UNIVERSITY OF THESSALY
SCHOOL OF ENGINEERING

DEPARTMENT OF
MECHANICAL ENGINEERING

ИНСТИТУТ ВЫСОКОТЕМПЕРАТУРНОЙ ЭЛЕКТРОХИМИИ
Уральского Отделения Российской Академии Наук

Direct Ethanol Fuel cells

By Panagiotis Tsiakaras

Yekaterinburg, April 2014

OUTLINE OF THE PRESENTATION

Research Activity of the

Laboratory of Alternative Energy Conversion Systems

Electrochemical Cells based on Solid Electrolytes

Passive and Active Operation of the electrochemical cells

Passive Operation – Fuel cells

Fuels for Fuel Cells

Green Energy- Biofuels

Motivation of direct ethanol fuel cells

Direct Ethanol Proton Exchange Membranes Fuel Cells (DE-PEMFC)

Direct Ethanol Fuel: Proton Exchange Membranes vs Anion Exchange Membranes

Direct Ethanol versus Hydrogen PEM fuel Cells

Conclusions

Laboratory of Alternative Energy Conversion Systems

RESEARCH ACTIVITIES

- **Fuel Cells (PEMFC & SOFC) Direct Hydrogen or**

  Direct Alcohol Fuel Cells

- **Preparation, Characterization and testing of Low Pt and Pt-free electrocatalysts**

- **Electrochemical promotion**

  With IHTE - YKT

- **Ionic – Mixed Co-ionic conductors**

  Solid Oxide Electrolyzers & Sensors

  With IHTE-YKT

- **Catalysis and Kinetics of Difficult Reactions (i.e. Aqueous Phase Reforming)**

Mathematical Modeling

- **Second Law Analysis, Exergy analysis of a FC based electricity generating systems**

- **Mass transport of ethanol, water, oxygen in PEM fuel cell components (diffusion layers, catalyst layers & Proton Exchange Membrane)**

- **Simulation and prediction of a FC operation (V-I, P-I).**

ИВТЭ ИНСТИТУТ ВЫСОКОТЕМПЕРАТУРНОЙ ЭЛЕКТРОХИМИИ
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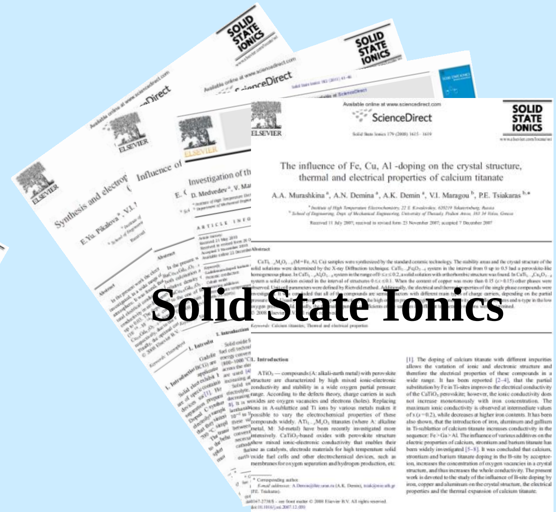
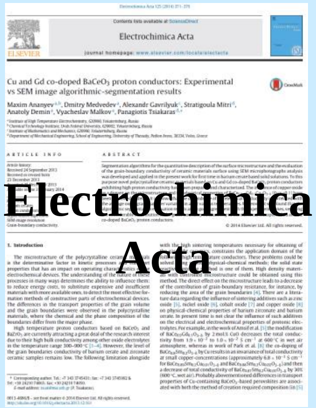
Collaboration Since 2000*
more than 30 common publications & 3 common projects


Journal of Power Sources


Solid State Ionics


International Journal of Hydrogen Energy


Electrochimica Acta

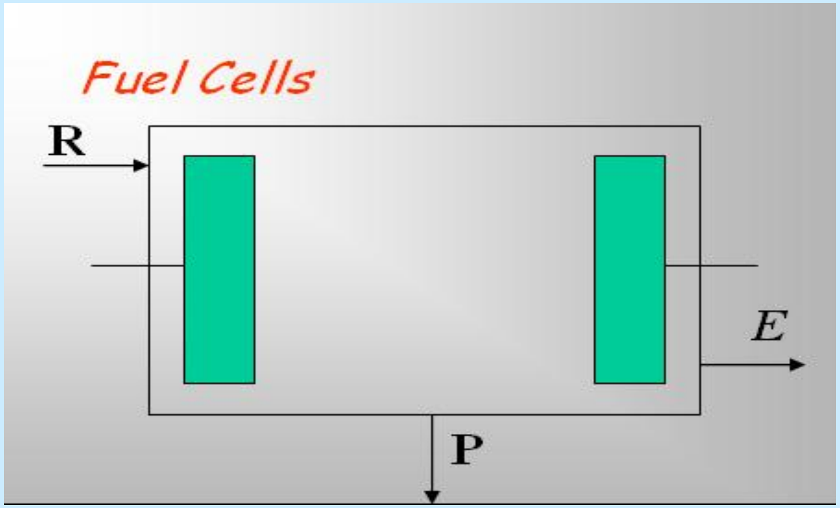

Progress in Materials Science

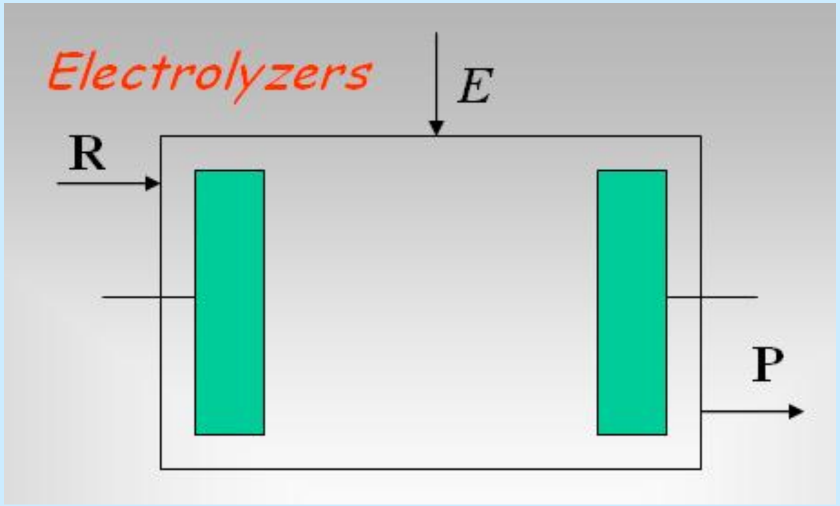
Current Project funded from the Russia Federation:
Development of solid oxide electrochemical cells with supported and thin layer proton electrolytes for electrochemical devices
(№ 14.Z50.31.0001)

***Last five years common publications**

Two of the main Applications of the Solid Electrolytes

Electrochemical Cell Passive Operation (Galvani mode)	Electrochemical Cell Active Operation (Volta mode)

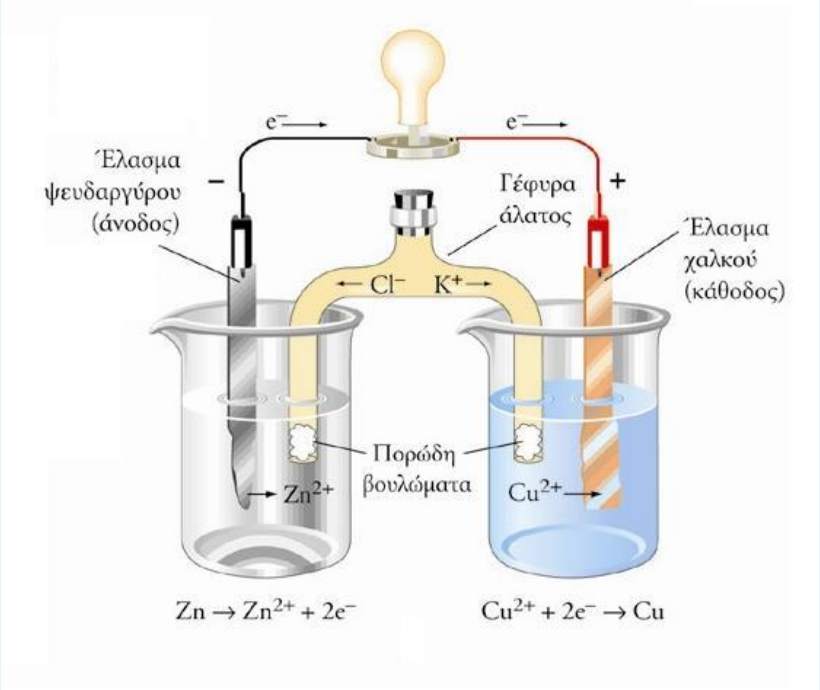




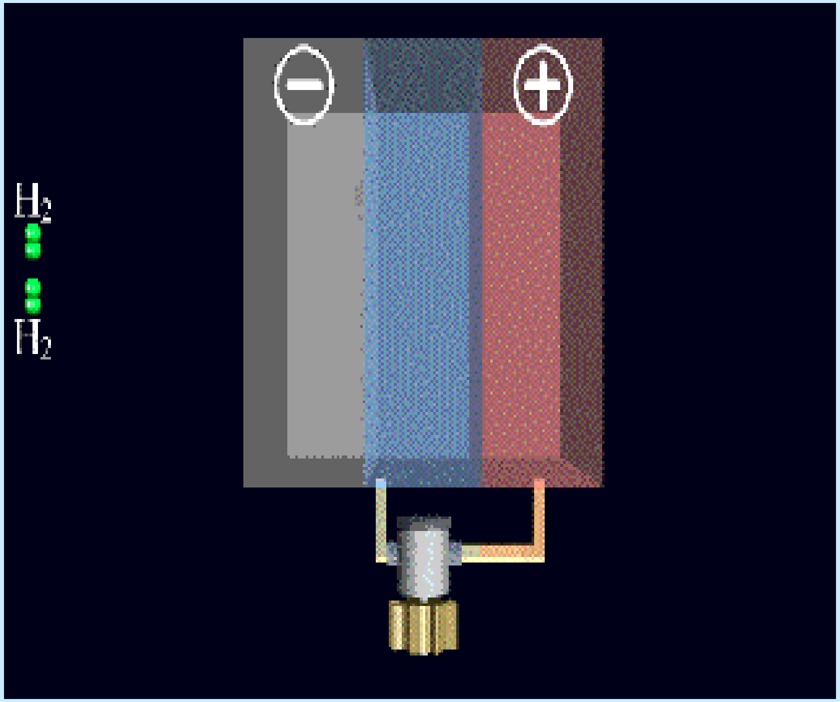
PASSIVE OPERATION
OF AN ELECTROCHEMICAL CELL

Fuel Cells

Galvani Cells



Fuel Cells



FUEL CELLS AND FUEL OPTIONS

Fuel Cells have the advantage **of being fed with a variety of fuels**.
Among the others, the most commonly used are the following:

H_2 and Hydrocarbons

Hydrogen is the optimum choice for use at fuel cells. Maximum power density values are obtained when the hydrogen is fed at these electrochemical devices. However, it is not found free at nature and there are still many problems concerning its storage and distribution. Light hydrocarbons can be also used in SOFCs.

Alcohols

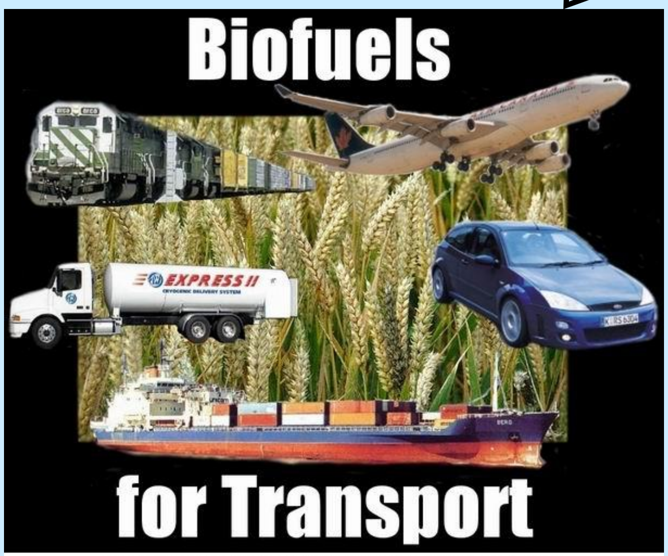
Alcohols have been studied intensively over the last 10 years due to their flexibility for use in a Fuel Cell operating at low temperature. Especially, the use of ethanol in fuel cells is of great importance because of its advantages.

