CPERI/CERTH KIT/IMVT YTU

H_2S - PROTON

Hydrogen production from H_2S decomposition in micro-structured proton-conducting (H^+) solid oxide membrane reactors

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BS-ERANET: Networking on Science and Technology in the Black Sea Region

Bucharest, December 11-12, 2012

Outline

- **Introduction**
- **Hydrogen Economy- Black Sea Rich in H_2S**
- **Project Summary**
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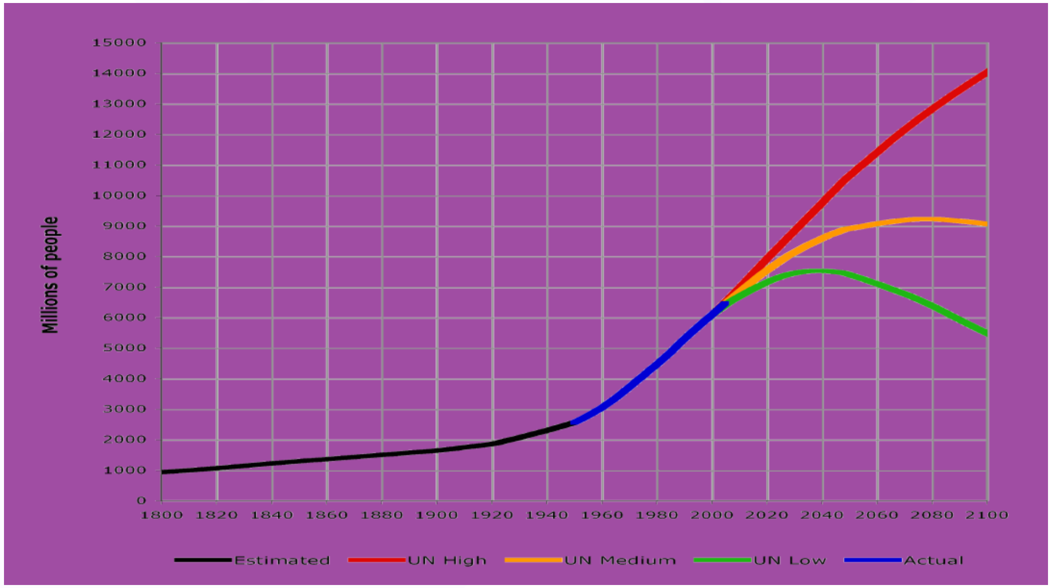
- **Project Coordinator and Partners**
- **Challenges of the Proposed Concept**
- **Main Objectives and Expected Results of the Project**
- **WP's Description**
- **Work Performed**

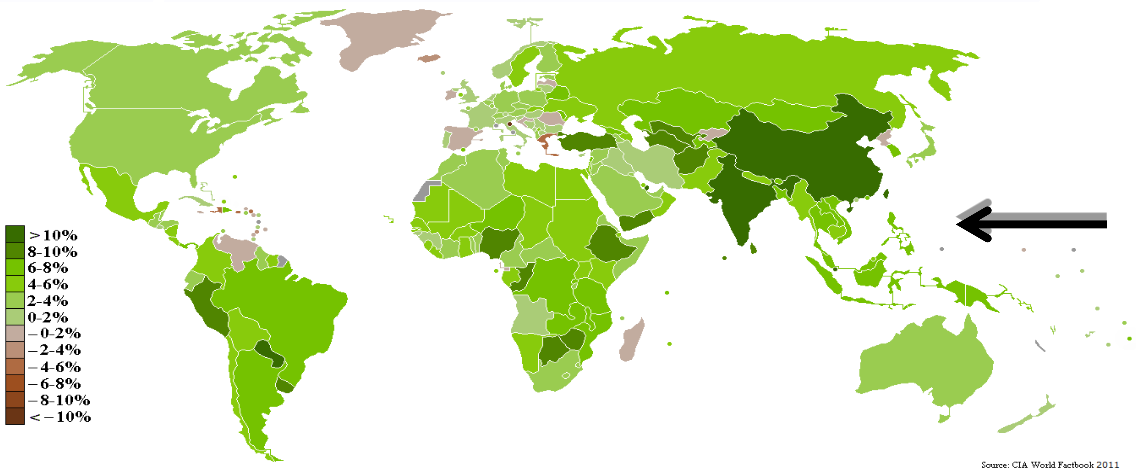
Introduction

World energy requirements are increasing

- Increase of population
- Technological development
- Living standards

World population





World growth (2010)

CE.R.T.H.

