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).
Collaboration Since 2000*
more than 30 common publications & 3 common projects

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)
Two of the main Applications of the Solid Electrolytes

**Electrochemical Cell**
- Passive Operation (Galvani mode)

**Electrochemical Cell**
- Active Operation (Volta mode)

*Fuel Cells*

*Electrolyzers*
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:

**H₂ 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  
USE OF BIOFUELS

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

H₂

Fuel Cells

mobile applications
stationary applications
portable applications

Reforming for H₂ production
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 $\eta$ 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 CHARACTERIZING 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…

Exergy

Anergy

Energy or Exergy Crisis?

Theoretical Potential

Losses
First attempts of Direct Ethanol Fuel Cells

1995: Wang and his coworkers compared the performance of fuel cells employing an $\text{H}_3\text{PO}_4$-doped polybenzimidazole membrane and PtRu (2.6 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$) as anode catalyst operating on various methanol-alternative fuels. **Cathode**: Pt/C (4 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$), 1 atm.


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 $\text{C}_2\text{H}_5\text{OH}$, 4.0 atm (abs); cathode 5.5 atm (abs) $\text{O}_2$. **Anode Pt-Ru (1:1)/C, 2 mg$_{\text{Pt}}$ cm$^{-2}$**;
**Cathode** Pt/C, 2 mg$_{\text{Pt}}$ cm$^{-2}$.

Anodes and Cathodes for Direct Ethanol PEM-Fuel Cells

Pt-based Electrocatalysts
- Pt-M
- Pt-M1-M2
- Low Pt

Non-Pt Electrocatalysts
- Pd/C, Carbon nanotubes, Ti
- Ir
- Ir-Sn

\[
\begin{align*}
\text{ANODE} & : & \text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} & \rightarrow 12 \text{H}^+ + 12 \text{e}^- + 2 \text{CO}_2 \\
\text{CATHODE} & : & 3 \text{O}_2 + 12 \text{H}^+ + 12 \text{e}^- & \rightarrow 6 \text{H}_2\text{O} \\
\text{OVERALL} & : & \text{C}_2\text{H}_5\text{OH} + 3 \text{O}_2 & \rightarrow 3 \text{H}_2\text{O} + 2 \text{CO}_2
\end{align*}
\]

\[ \begin{align*} 
-2\text{e} & \quad -2\text{e} & \quad -8\text{e} \\
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CHO} & \rightarrow \text{CH}_3\text{COOH} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} 
\end{align*} \]

The best catalyst will permit the complete electro-oxidation of ethanol to \( \text{CO}_2 + \text{H}_2\text{O} \) offering 12 electrons!

However………. 
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.**

The Case of Pt-Sn Anodes

(A) A typical TEM image of Pt$_2$Sn$_1$/C catalyst and (B) PtSn particles size distribution*.

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


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$_x$Sn$_y$/C catalyst at different operating temperatures.
The Effect of the Cell Discharge Current (produced electricity) on Products’ Distribution

ETHANOL CONVERSION

PRODUCTS SELECTIVITY

CH$_3$CH$_2$OH $\rightarrow$ CH$_3$CHO $\rightarrow$ CH$_3$COOH $\rightarrow$ CO$_2$ + H$_2$O

ACETALDEHYDE YIELD

ACETIC ACID YIELD

CARBON DIOXIDE YIELD

Difficulty of C-C bond cleavage over Pt$_x$Sn$_y$

XRD patterns of the as-prepared Pt$_x$Sn$_y$/C and Pt/C electrocatalysts.

TEM images of (a) Pt$_1$Sn$_1$/C, (b) Pt$_2$Sn$_1$/C, (c) Pt$_3$Sn$_2$/C, and (d) Pt/C.

Ethanol electro-oxidation rate in terms of current density in 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) + 1.0 mol L\(^{-1}\) C\(_2\)H\(_5\)OH aqueous solution recorded at a sweep rate of 50 mV s\(^{-1}\).
Acetaldehyde electro-oxidation: 0.5 mol L$^{-1}$ H$_2$SO$_4$ + 0.5 mol L$^{-1}$ CH$_3$CHO aqueous solution; sweep rate of 50 mV s$^{-1}$.

Acetic Acid Electro-oxidation: very small reaction!

**Acetic acid electro-oxidation:** $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{CH}_3\text{COOH}$ 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/cm². Membrane is Nafion®-115.

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

Arico, 1998
M.Zhiani, 2009
J.Datta, 2012
DEFC-Maximum power density (mW cm\(^{-2}\))

0.26 mWµg\(^{-1}\)

0.092 mWµg\(^{-1}\)

0.045 mWµg\(^{-1}\)

Total metal loading (µg cm\(^{-2}\))
The state-of-the-art of Direct Ethanol PEM Fuel Cells vs H\textsubscript{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

* A Brouzgou, S. Song, P Tsiakaras, *Applied Catalysis B: Environmental* 127, 371-388
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
- Larissa
- Trikala
- Karditsa
- Magnesia

Magnesia
- Volos
- PAGASSITIKOS GULF
- Evia Island
Photos of Thessaly
Volos
Sporades Islands
The Ionian
Ancient Heritage
Classical Art
Modern Art
Greek Food
Acknowledgments

To my Collaborators

Kontou S.    Song S.    Mitri E.    Seretis A.    Andreadis G.    Stergiopoulos V.

Brouzgou A.    Tzorbatzoglou F.    Papageridis K.    Polymeros G.    Kourenta K.
Большое спасибо за внимание!

tsiak@uth.gr
http://www.mie.uth.gr/n_labs_main.asp?id=4&lang=en&lc=1