P Tsiakaras, A Demin, Journal of Power Sources 102 (1), 210-217
S Douvartzides, F Coutelieris, A Demin, P Tsiakaras, International Journal of Hydrogen Energy 29 (4), 375-379

Green Energy- Biofuels - Fuel Cells - Applications

USE OF BIOFUELS

Direct use or as a mixture with the conventional fuels (i.e. gasoline) Biodiesel



www.esru.strath.ac.uk/EandE/Web_sites/02-03/biofuels/front.jpg

Reforming for H_2 production

H_2

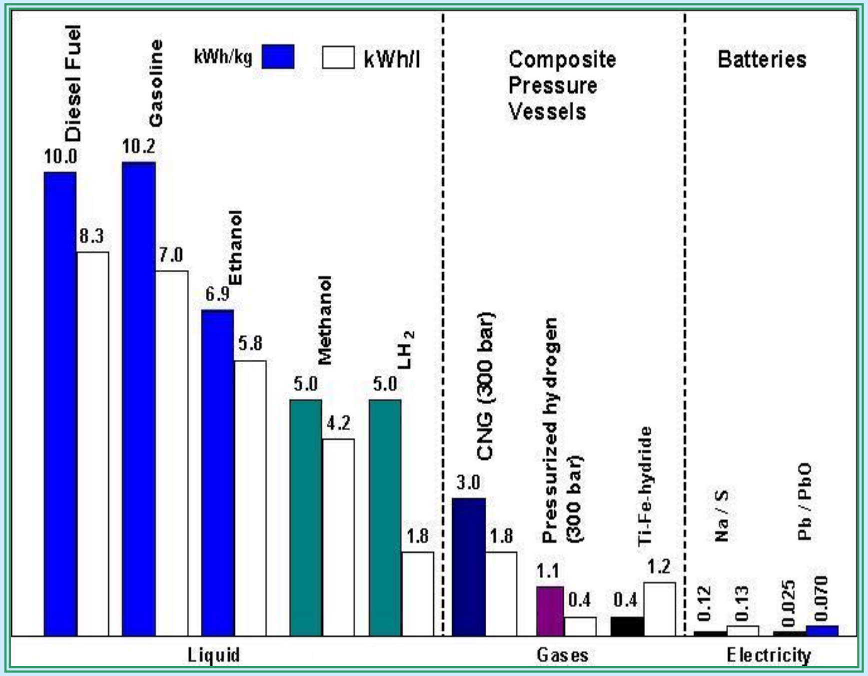
Fuel Cells

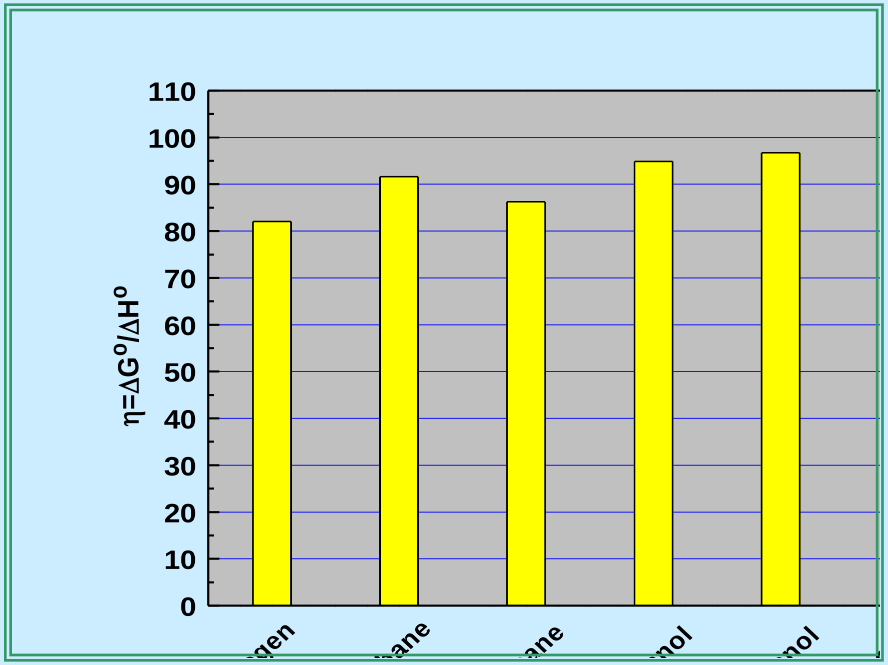
mobile applications

stationary applications

portable applications

Motivation for Direct Ethanol Fuel Cells





- There is no free Hydrogen in the nature.
- As yet, there is no widespread infrastructure for the distribution and storage of hydrogen.
- Ethanol is connected with a higher thermodynamic conversion efficiency **η** as compared to hydrogen.
- The energy density of ethanol is higher to the one of hydrogen.
- Less toxic than methanol.

Further benefits of Ethanol

Available as a renewable fuel from biomass.

Domestic ethanol production reduces demand for imported oil.

Benefit farm communities who produce Biomass feedstock.

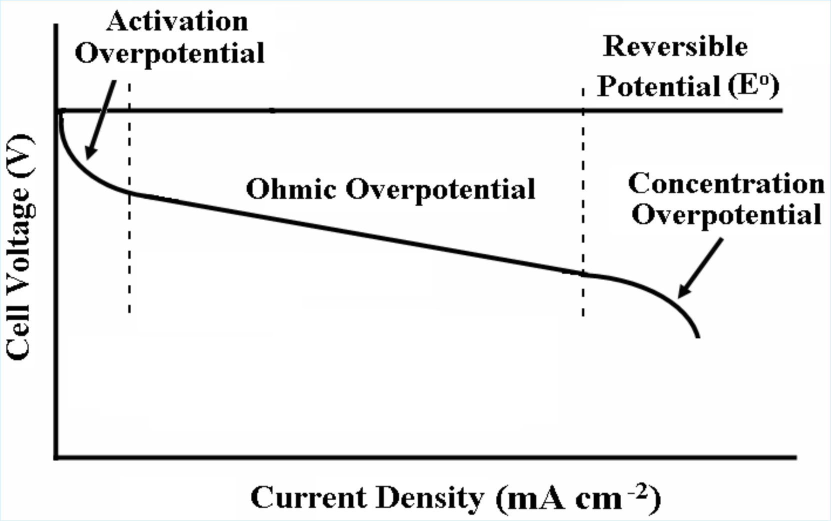
Reduces air pollution.

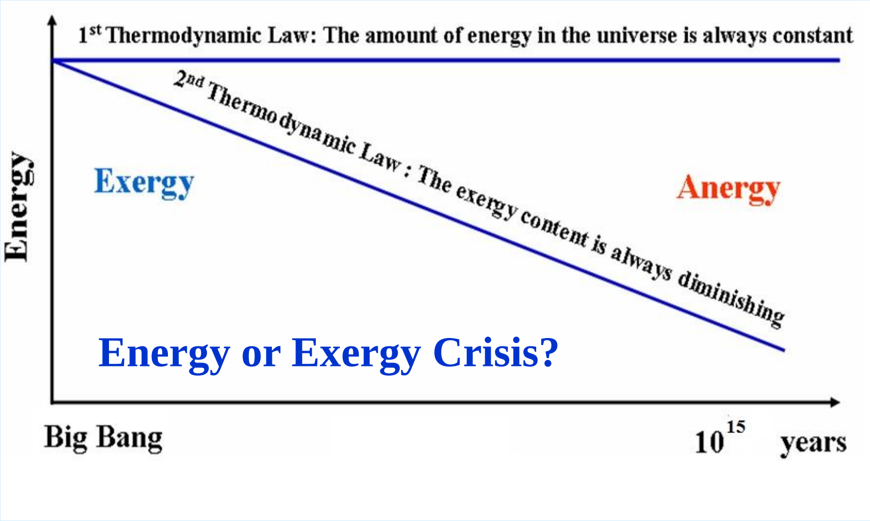
The Ethanol industry will be responsible for new jobs.

WHICH IS THE MEANING OF THE CHARACTERISTING CURVES OF A FUEL CELL OPERATION (V-I)