Introduction

Increasing energy demands

↓

Depletion of fossil fuels

↓

Environmental pollution

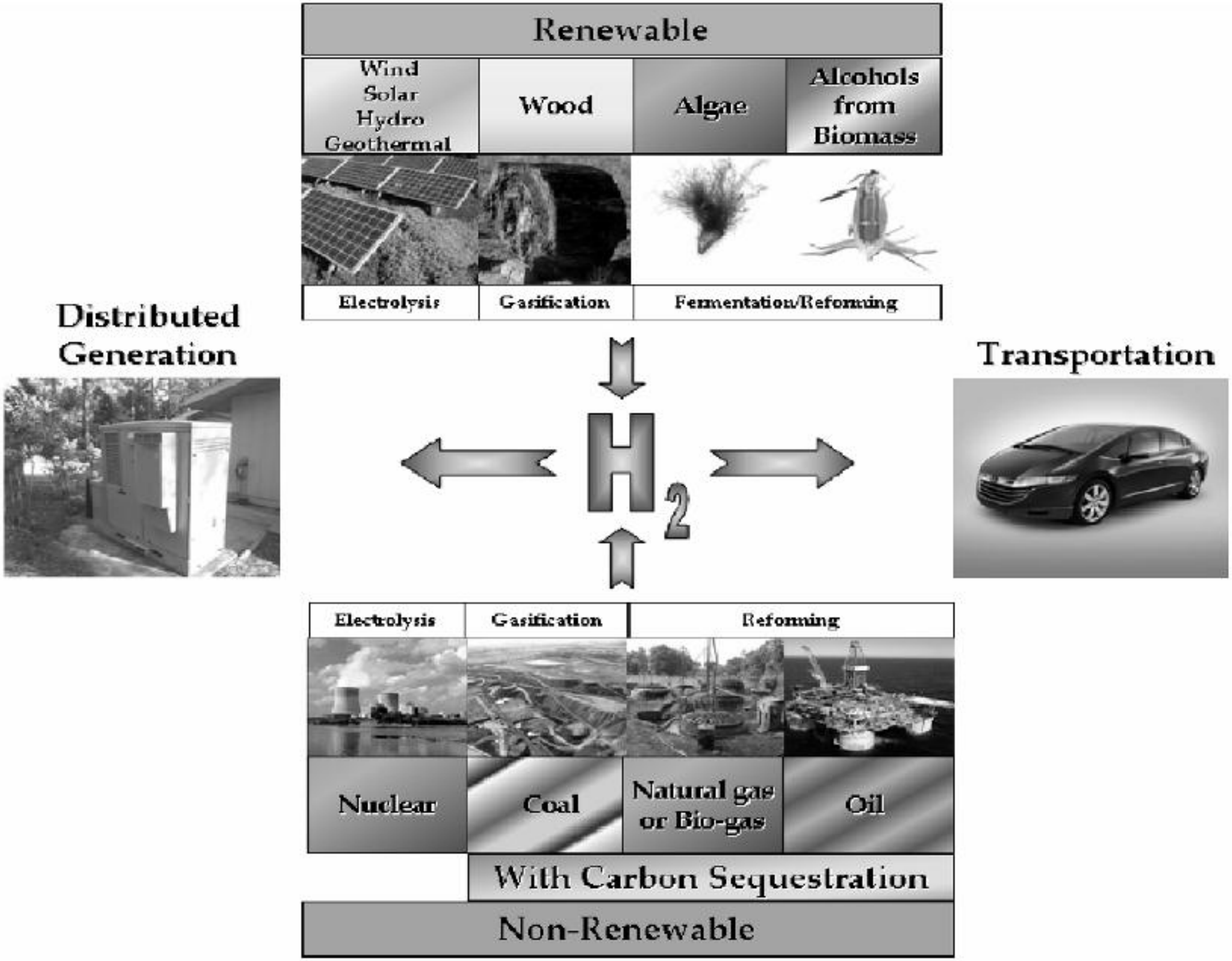
(greenhouse effect, ozone depletion, acidification, photochemical smog)

↓

EU Directive 20-20-20 (2008)

20% reduction of GHG emissions
20% energy savings
20% increase of RES portion in the energy mix

