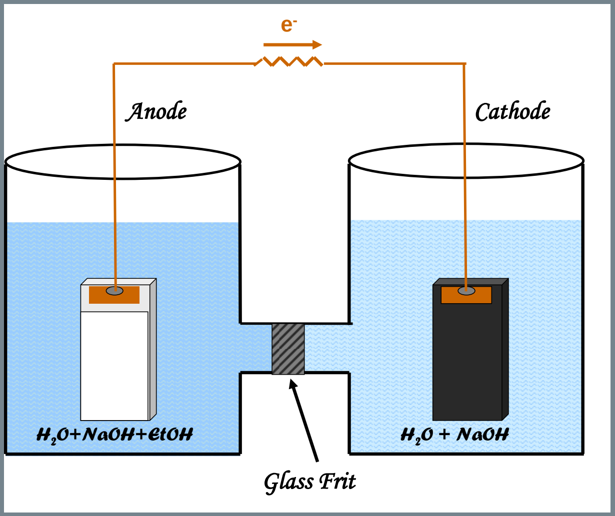


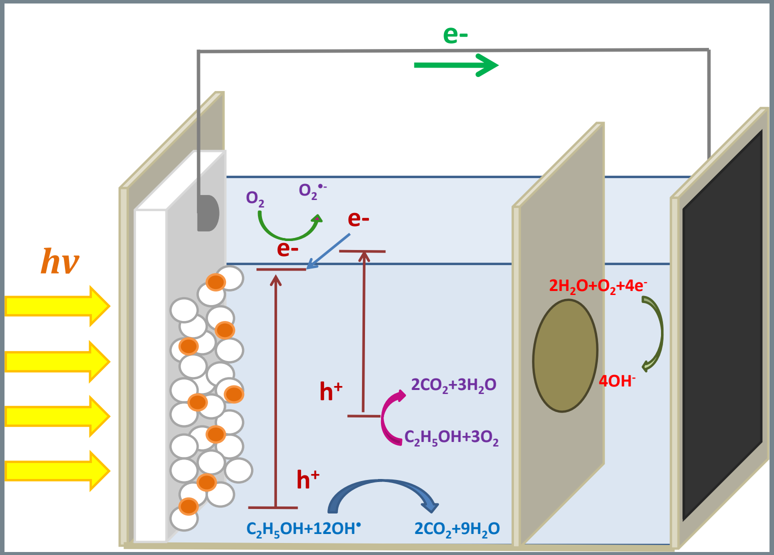


FE-SEM image of a TiO_2 film

Photocatalytic and photoelectrocatalytic hydrogen and electricity generation

- The photodegradation of organic wastes, for example, those produced by the biomass-processing industry, can be used to generate H_2 and/or electricity in the presence of photocatalysts and under solar irradiation.





- Photoreforming and the construction of photoactivated fuel cells has been recently studied.

- Many ideas applicable to photo-fuel-cells have proven themselves valuable for optimizing DSSCs.

Research Projects – 1/2

- “Study of the Photoelectrochemical production of hydrogen and electricity by using hybrid organic-inorganic structure”, ERAKLEITOS, 2010-2013, 45000 €.
- “Innovative materials for nanostructured solar cells”. THALES, 2012-2015, 60000 €.
- “Solar-powered photoactivated fuel cells producing electricity by photocatalytically consuming water wastes”. ARISTEIA 2012-2015
- “Efficient wastewater treatment with nanocrystalline transition metal oxides modified with noble metals and non-metals”. GR-RO R&T cooperation, 2012-2014, 15000 €.
- “Graphene and nanocomposite materials. Production, properties and applications”. Participant, THALES, 2012-2015, 600000€

Research Projects – 2/2

- "Development of innovative photofuel cells for the production of electricity and hydrogen by consumption of wastes using solar radiation", THALES, 2012-2015, 600000 €
- "Energy autonomous smart greenhouse", SYNERGASIA 2013-2015 130 000 € (2.5 M€ total budget).
- "Innovative materials for solar cell design and demonstration", GR-DE cooperation program", 2013-2015 , 250000 €.
- "Development and pilot plant demonstration of hydrogen production from solar energy and biomass (waste) compounds and derivatives at ambient conditions mediated by nanostructured photocatalysts". (E.ON International Research Initiative 2009-2013) 400000 €.

Patents

- “Photoelectrochemical solid-state cell used for the photovoltaic conversion of solar energy” P.Lianos, Elias Stathatos, B.Orel, U.Lavrencic-Stangar, N.Groselj, Greece, No. 1003816, International Classification: H01G 9/20
- “Solar photoelectrochemical cell made of composite organic/inorganic nanostructured materials”, P. Lianos and E. Stathatos, Greece, No.1004545, International Classification: C01G 23/053
- “Photoelectrochemical solar cell made from nanocomposite organic-inorganic materials”, Applicants: P.Lianos and E.Stathatos, PCT/GR2004/000023/16.4.2004

Catalytic and Electrochemical Processes Statistics (2007-2013)

Number of papers:	>250
Citations:	~15000
Chapters in books:	15
Books:	2
No of research projects:	27
Budget	4.4 M€
Patents:	9