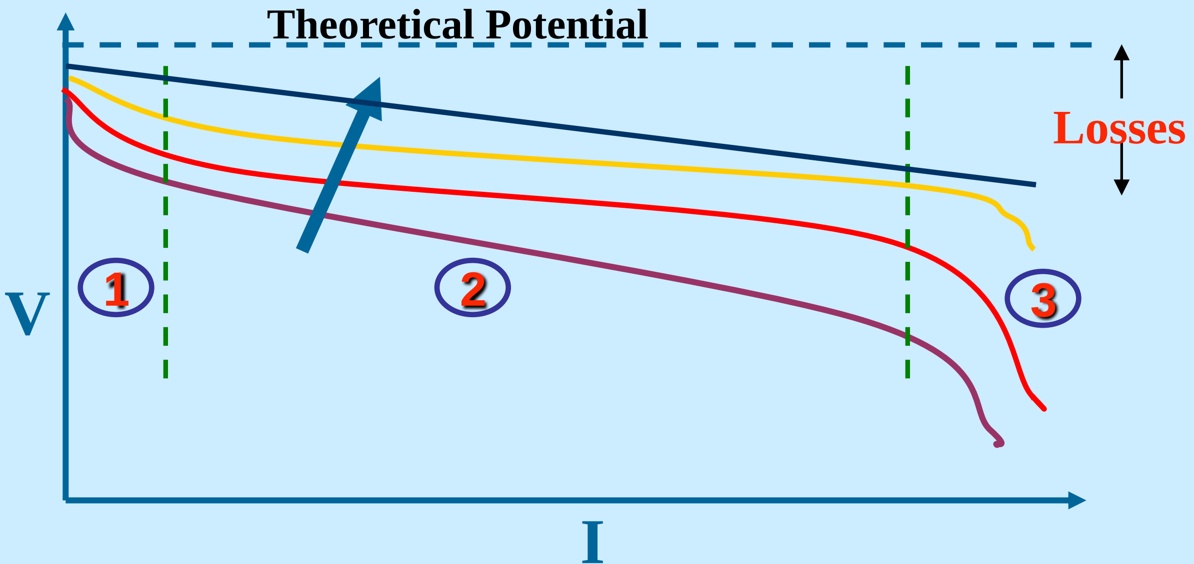
Energy = Exergy + Anergy

$\Delta H = \Delta G + T\Delta S$ GIBBS

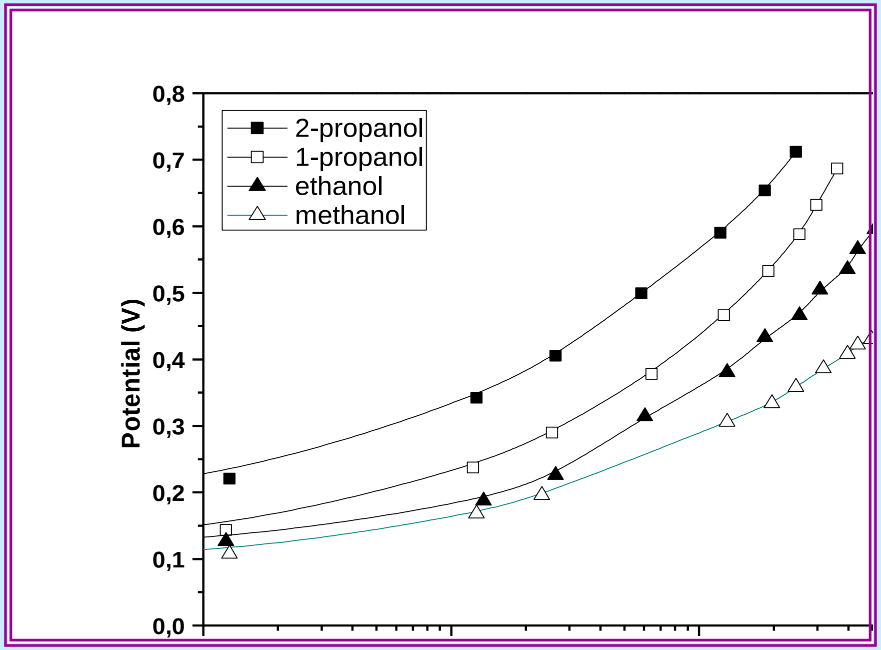




Our Research is oriented towards electrocatalyst optimization…

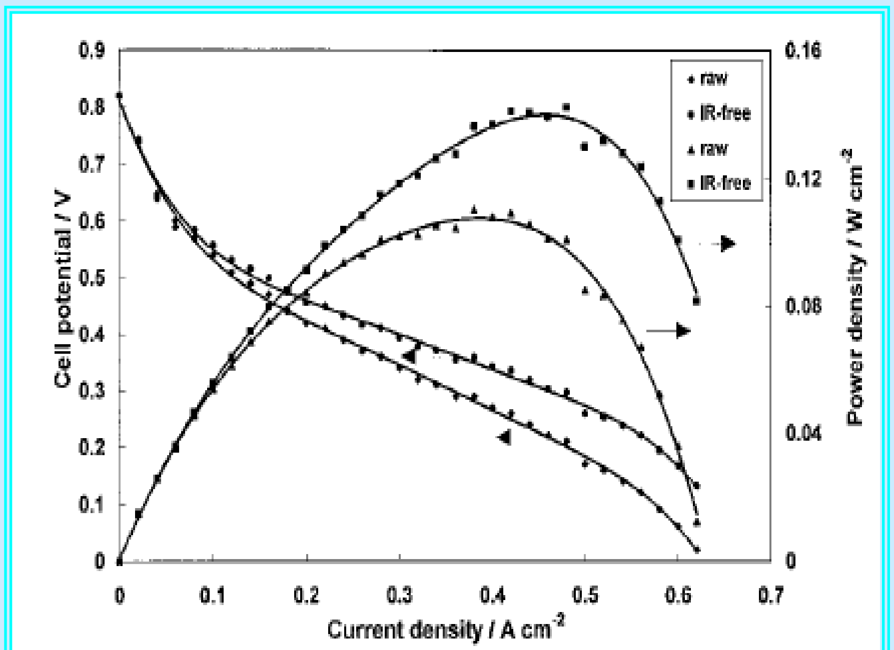


First attempts of Direct Ethanol Fuel Cells



1995: Wang and his coworkers compared the performance of fuel cells employing an H_3PO_4-doped polybenzimedazole membrane and **PtRu** (2.6 mg_{Pt} cm^{-2}) **as anode catalyst** operating on various methanol-alternative fuels.
Cathode: Pt/C (4 mg_{Pt} cm^{-2}), 1 atm.

J. Wang, S. Wasmus, R. F. Savinell, *J. of Electrochem. Soc.* 142 (12) (1995) 4218-4224.



1998: Arico, Antonucci and their coworkers:
Raw and iR-free polarization and power density data for the direct ethanol fuel cell at 145 C; anode 1 M C_2H_5OH, 4.0 atm (abs); cathode 5.5 atm (abs) O_2. **Anode Pt-Ru (1:1)/C, 2 mg_{Pt} cm^{-2}; Cathode Pt/C, 2 mg_{Pt} cm^{-2}.**

A. S. Aricò, P. Cretì, P. L. Antonucci, V. Antonucci, Electrochemical and Solid-State Letters, 1 (2) (1998) 66-68.

Anodes and Cathodes for Direct Ethanol PEM-Fuel Cells

Pt-based Electrocatalysts	Non-Pt Electrocatalysts
Pt-M Pt-M1-M2 Low Pt	Pd/C, Carbon nanotubes, Ti Ir Ir-Sn

ANODE $C_2H_5OH + 3\ H_2O \rightarrow 12\ H^+ + 12\ e^- + 2\ CO_2$

CATHODE $3\ O_2 + 12\ H^+ + 12\ e^- \rightarrow 6\ H_2O$

OVERALL $C_2H_5OH + 3\ O_2 \rightarrow 3\ H_2O + 2\ CO_2$

$$CH_3CH_2OH \xrightarrow{-2e} CH_3CHO \xrightarrow{-2e} CH_3COOH \xrightarrow{-8e} CO_2 + H_2O$$

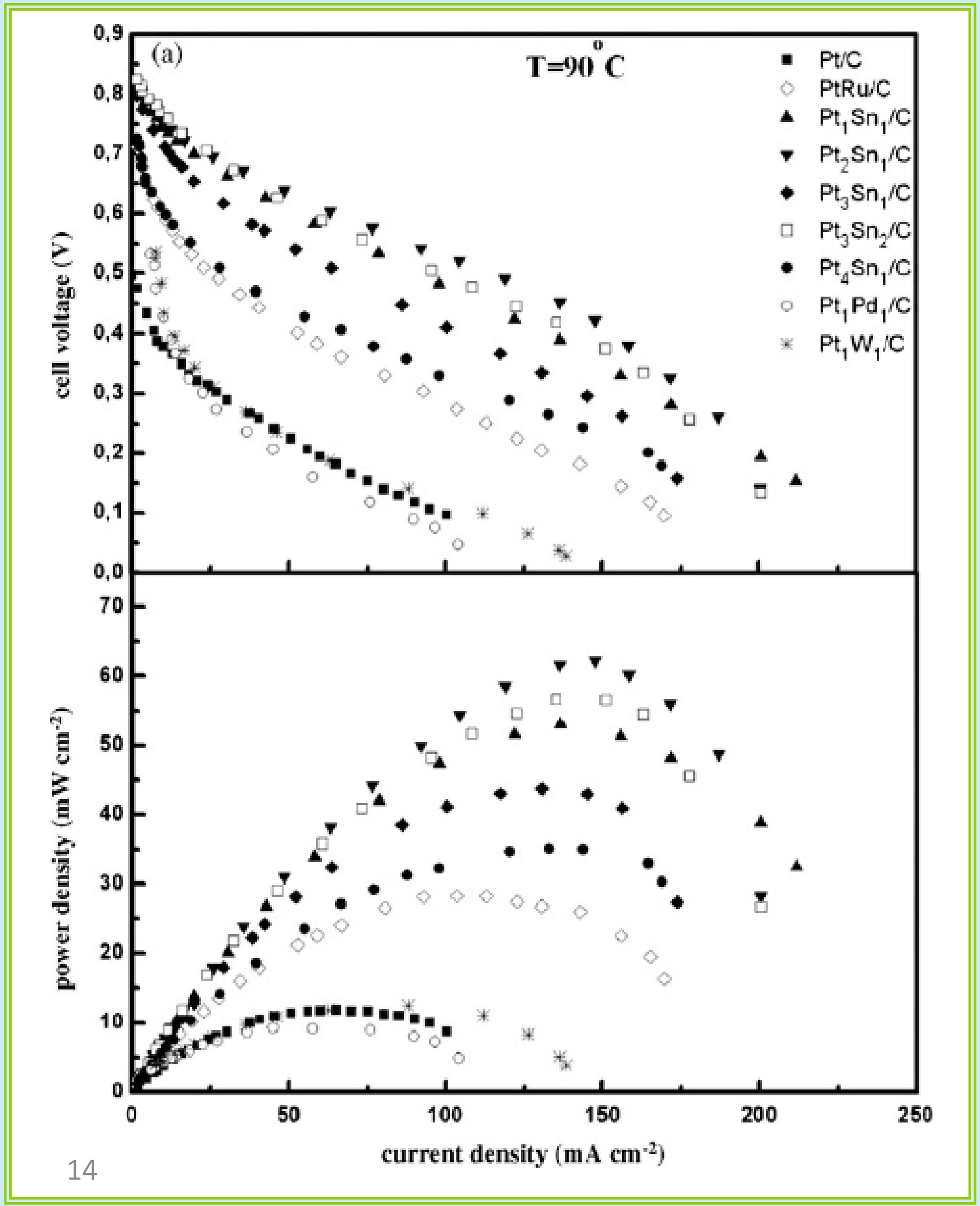
The best catalyst will permit the complete electro-oxidation of ethanol to $CO_2 + H_2O$ offering 12 electrons!

However………

Direct Ethanol PEM-Fuel Cells Performance on Binary Catalysts

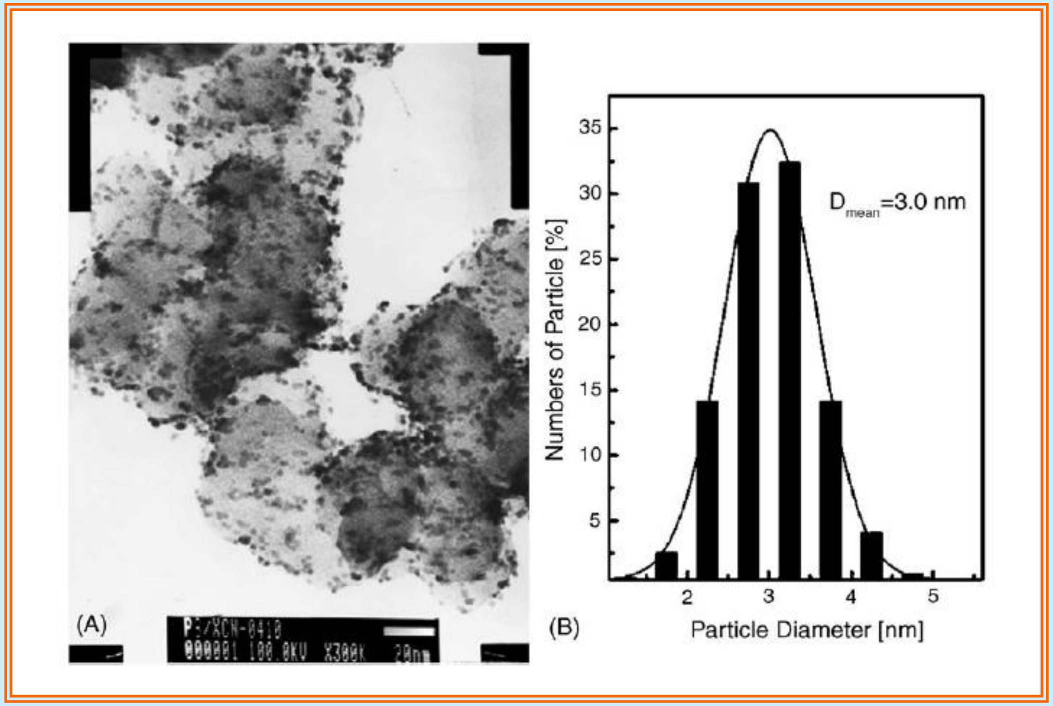
Direct ethanol fuel cell operation over different bimetallic anode catalysts at 90◦C.

Ethanol aqueous solution was 1.0 mol L^{-1} and its flow rate was 1.0 ml min^{-1}, **cathode catalyst was Pt/C**.