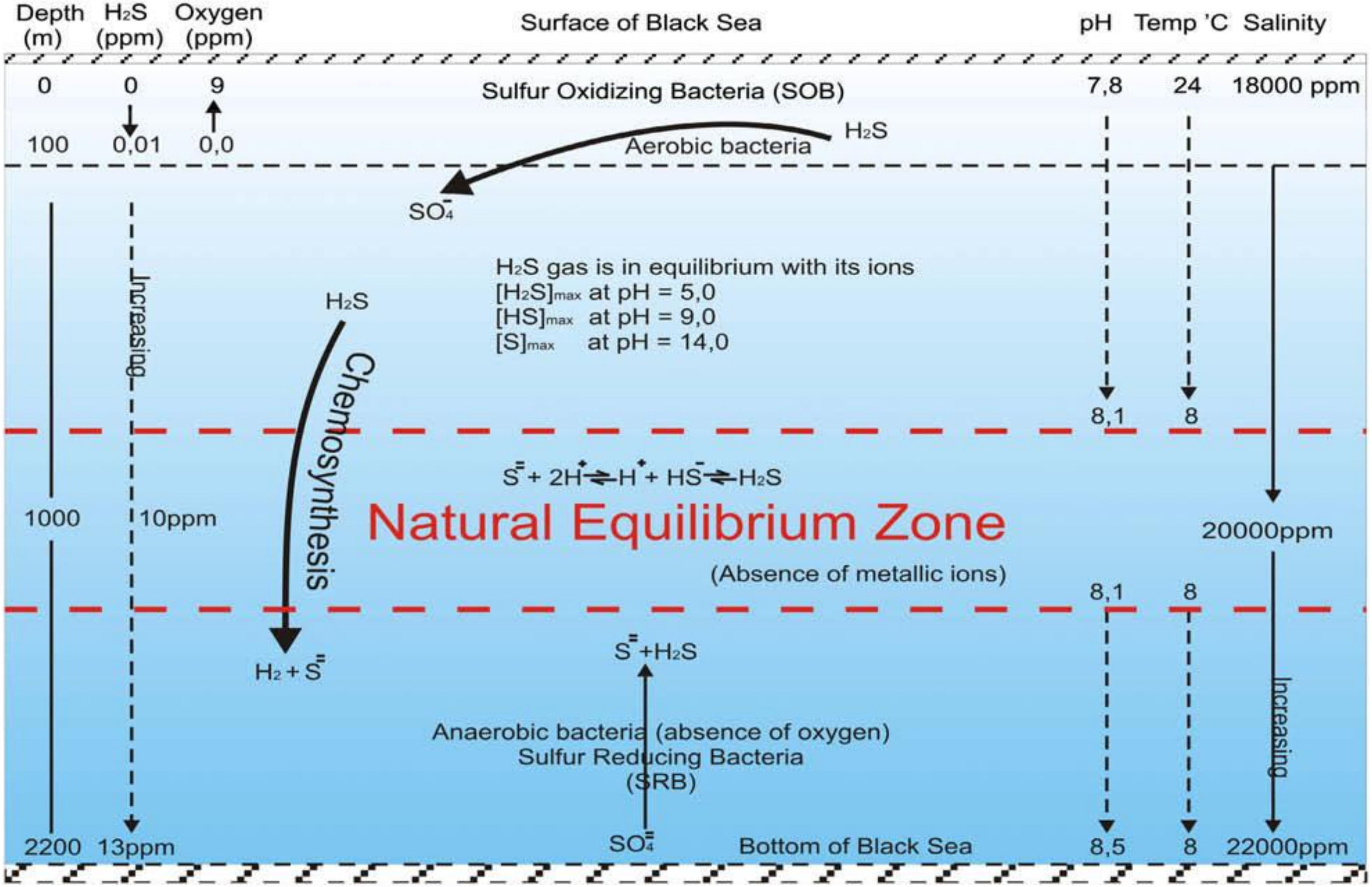
Hydrogen Economy



Black Sea Rich in H_2S

H_2S Concentration levels

- **Surface → 0 ppm**
- **Increase gradually after 100 m**
- **1000 m → 10ppm**
- **Bottom → 14ppm**



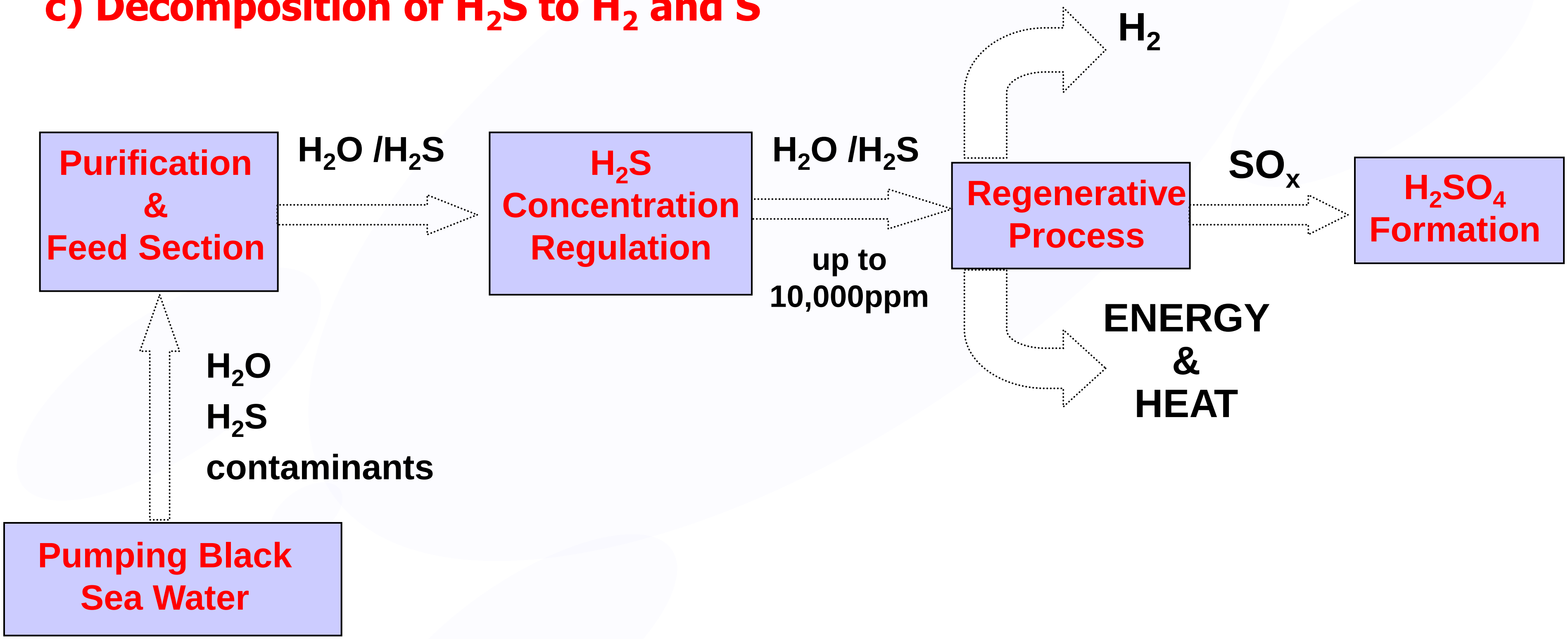
Project Summary

Hydrogen production from Black Sea consists of the following steps:

a) Pumping of sea water from ~1000m depth

b) Extraction of concentrated H_2S/H_2O mixtures

c) Decomposition of H_2S to H_2 and S



Project Summary

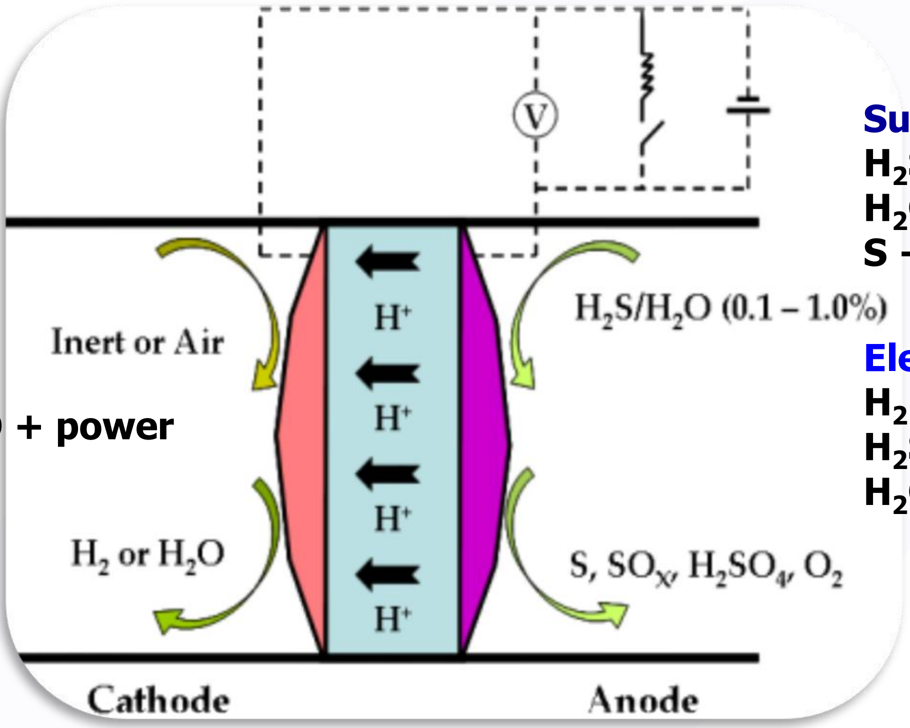
Decomposition of H_2S to H_2 and S

EMR Operation

$2H^+ + 2e^- \rightarrow H_2$

Fuel Cell Operation

$2H^+ + \frac{1}{2}O_2 + e^- \rightarrow H_2O$ + power



Surface Reactions

$H_2S \rightarrow H_2 + 1/n\ S_n$

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$

$S + O_2 + H_2O \rightarrow SO_2 + H_2SO_4$

Electrochemical Reactions

$H_2 \rightarrow 2H^+ + 2e^-$

$H_2S \rightarrow 2H^+ + 1/n\ S_n + 2e^-$

$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

- Anode is exposed to concentrated H_2S/H_2O mixtures (0.1-1% H_2S) and catalyzes the decomposition of H_2S to H^+ and S.
- H^+ are transferred through the dense solid electrolyte membrane to the cathode, where they are converted:
  - either to H_2 (pumping mode) or
  - to H_2O generating power (fuel cell mode).
- If O_2 is present at the anode, the generated S_n (n = 1-8) will react to SO_2/SO_3 and further with excess H_2O to H_2SO_4.

Project Scope

The project addresses the priority :

"Hydrogen production from H_2S rich Black Sea Water",

aiming to develop a micro-structured proton conducting electrochemical membrane reactor that will enable the efficient exploitation of Black Sea's water for H_2 production (~270 Mtn).

Project Coordinator and Partners

	Participant Name	Partner	Role
1	Prof. George Marnellos		Project Coordinator
2	Dr. Spyros Voutetakis		
3	Prof. Simira Papadopoulou		
4	Prof. Michael Stoukides	CPERI/CERTH	
5	Dr. Martha Ouzounidou		
6	Dr. Dimitris Ipsakis		
7	Ms. Jouliana Kraia		
8	Prof. Roland Dittmeyer		Team Leader
9	Dr. Andreas Dubbe	KIT/IMVT	
10	Dr. Katja Haas-Santo		
11	Prof. Sema Baykara		Team Leader
12	Dr. Zehra Altin		
13	Dr. Berceste D. Beyribey	YTU	
14	Prof. Burcu Corbacioglu		
15	Dr. Halit Eren Figen		

CPERI/CERTH — **Chemical Process & Energy Resources Institute/ Centre for Research and Technology Hellas**

KIT/IMVT — **Institute for Micro Process Engineering/ Karlsruhe Institute of Technology**

YTU — **Chemical Engineering Department/ Yildiz Technical University**

H2S PROTON

Challenges of the Proposed Concept

- **Production of pure H_2 (at the cathode)** from H_2S with 100% selective separation in a single device.

- **Co-generation of H_2SO_4 (at the anode)**.

- **Enhancement of H_2 generation rate** by shifting the equilibrium of the decomposition reactions and through the electrochemical promotion approach (EPOC).

- **Simultaneous production and use of hydrogen** for the generation of heat and power (during fuel cell operation mode).

- **Autonomous thermal operation**.

- **Flexible process modules**.

Main Objectives and Expected Results of the Project

- Preparation of H_2S-tolerant H^+-conducting ceramics with high ionic conductivity (>10 mS/cm) at intermediate temperatures (700-1000 K) and adequate chemical stability/mechanical strength.

- Preparation of H_2S-tolerant and conductive anodic composites with high catalytic activity towards H_2 ($> 4 \cdot 10^{-7}$ moles.cm^{-2}.s^{-1}) production.

- Preparation of cathodes with high electronic conductivity (0.5-0.05 OHMcm^2).

- Construction of corrosion resistant ceramic or metal supported micro-cells using advanced fabrication techniques that will lead to flexibility.

- Simulation of transport phenomena taking place in the H^+-conducting cell.

- Optimization and economical evaluation of a scaled-up integrated system.

CE.R.T.H.

WP's Description

WP 1: Preparation and characterization of materials (CPERI, KIT, YTU)

2012											2013
2	3	4	5	6	7	8	9	10	11	12	1

1.1 Preparation and selection of solid electrolytes (CPERI)

1.2 Preparation of electrodes (YTU, CPERI)

1.3 Physicochemical characterization (CPERI, KIT, YTU)

1.4 Characterization of interfaces (KIT)

Deliverables

Solid electrolytes. Preparation protocol and selection of best materials

Electrodes/catalysts. Preparation protocol of anodes and cathodes

Report on materials properties

Report on corrosion and failure mechanisms in interface

Milestones

Selection of solid electrolyte membranes

WP's Description

WP 2: Anodic electrodes selection (CPERI, YTU)

2012						2013						
7	8	9	10	11	12	1	2	3	4	5	6	7

2.1 Activity and stability tests on H_2S decomposition (YTU, CPERI)

2.2 Activity and stability tests for H_2SO_4 production (YTU, CPERI)

2.3 Surface chemistry analysis and mechanistic considerations (CPERI, YTU)

Deliverables

Activity list of catalysts/electrodes for both reactions

Report on reaction mechanism for both reactions

Milestones

Selection of most promised anodic composites

CE.R.T.H.