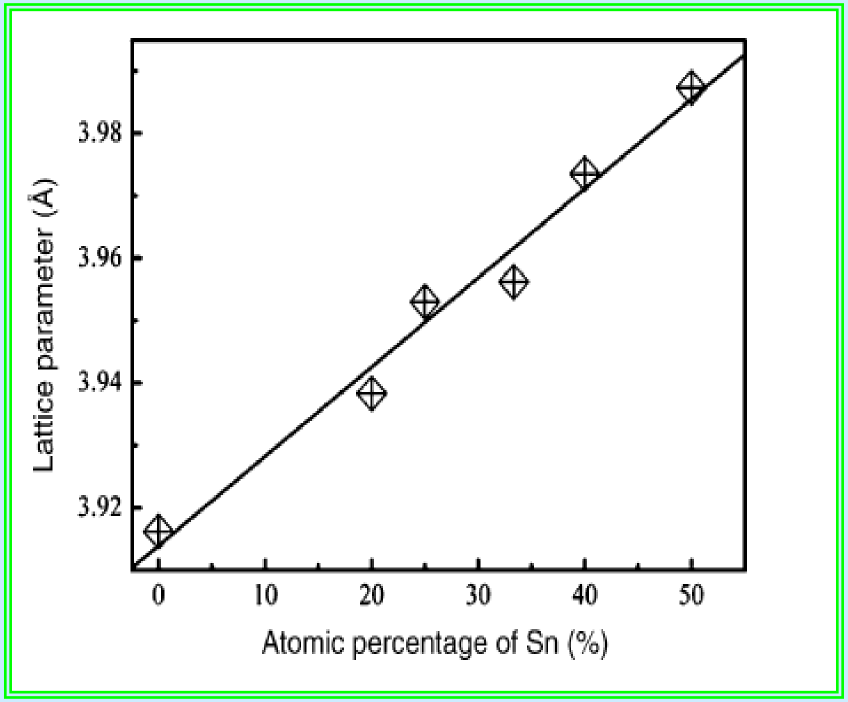


P. Tsiakaras, J. Power Sources 171 (2007) 107-112.

The Case of Pt-Sn Anodes



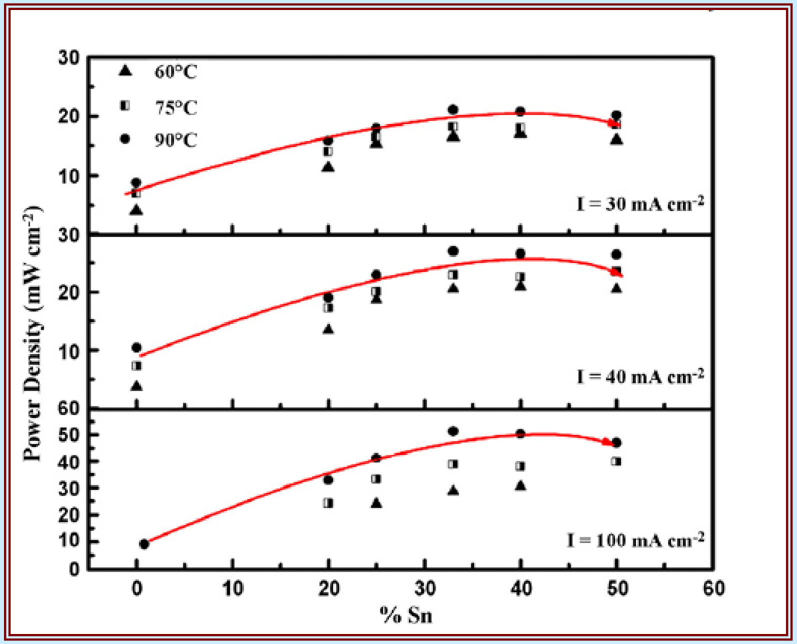
(A) A typical TEM image of Pt_2Sn_1/C catalyst and
(B) PtSn particles size distribution*.



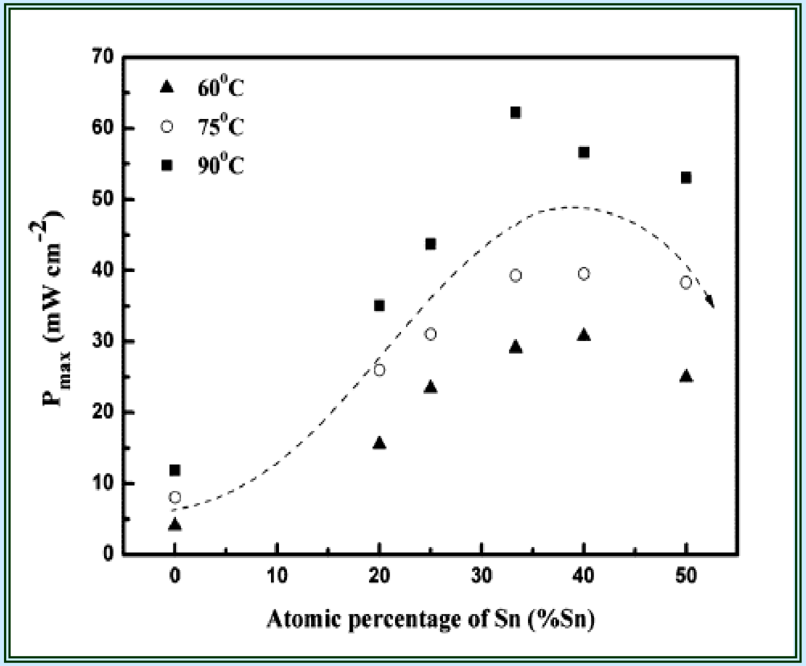
The relation between lattice parameter and Sn content in different PtSn/C catalysts**.

*W.J. Zhou, S.Q. Song,. Douvartzides, P. Tsiakaras, J. Power Sources 140 (2005) 50-58.
**W. Zhou, S. Song, P. Tsiakaras, Appl. Catal. B: Environ. 46 (2003) 273-285.

The Sn Effect on Direct Ethanol Fuel Cells Performance



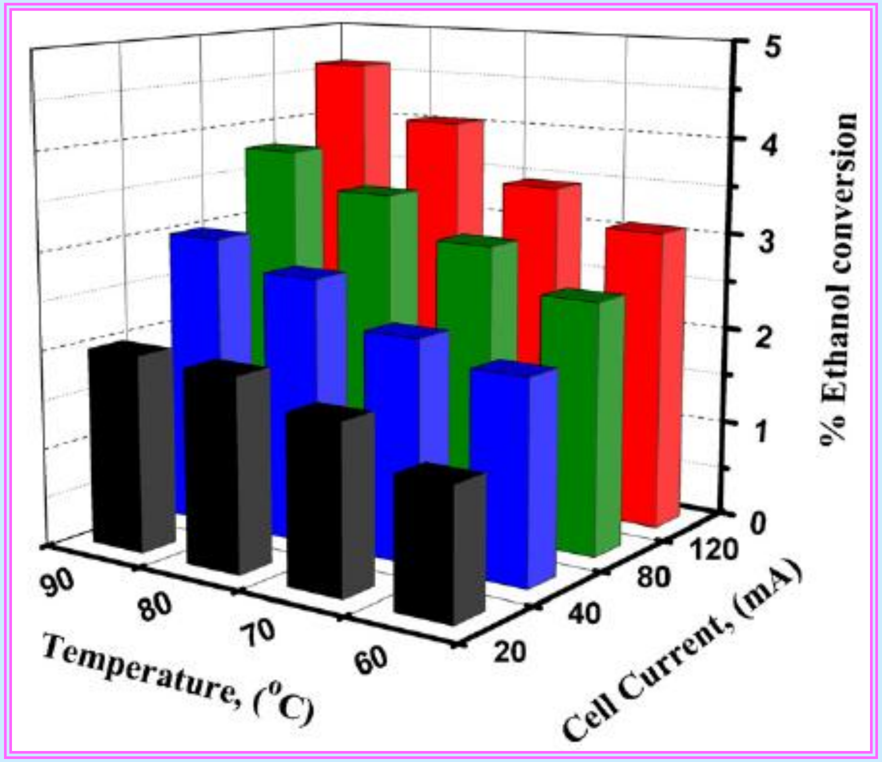
The effect of Sn percentage on the DEFC power density for different current density values at three different operating temperatures.



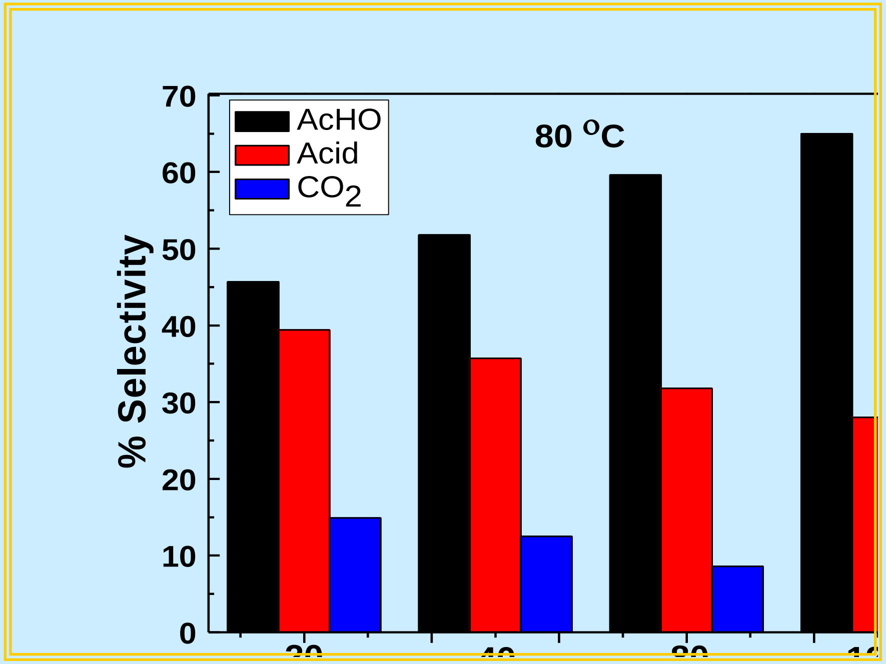
Maximum power density along with the atomic percentage of Sn in a Pt_xSn_y/C catalyst at different operating temperatures.

The Effect of the Cell Discharge Current (produced electricity) on Products' Distribution

ETHANOL CONVERSION



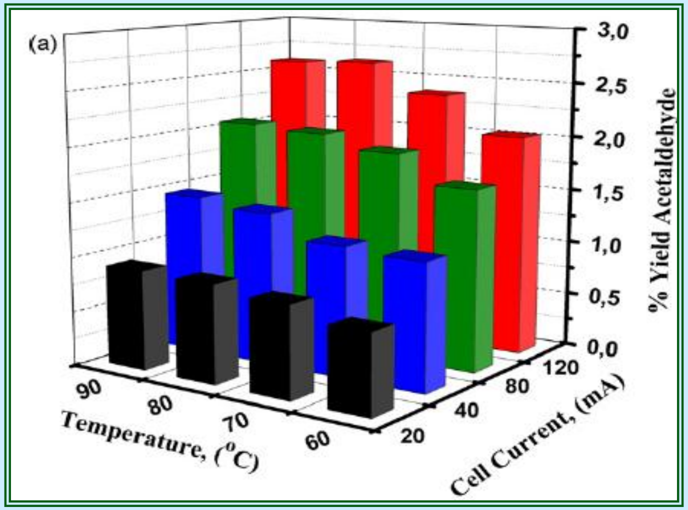
PRODUCTS SELECTIVITY



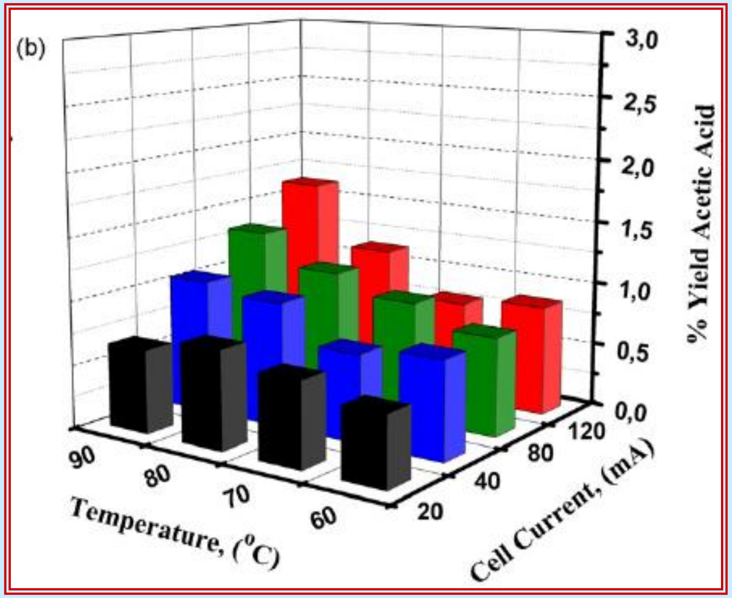
G. Andreadis, V. Stergiopoulos, S. Song, P. Tsiakaras, Appl. Catal. B: Environ. 100 (2010) 157-164.