WP's Description

WP 3: Single cell fabrication and electrochemical characterization (CPERI, KIT, YTU)

2013												2014
1	2	3	4	5	6	7	8	9	10	11	12	1

3.1 Development of a metallic support system for the micro reactor (KIT)

3.2 Fabrication of micro reactors and electrochemical cells (KIT)

3.3 Chemical/electrochemical characterization of micro-reactors (KIT, CPERI, YTU)

Deliverables

Development of the metallic support system

Cell fabrication

Report on the chemical and electrochemical characterization of micro-reactors

Milestones

Micro-reactor ready for use

WP's Description

WP 4: Reactor and fuel cell studies (CPERI, KIT, YTU)

2013						2014									
7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10

4.1 Open and closed circuit electrocatalytic measurements (CPERI, YTU, KIT)

4.2 Fuel cell measurements (CPERI, KIT)

4.3 Long-term stability tests (CPERI)

4.4 Process modeling (CPERI, KIT)

Deliverables

Report on the open and electro-catalytic measurements for H_2 production

Report on fuel cell measurements

Report on degradation and flexibility of operation

Report on the CFD and dynamic simulation results and control analysis

Milestones

Flexible operation with minor degradation for 100 h of operation

Dynamic modeling and control of a regenerative based on H^+ conductors

WP's Description

WP 5: System Integration and TEE (CPERI, KIT, YTU)

2013			2014												2015
10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1

5.1 Techno- economic evaluation(CPERI)

5.2 Design and optimization of the scaled–up integrated process (CPERI)

Deliverables

Report of the methods and requirements for H_2S from Black Sea deep waters

Report on the techno-economical analysis of the integrated scaled-up process

Report on the steady-state model, integrated scaled-up process

Milestones

Techno-economic evaluation

Proposed optimized flow-sheet

WP's Description

WP 6: Project management and results dissemination (CPERI, KIT, YTU)

2012											2013												2014												
2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1

6.1 Project management (CPERI)

6.2 Results dissemination (CPERI)

6.3 Exploitation of project results and TIP(CPERI)

Deliverables

- Consortium Agreement
- Project web-site
- 1st year progress report &meeting
- Midterm progress report & meeting
- 2nd year progress report & meeting
- Final report & meeting
- Technology Implementation Plan

Milestones

- Consortium Agreement
- Midterm progress report
- Final report
- Technology Implementation Plan

Work Performed

WP1 PREPARATION AND CHARACTERIZATION OF MATERIALS (1 - 12)

2012	2013	2014	2015
2 3 4 5 6 7 8 9 10 11 12	**1** 2 3 4 5 6 7 8 9 10 11 12	1 2 3 4 5 6 7 8 9 10 11 12	1ta

1. Preparation and selection of solid electrolytes (01-09)

- ✓ Based on literature, we selected the $BaZr_{0.85}Y_{0.15}O_{3-\delta}$, BZY, proton-conducting perovskite as solid electrolyte due to its mechanical/chemical stability and good performance under H_2S atmosphere.
- ✓ $BaZr_{0.85}Y_{0.15}O_3$ electrolyte was synthesized employing the solid state reaction method. The formation of barium carbonate was prevented by sintering at 1450 °C in a compacted form.

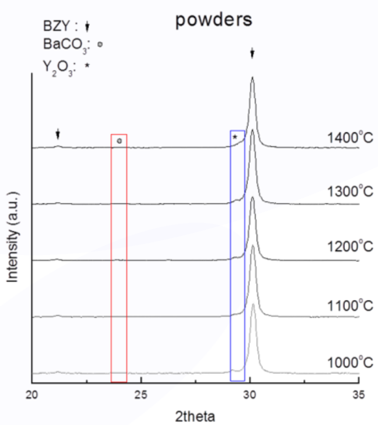
POWDER form:

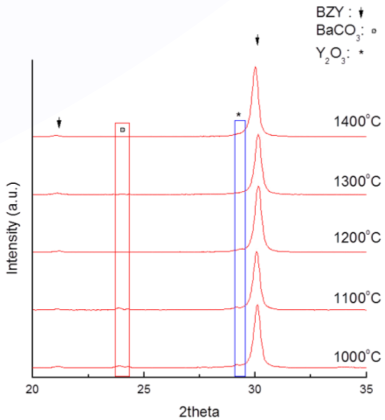
Impurities in traces up to 1400° C

Not a pure perovskite

$BaCO_3$ traces up to 1300° C

Y_2O_3 traces persistent up to 1400° C





Protected Pellets :

$BaCO_3$ traces up to 1100° C &

Y_2O_3 traces up to 1100° C

Work Performed

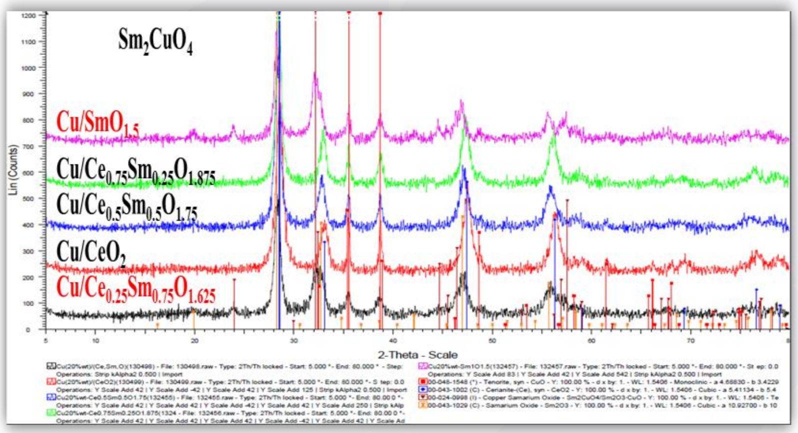
WP1 PREPARATION AND CHARACTERIZATION OF MATERIALS (1 - 12)

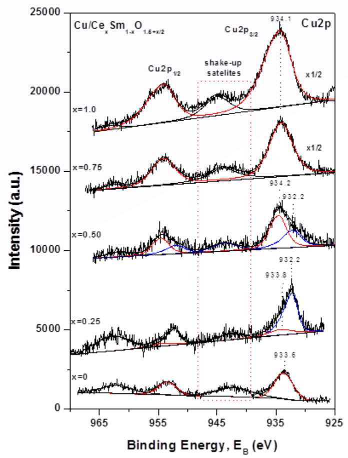
2012	2013	2014	2015
2 3 4 5 6 7 8 9 10 11 12	**1** 2 3 4 5 6 7 8 9 10 11 12	1 2 3 4 5 6 7 8 9 10 11 12	1

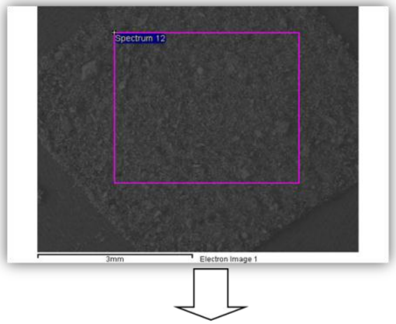
2. Preparation of electrodes (01-09)

3. Physicochemical characterization (3-12)

- ✓ Synthesis (impregnation) and physicochemical characterization (BET, ICP, XRD, XPS, SEM) of 20%Cu/$Ce_{1-X}Ln_XO_Z$ anodic composites (where Ln: Gd, Sm, Pr, La, Nd) and LaSrMoO – LaSrVO perovskites (citrate method).







Element	Weight %	Atomic %
Mo	42.42	19.00
La	31.01	9.59
O	26.58	71.40
Total	100.0	

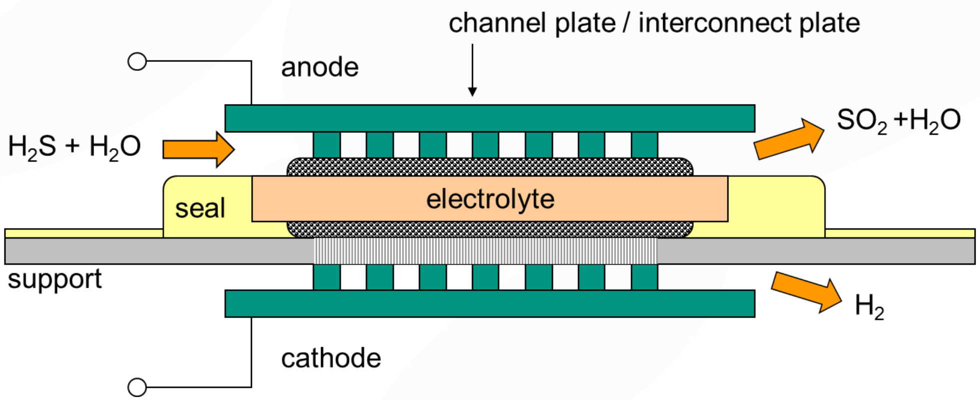
Work Performed

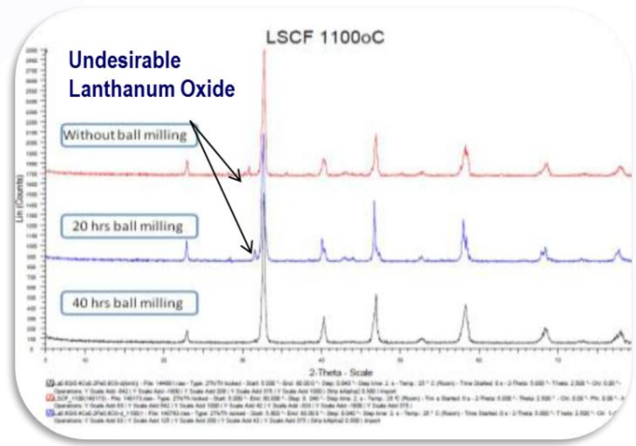
WP1 PREPARATION AND CHARACTERIZATION OF MATERIALS (1 - 12)

2012	2013	2014	2015
2 3 4 5 6 7 8 9 10 11 12	**1** 2 3 4 5 6 7 8 9 10 11 12	1 2 3 4 5 6 7 8 9 10 11 12	1

4. Characterization of interfaces (3-12)

- ✓ LSCF perovskite (cathode) was prepared using the citrate method with sufficient phase purity at T>1100 °C and 40 h ball milling before calcination.
- ✓ All materials will be checked concerning interface integrity and corrosion rates.