$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CH_3COOH \rightarrow CO_2 + H_2O$

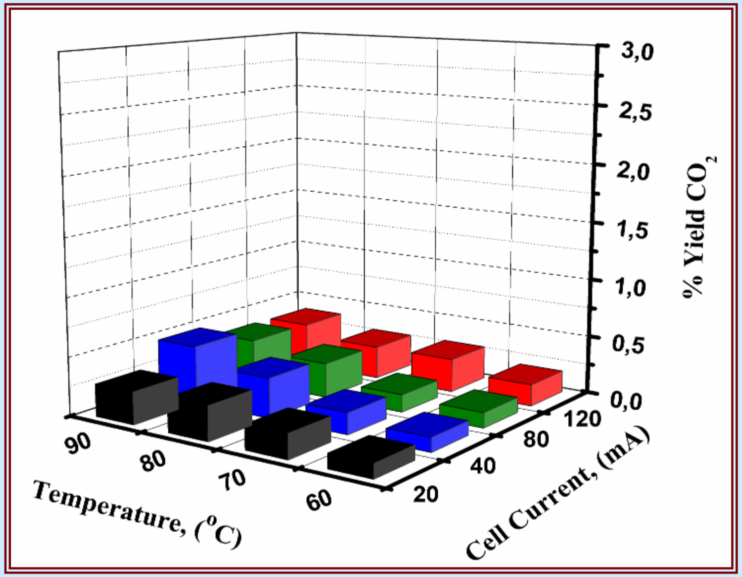
ACETALDEHYDE YIELD



ACETIC ACID YIELD

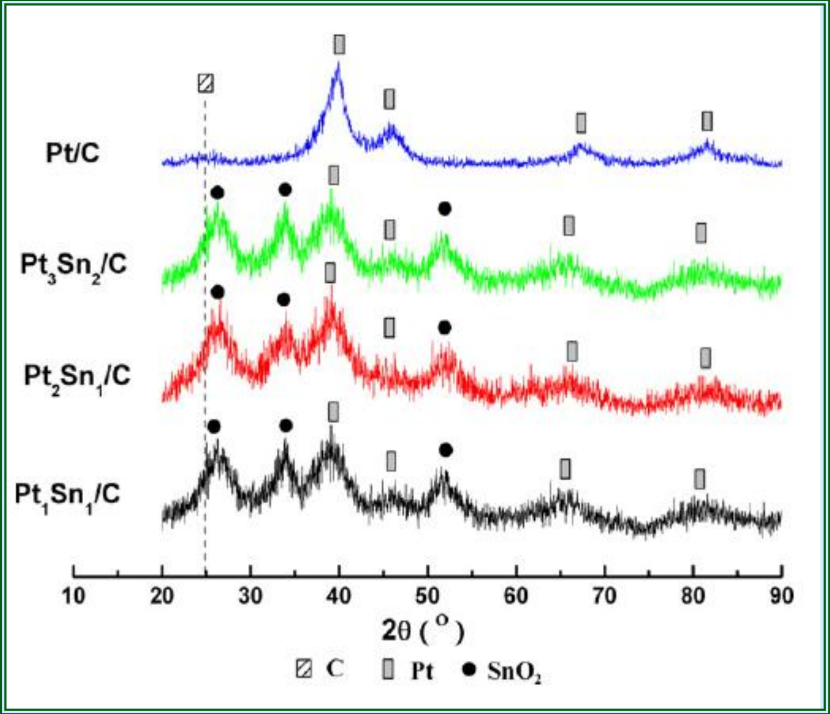


CARBON DIOXIDE YIELD

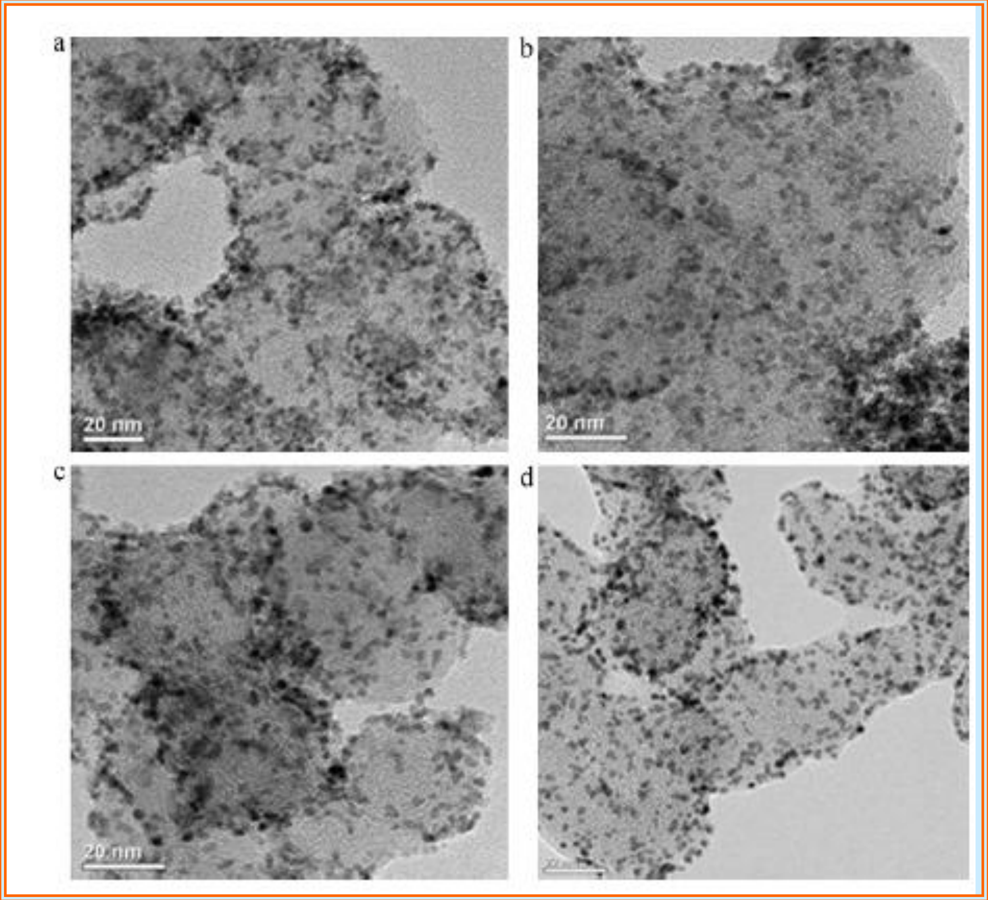


G. Andreadis, V. Stergiopoulos, S. Song, P. Tsiakaras, Applied Catalysis B: Environ. 100 (2010) 157-164.

Difficulty of **C-C** bond cleavage over Pt_xSn_y



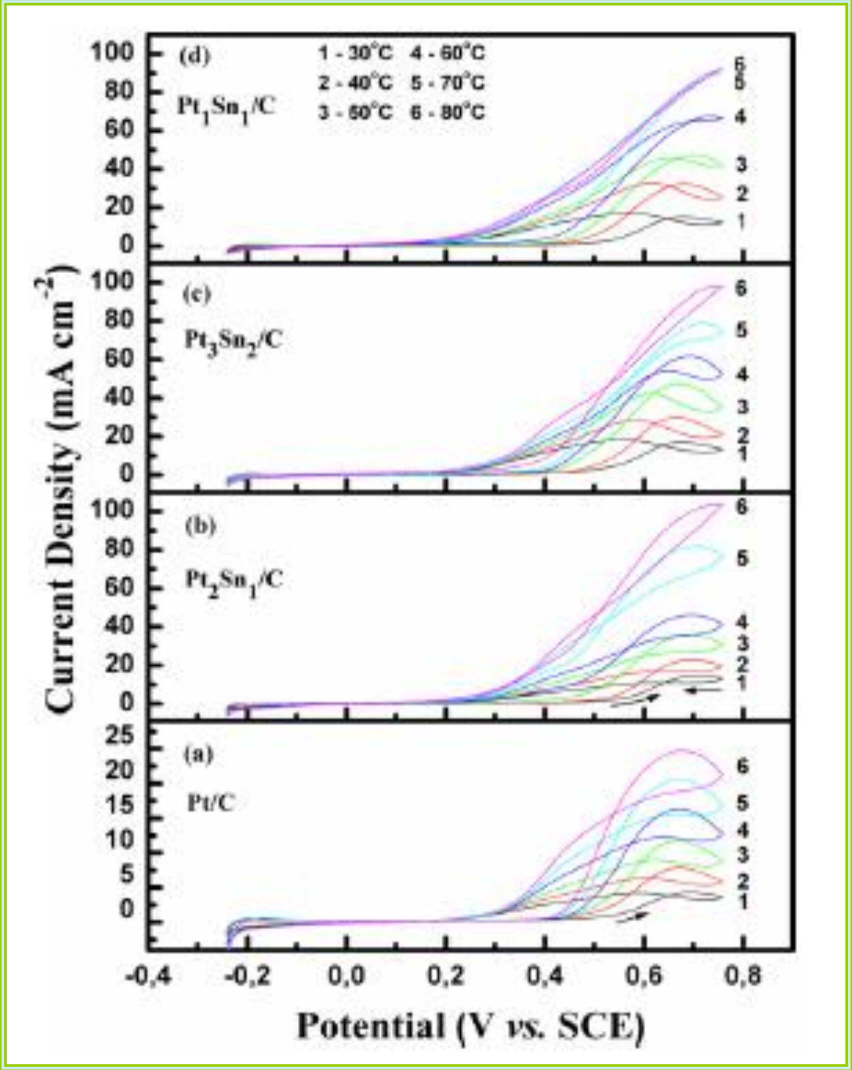
XRD patterns of the as-prepared Pt_xSn_y/C and Pt/C electrocatalysts.

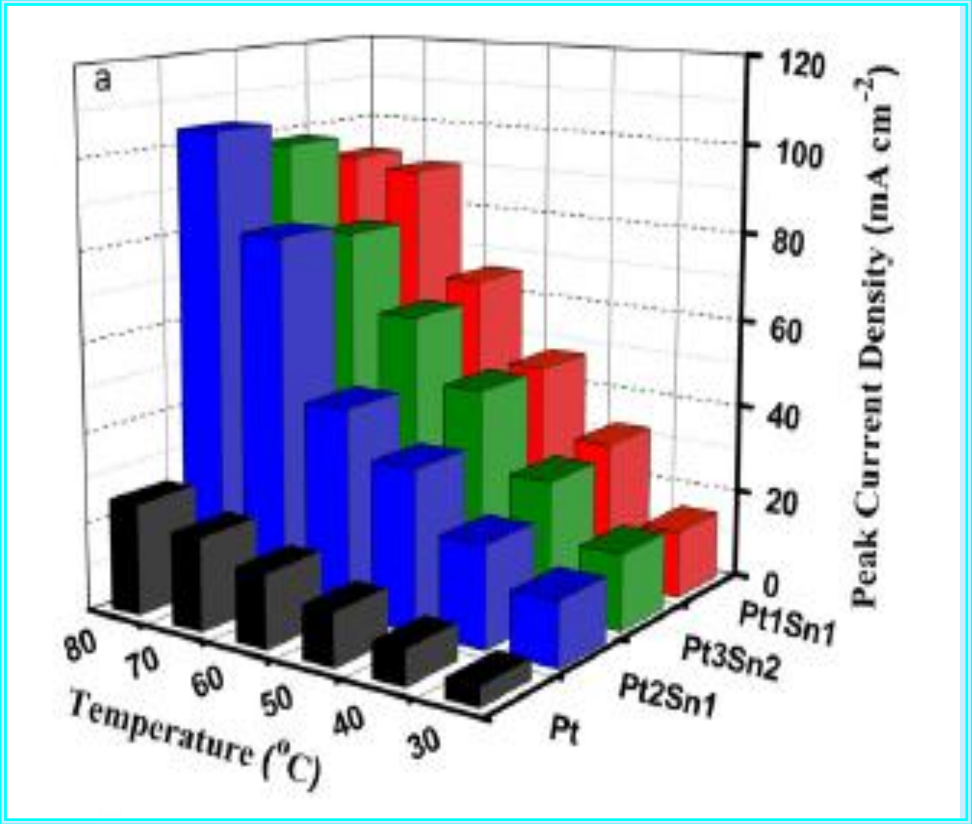


TEM images of (a) Pt_1Sn_1/C, (b) Pt_2Sn_1/C, (c) Pt_3Sn_2/C, and (d) Pt/C.

Y. Wang, S. Song, G. Andreadis, H. Liu, P. Tsiakaras, J. Power Sources 196 (2011) 4980-4986.

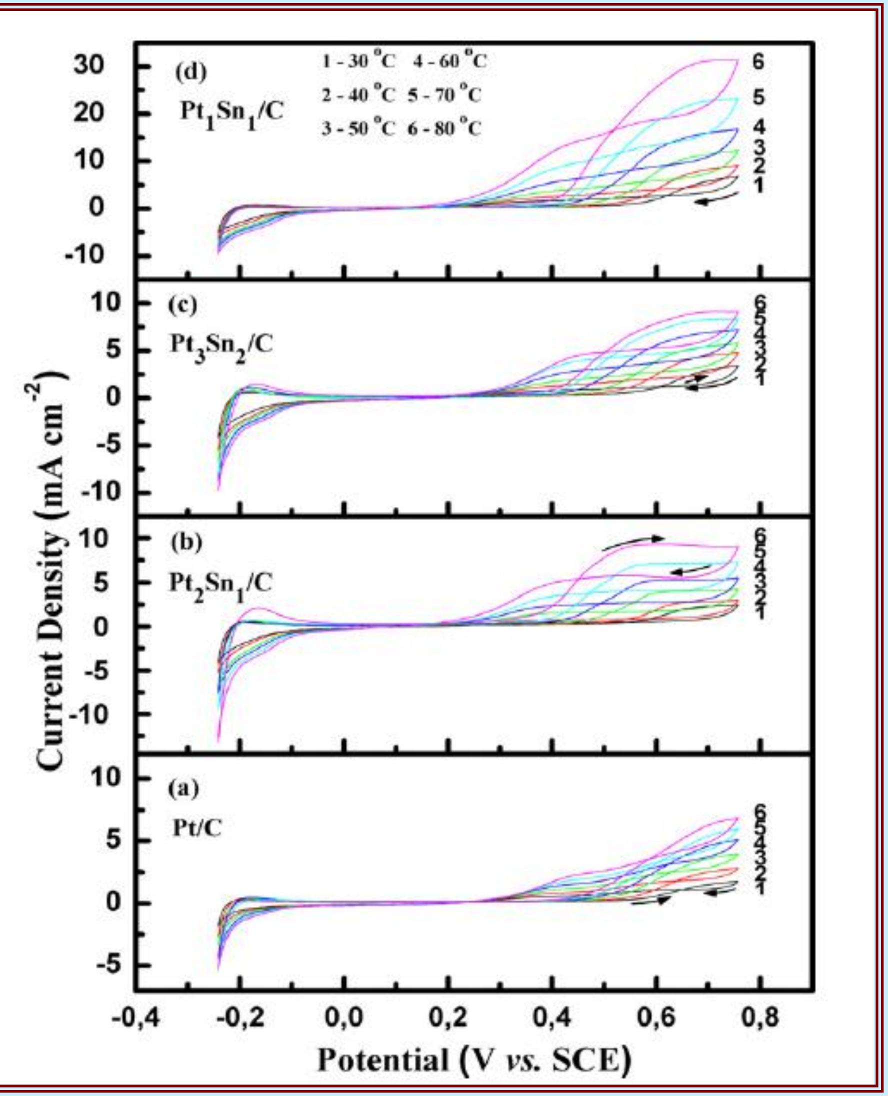
Ethanol Electro-oxidation

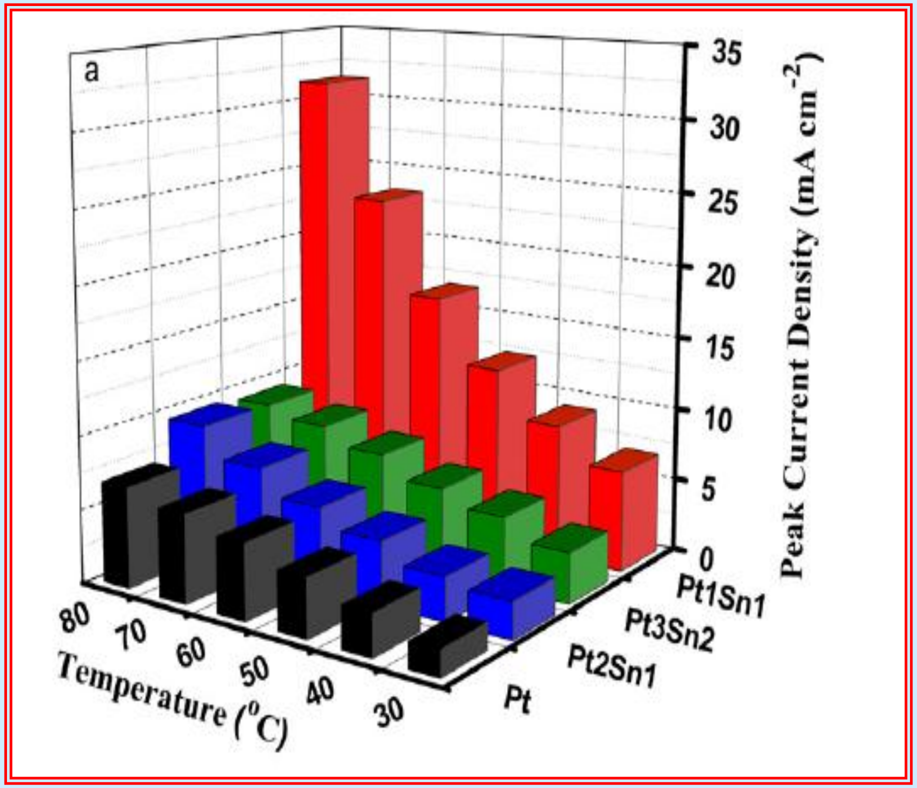




Ethanol electro-oxidation rate in terms of current density in 0.5 mol L^{-1} H_2SO_4 + 1.0 mol L^{-1} C_2H_5OH aqueous solution recorded at a sweep rate of 50 mV s^{-1}.

Acetaldehyde Electro-oxidation

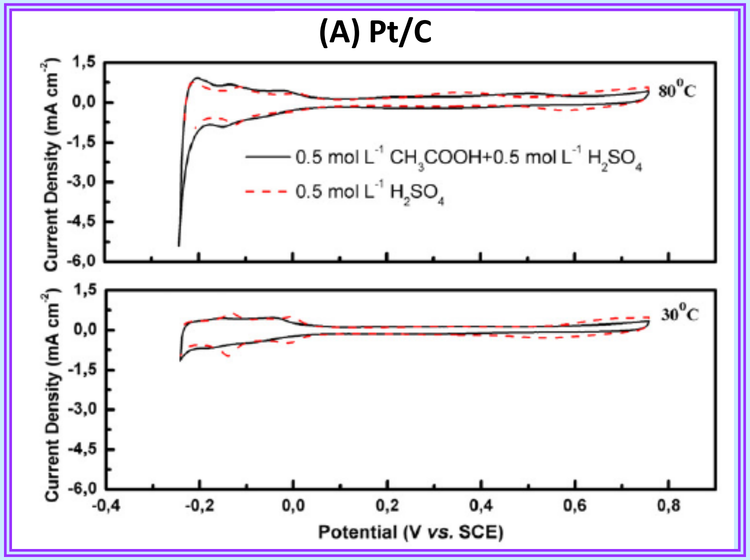


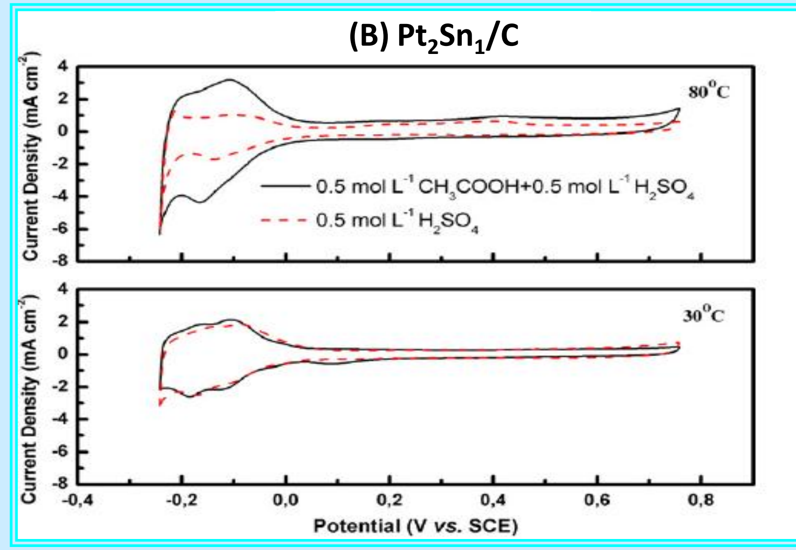


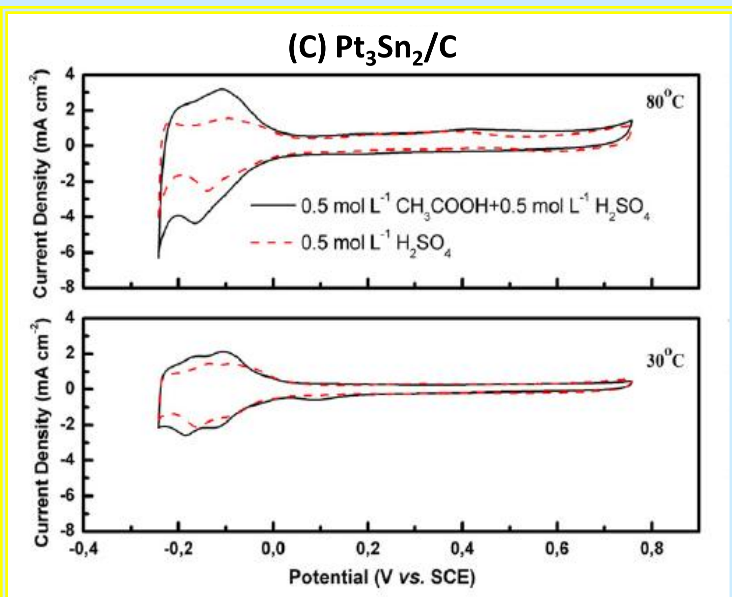
Acetaldehyde electro-oxidation: 0.5 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} CH_3CHO aqueous solution; sweep rate of 50 mV s^{-1}.

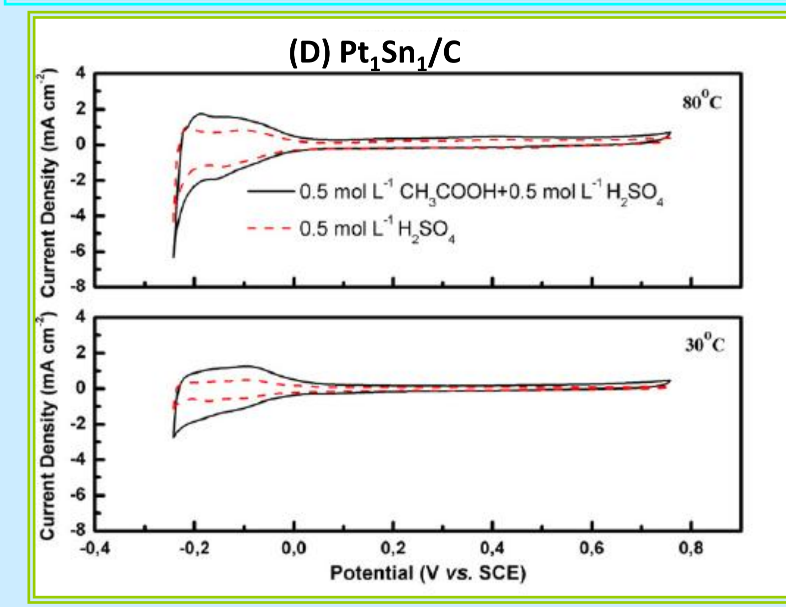
Y. Wang, S. Song, G. Andreadis, H. Liu, P. Tsiakaras, J. Power Sources 196 (2011) 4980-4986.

Acetic Acid Electro-oxidation: very small reaction!