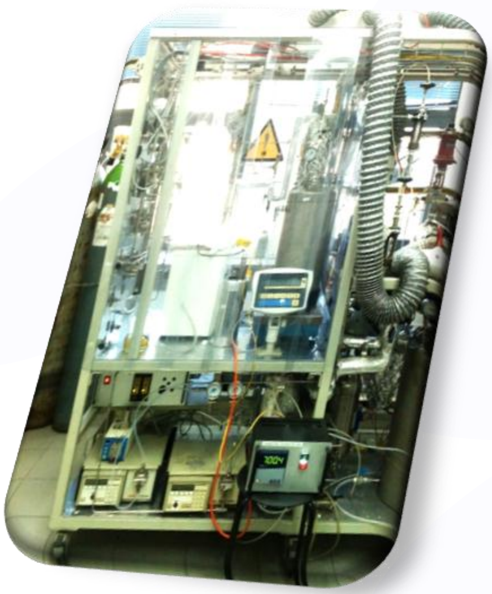
Work Performed

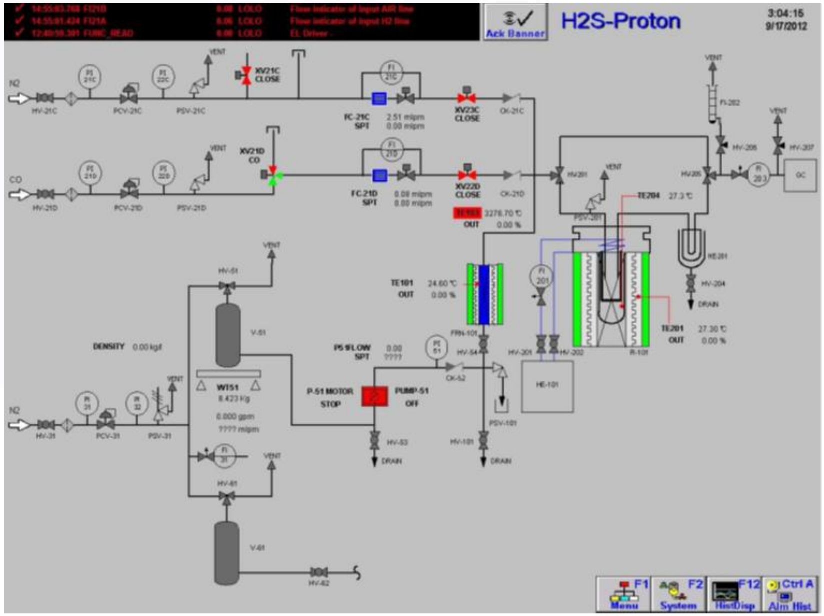
WP2 ANODIC ELECTRODES SELECTION (6 - 18)

2012	2013	2014	2015
2 3 4 5 6 **7 8 9 10 11 12**	**1 2 3 4 5 6 7** 8 9 10 11 12	1 2 3 4 5 6 7 8 9 10 11 12	1

1. Activity and stability tests on H_2S decomposition (6-12)

- ✓ Preparation of the experimental set-up
- ✓ Activity/Stability tests in the absence and presence of H_2O





Work Performed

WP2 ANODIC ELECTRODES SELECTION (6 - 18)

2012	2013	2014	2015
2 3 4 5 6 **7 8 9 10 11 12**	**1 2 3 4 5 6 7** 8 9 10 11 12	1 2 3 4 5 6 7 8 9 10 11 12	1

1. Activity and stability test on H_2S decomposition (6-12)

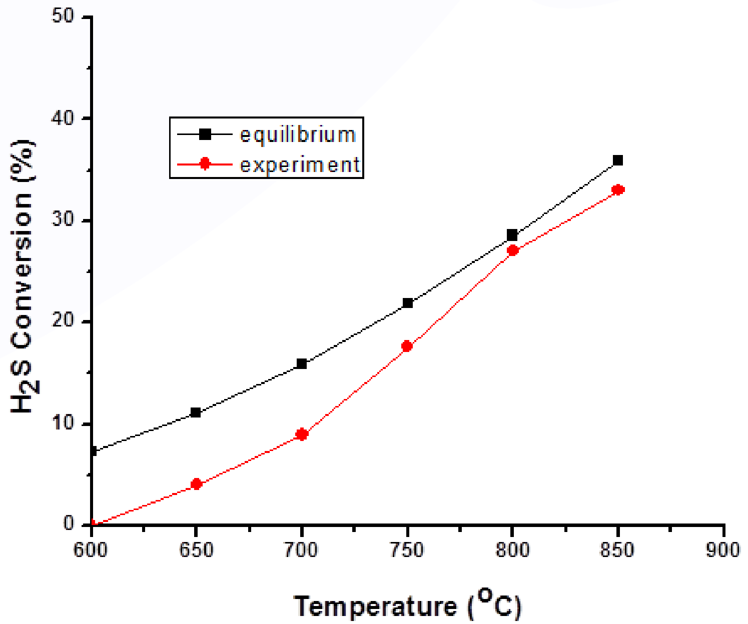
- ✓ Preparation of the experimental set-up
- ✓ Activity/Stability tests in the absence and presence of H_2O

Catalyst – 20%Cu/CeO_2

Weight – 250 mg (+ 250 mg quartz)

Flow rate – 100 cm^3/min

Reacting mixture – H_2S/Ar (1%)

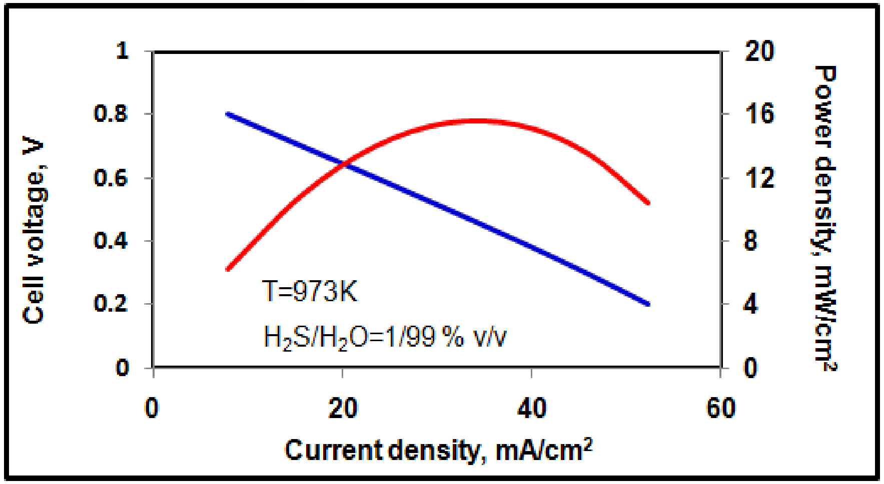


Work Performed

WP4-5 Reactor and fuel cell studies System Integration and TEE (18-36)

- CFD modelling overview concerning species and temperature distribution.
- Process modelling requirements in a scaled-up regenerative process.
- Process control issues regarding effective model based advanced strategies.
- System integration on the framework of an integrated system with multiple units effectively connected to each other.
- Technoeconomic analysis ranging from H_2S extraction up to product exploitation.

A feed concentration of ca. 0.5% H_2S in H_2O is thermodynamically optimal for the electrochemical reactor and that the heat management is crucial for an economical operation.