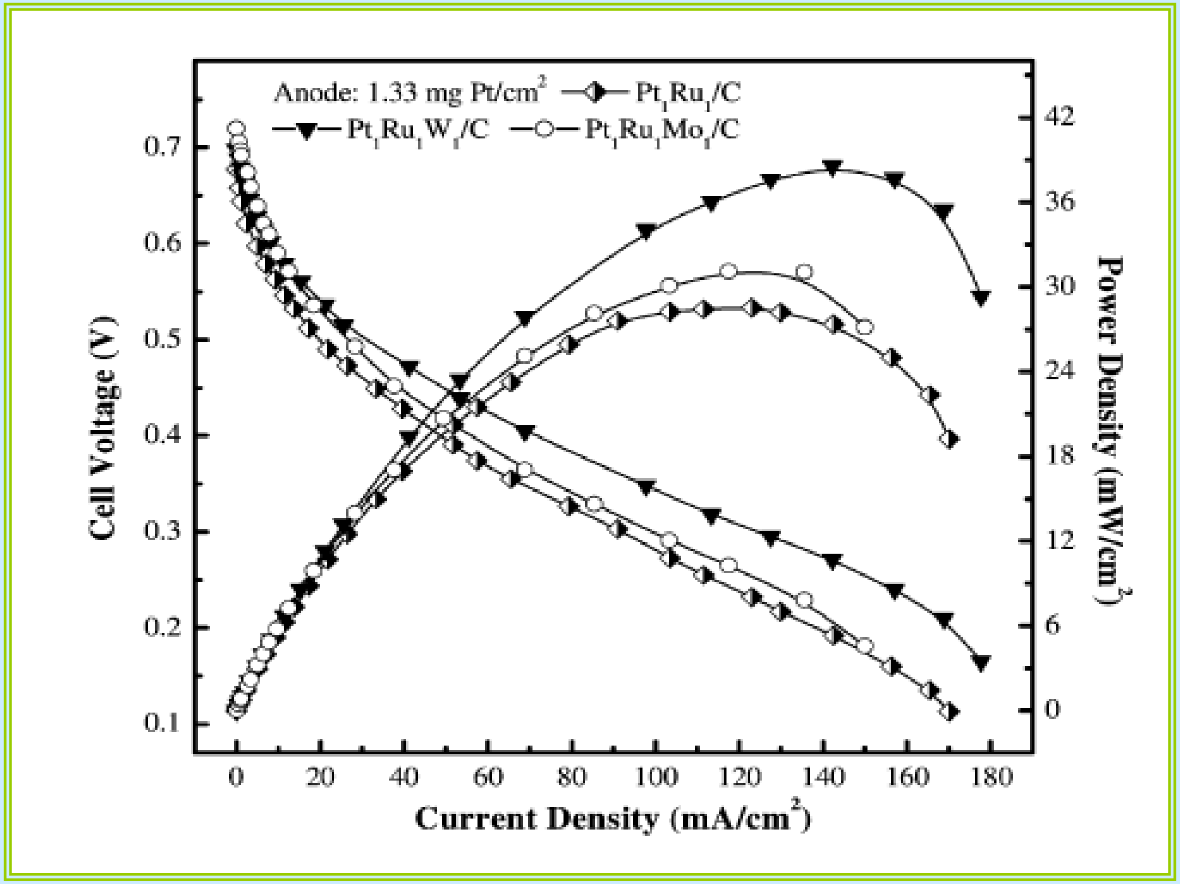






Acetic acid electro-oxidation: 0.5 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} CH_3COOH aqueous solution; sweep rate of 50 mV s^{-1}.

DEFCs' Performance for Ternary Catalysts



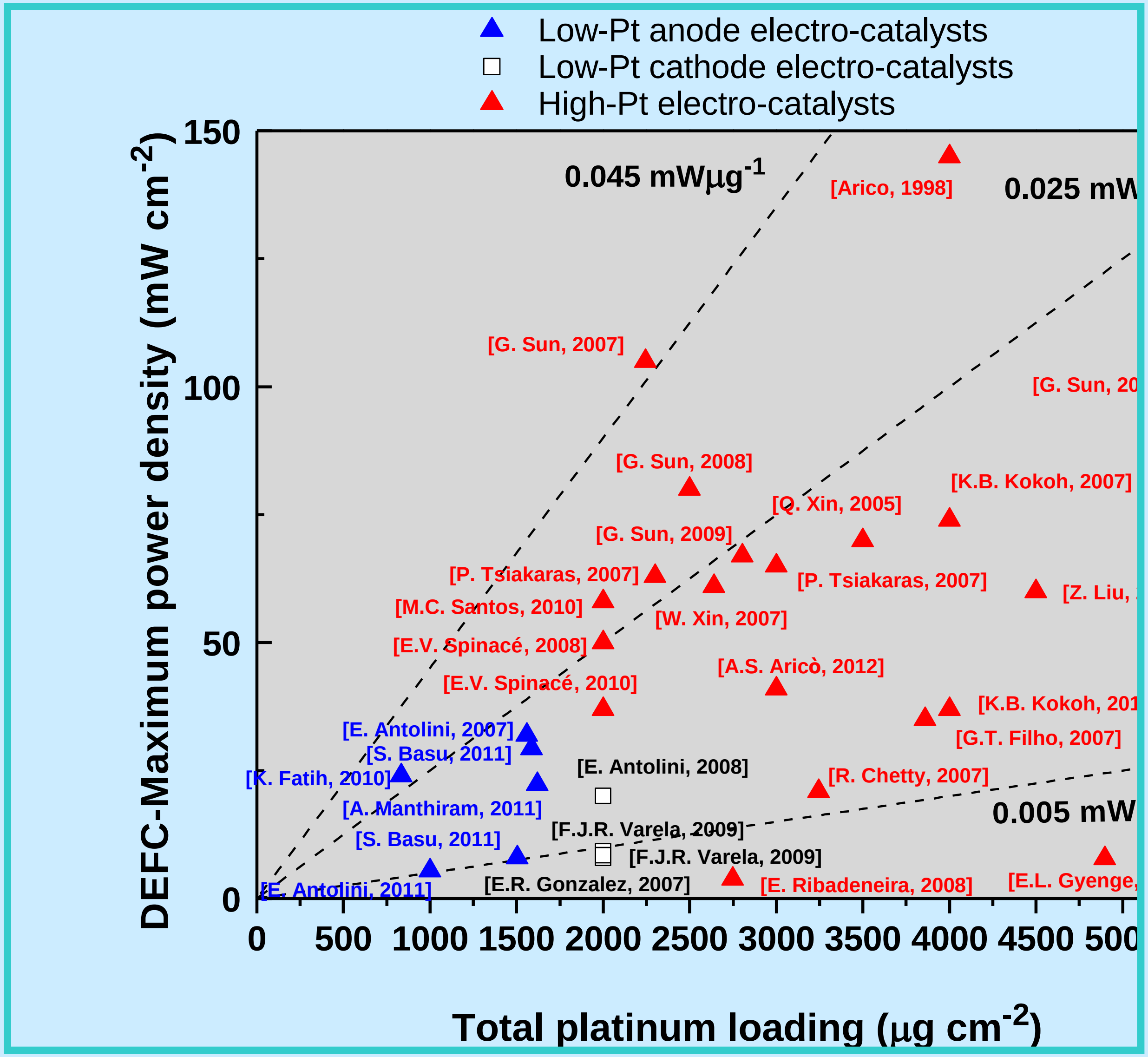
PtRuW, PtRuMo vs PtRu

PtRu-based anode catalysts at 90 C. Ethanol aqueous solution is 1.0 mol/l and its flow rate is 1.0 ml/min; Cathode contains Pt/C (Johnson Matthey Co.) with 1.0 mg_{Pt}/cm^2. Membrane is Nafion®-115.

P. Tsiakaras, J. Power Sources 171 (2007) 107-112.

State-of-art of Direct Ethanol Fuel Cells performance:

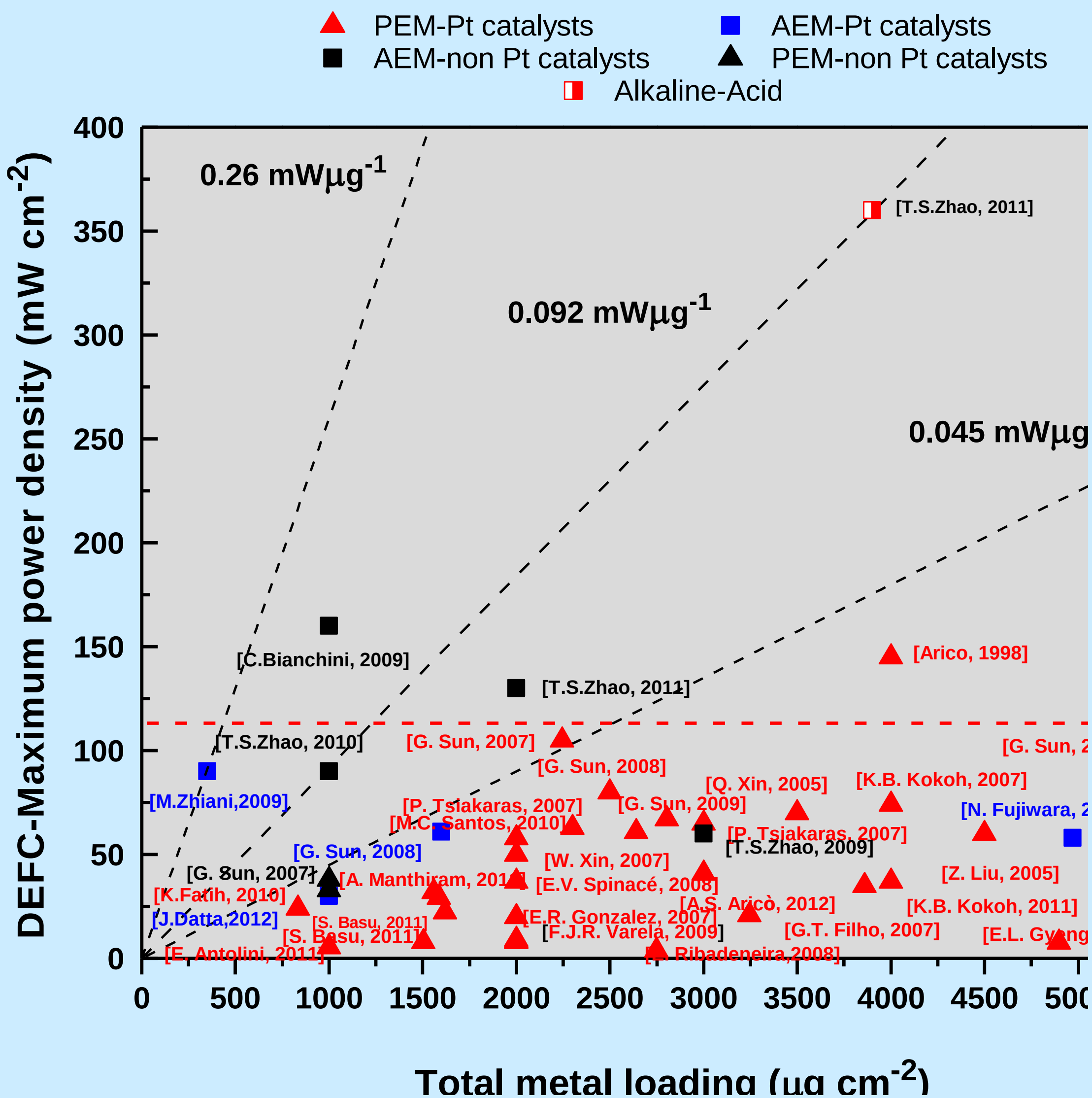
Proton Exchange membrane



A. Brouzgou, S. Song, P. Tsiakaras, accepted to Applied Catalysis B: Environmental, 2012.

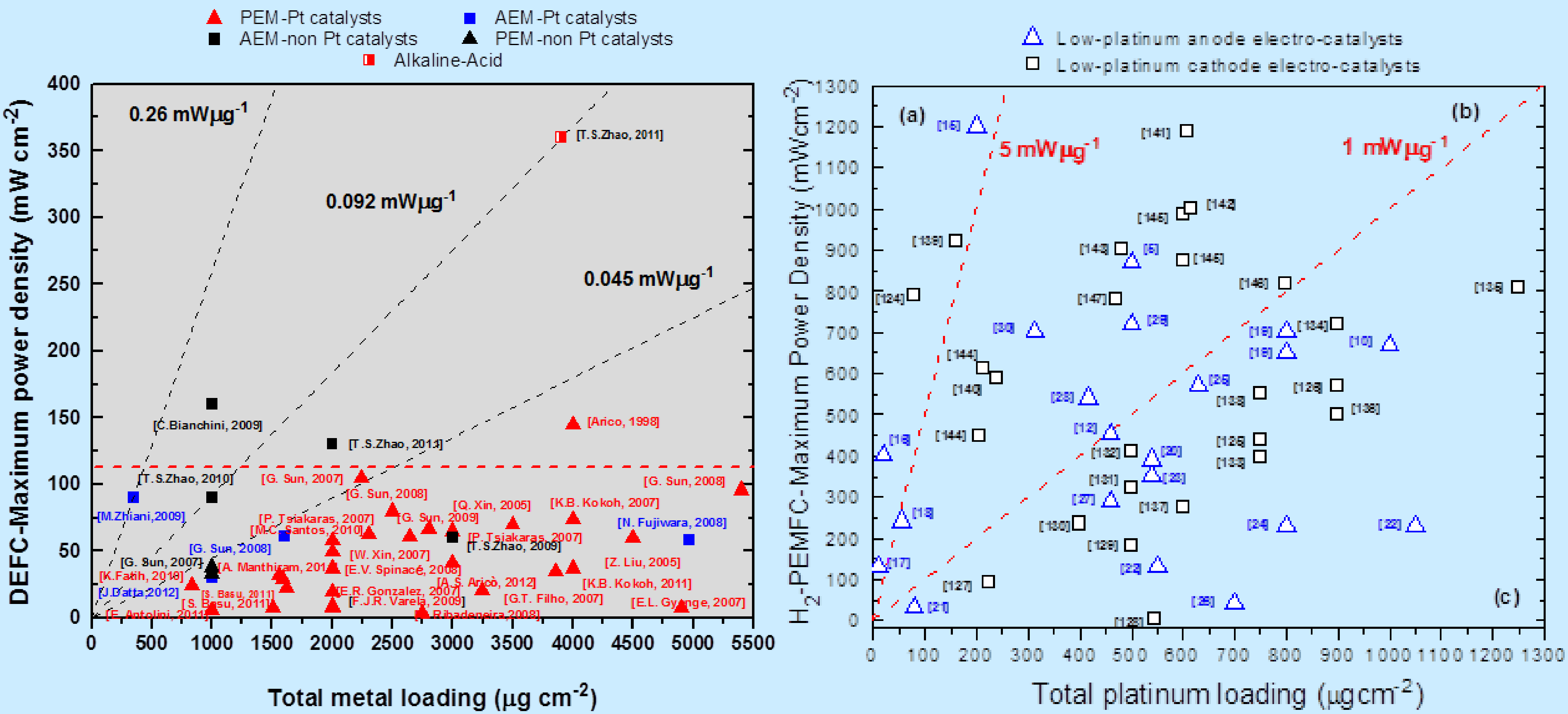
Direct Ethanol Fuel Cells Performance:

Proton vs Anion exchange membrane



A Brouzgou, A Podias, P Tsiakaras, Journal of Applied Electrochemistry 43 (2), 119-136

The state-of-the-art of
Direct Ethanol PEM Fuel Cells vs H_2-PEM Fuel Cells



THE SPECIFIC POWER IS MORE THAN **20 TIMES** HIGHER
IN H-PEMFC THAN IN DE-PEMFCs

A Brouzgou, S Song, P Tsiakaras, Applied Catalysis B: Environmental 127, 371-388.

Advantages and Disadvantages of Direct Ethanol PEMFCs*

Advantages

- Ethanol has high energy density (8.01 KWh/kg)
- It can be produced in great quantities by the fermentation of sugar containing raw materials
- Ethanol is ecological fuel, as a biofuel
- Safer when used in comparison to widely used in nowadays methanol

Disadvantages

- It is difficult to brake the C-C bondage
- Ethanol price is still high in contrast to the conventional fuels as there is no mass production yet
- During its electro-oxidation there is CO production that poisons the anode catalyst, thus affecting the fuel cell power density
- Ethanol permeates through the membrane leading to mixed potential at the cathode side of the cell

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* A Brouzgou, S. Song, P Tsiakaras, **Applied Catalysis B: Environmental** 127, 371-388
S. Song and P. Tsiakaras, **Appl. Cat. B: Environ.** 63 (2006) 187-193

Research Issues for PEM-DEFC Electrodes

Electrocatalysts (cost & performance)

ANODES

– Issues: limited performance, High cost, Poisoning by CO, reduce qty.

– Solution: New and more active (for C-C breaking) catalysts, better distribution of catalyst on support – novel support materials, **Low Platinum** or **non-noble metal catalysts.**

CATHODES

Issues: Limited performance, High cost, Poisoning by (crossovered) ethanol, reduce qty.

Solution: New and more active catalysts, Ethanol inert materials, better distribution of catalyst on support – novel support materials,

Low Platinum, non-noble metal catalysts .

MOREOVER:
Water management and Ethanol Crossover Issues should also be considered

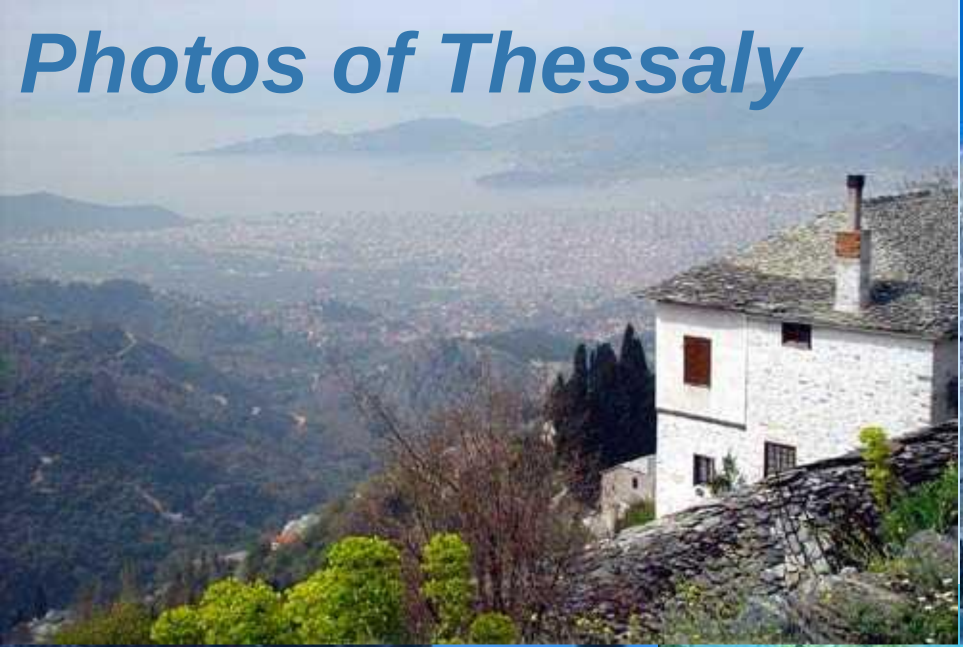
WHERE WE ARE - Regional Maps

Greece

Thessaly

Magnesia

Photos of Thessaly



Volos

Volos

Sporades Islands

The Aegean

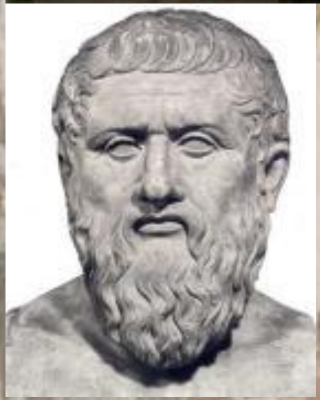
The Ionian

Ancient Heritage

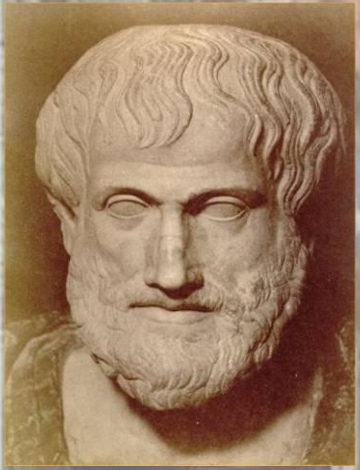
Classical Art

Philosophy & Science

Socrates



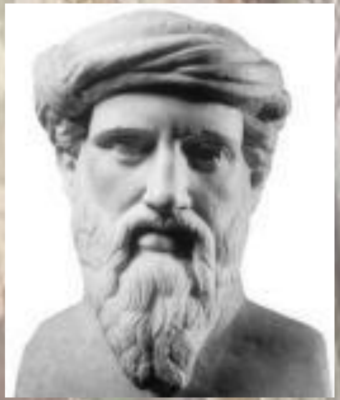
Plato



Aristotle

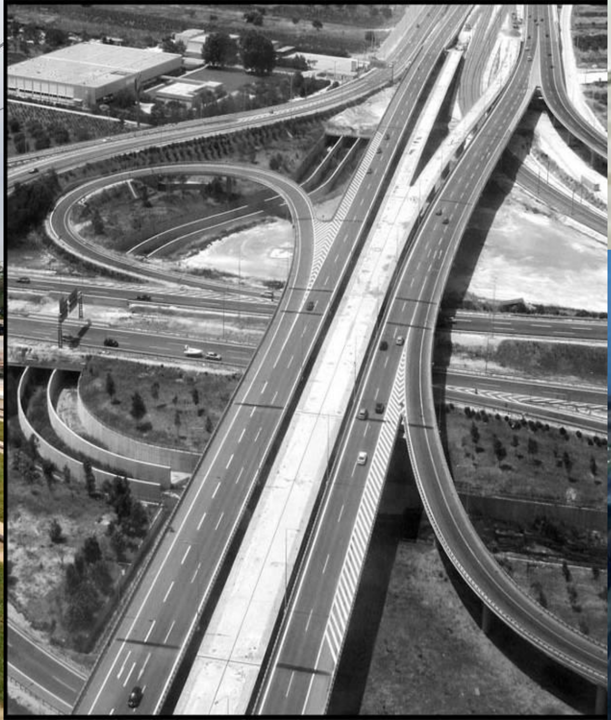
Archimedes

Pythagoras

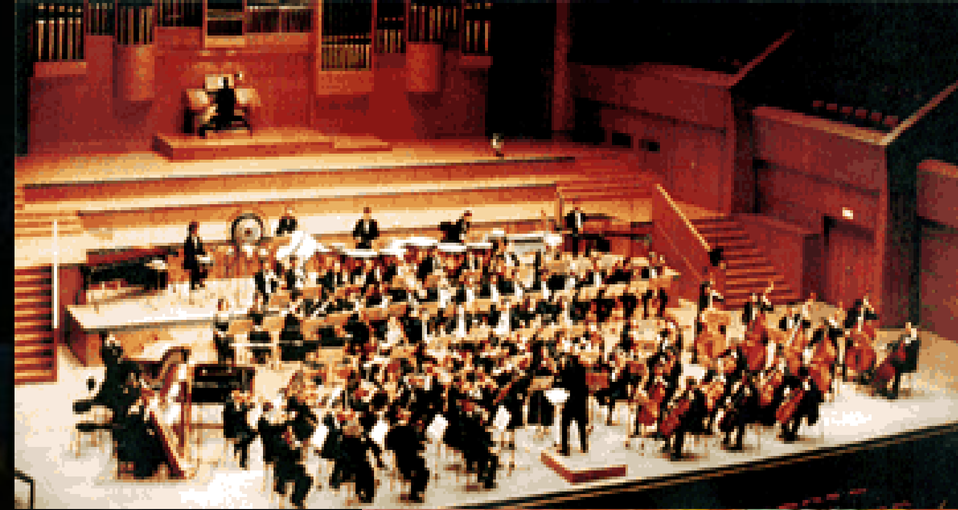


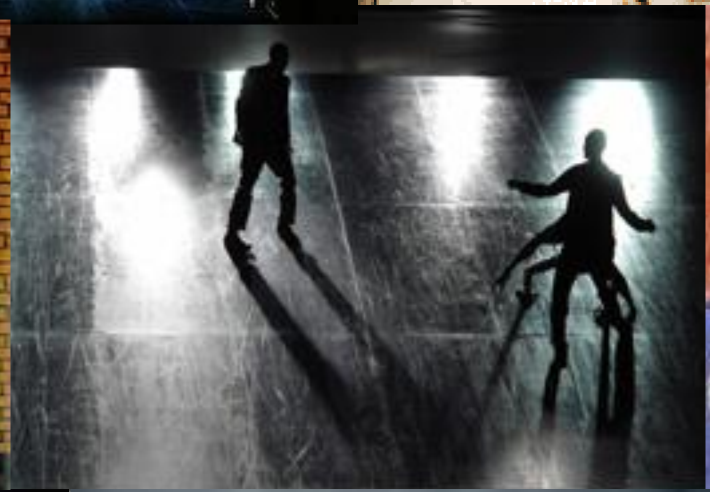
Democritos

Modern Greece



Modern Art




Greek Entertainment

Modern Greek scientists and philosophers

Greek Food

Acknowledgments

To my Collaborators

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Большое спасибо за внимание!

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