Work Performed

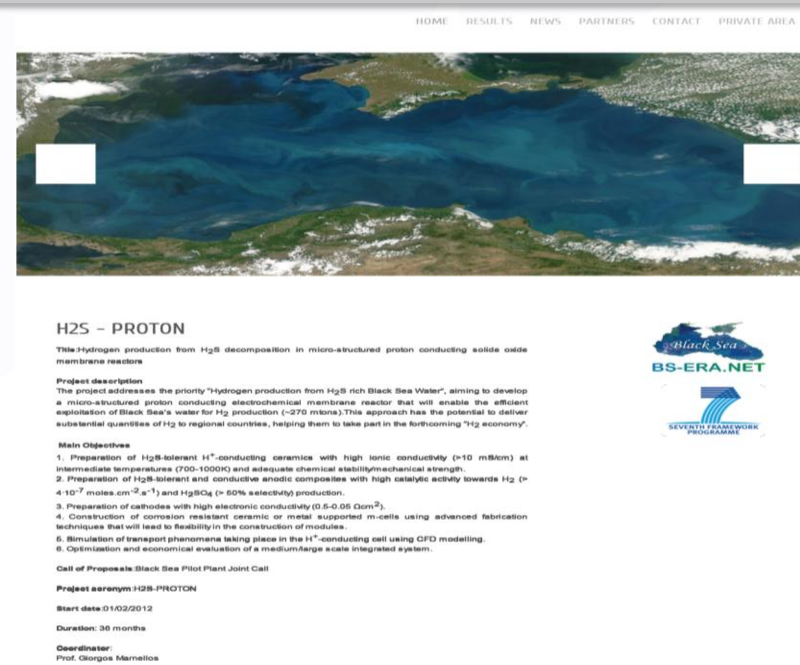
WP6 Project management and results dissemination (1-36)

2012	2013	2014	2015
2 3 4 5 6 7 8 9 10 11 12	1 2 3 4 5 6 7 8 9 10 11 12	1 2 3 4 5 6 7 8 9 10 11 12	1

1. **Project Management**
2. **Results dissemination**
3. **Exploitation of project results and TIP**

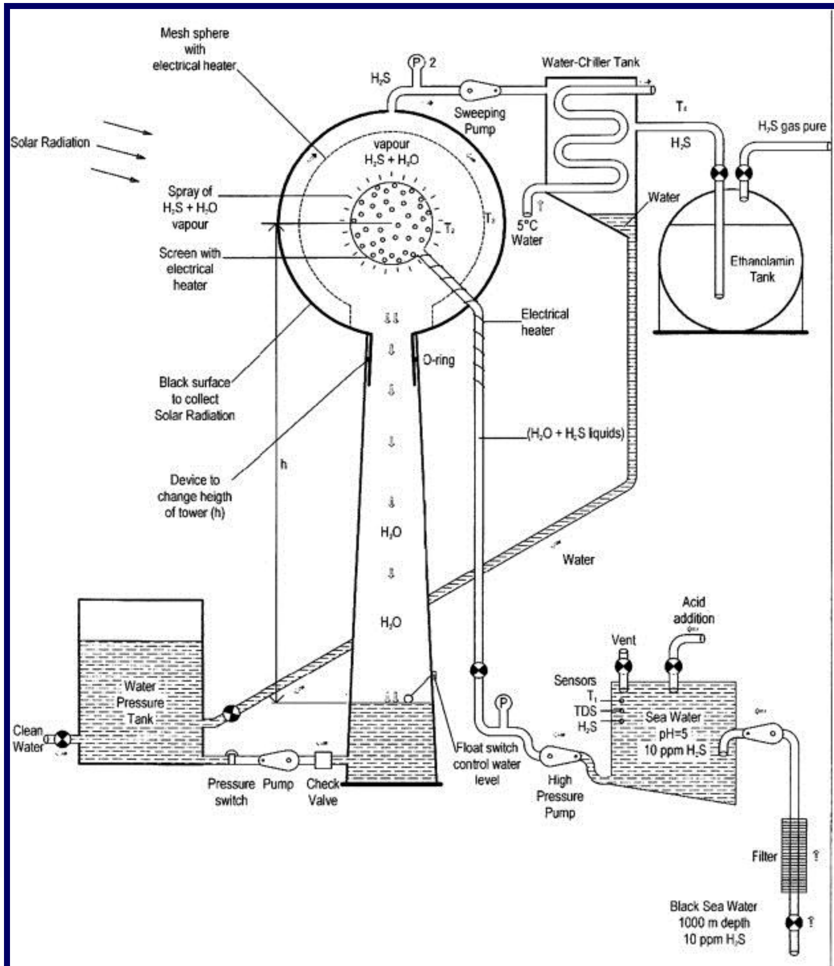
- **Consortium Agreement**
- **Umbrella Agreement**
- **Kick- off Meeting**
- **6th month Meeting**
- **Skype Meeting**
- **Project web-site**

h2sproton.cperi.certh.gr



THANK YOU FOR YOUR ATTENTION

PROGRESS COMPARISON FOR H_2S EXTRACTION



H_2S EXTRACTION

Pumping water containing H_2S from the correct sea depth.

Collect sea water at a surface tank.

Separation of water and H_2S through solar heating and/or electrical heaters.

H_2S decomposition through the proposed electrochemical method (regenerative mode).

outside and inside Black Sea water *

	Inside
	Only pipes for transferring H_2S to the surface
	No tanks for water storage
	Unit operation pressure 100 atm
	No pumping stations, just a small pump
…pe	No pollution due to H_2S escape
Pump with specific characteristics	Immersion pump with same power

S.A. Naman, I.E. Ture, T.N. Veziroglu, Industrial extraction pilot plant for stripping H_2S gas from Black Sea water Int. J. Hydrogen Energy, 33 (2008) 6577-6585.