Russian R&D in Hydrogen Energy

2nd Implementation-Liaison Committee-Meeting of the IPHE
Reisensburg Castle, Germany
01 March 2004 – 03 March 2004

In present Russian R&D in Hydrogen Energy is carried out within the Programs supported by:

- Ministry of Industry, Sciences and Technology
- Ministry of Atomic Energy
- Russian Aviation and Space Agency
- Russian Academy of Sciences

Lately private investors are facing to the Hydrogen Energy
(Norilskii Nikel has announced a $40 million program in Hydrogen Energy)

Basic R&D directions

- Novel hydrogen production technologies
- Hydrogen purification technologies
- Hydrogen storage
- Fuel Cells
- New catalytic systems
- New proton exchange membranes
- Hydrogen combustion systems
- Infrastructure
- Safety and standards

HYDROGEN PRODUCTION

- On-board and on-site H_2 and syn-gas production from hydrocarbon materials on the basis of plasma catalysis
- Plasmachemical large scale H_2 production from methane and acid gas in non-equilibrium SHF-dischargers
- Natural gas thermal decomposition and wood processing
- New catalytic systems and small scale fossil fuel processors
- Advanced electrolysis (SPE and alkaline)
- Advanced technologies for LH_2 production, storage and transportation

PEM-electrolyzers

Small scale production of PEM-electrolysers of different productivity (up to 10 m^3/h) was organized by RRC “Kurchatov institute” together with GUP Company MATYS. At present time electrolyzers are operating at current up to 1 A/cm^2 with energy consumption 3,9-4,2 $kW{\cdot}h/m^3$, platinum group metals loading is 1,6-3,5 mg/cm^2. Proved lifetime is 20000 hours.

The goals of proposed project – development of new generation of PEM-electrolysers for different pressures up to 30 atmospheres, with specific productivity up to 2 A/cm^2 with reduced energy consumption (3,7-4,0 $kW*h/m^3$) and price (to reach same price as for alkaline electrolyzers).

New membrane materials, modified platinum and not-platinum electrocatalysts, other construction materials, optimization of heat and mass transfer, improved design of electrolysis stack and the installation will be the subject of the R&D in the frame of the project.

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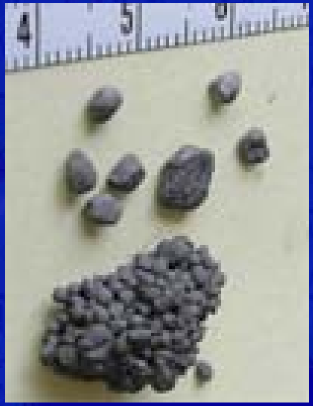
NATURAL GAS PROCESSING

FOR PRODUCTION OF HYDROGEN AND PURE CARBON MATERIALS

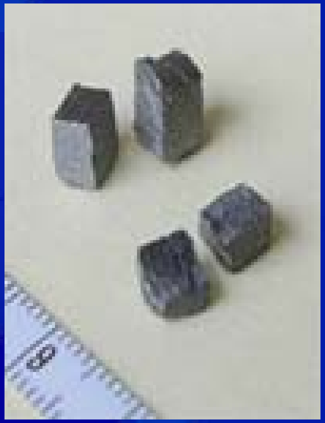
On the basis of two-stage pyrolysis of natural gas the technology to produce hydrogen from natural gas simultaneously with pure carbon material for broad commercial applications has been developed.

Thermal decomposition of natural gas is carried out in the heated porous matrix and according to the heterogeneous mechanism the pyrocarbon is formed in the pores of the matrix. As a result a solid carbon monolith is produced.

As a porous carbon skeleton for pyrocarbon stuffing other carbon containing materials can be used (e.g. wood waste products, generally the vegetable origin waste).



0.01	Moisture content,%	0.52
0.43	Volatile, %	1.12
0.04	Ash, %	1.54
0.02	Sulphite, %	0.30
99.56	C,%	97.38
0.25	H, %	0.27
33.18	Calorific value, MJ/kg	32.57
1.62	Density, g/cm^3	0.743



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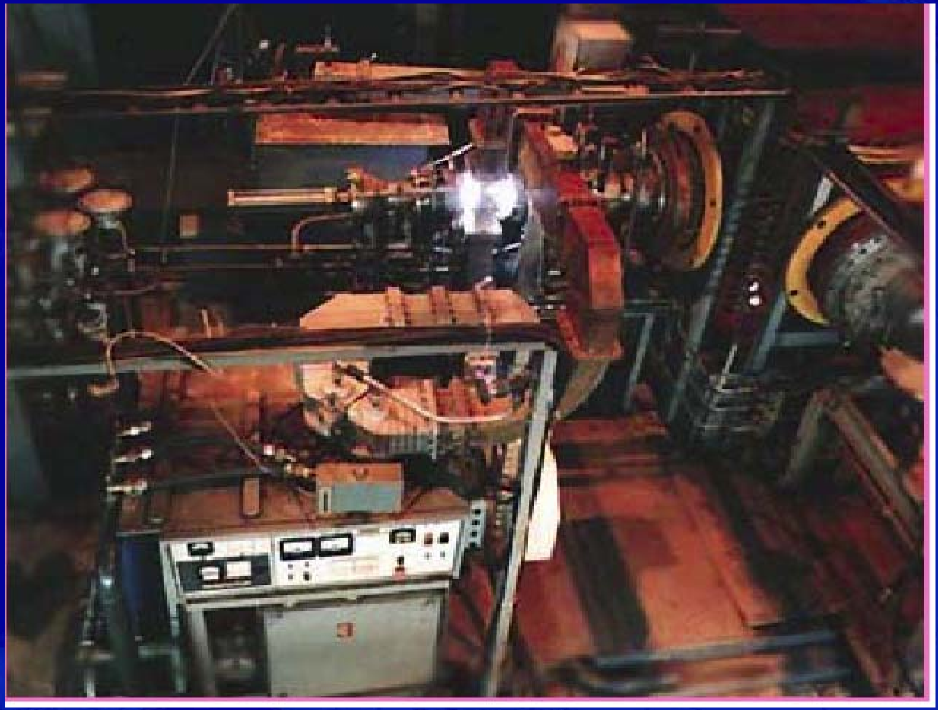
RRC "Kurchatov Institute's" Test Facility "POVOD" for Development and Scaling of Plasma Assisted Processes of Hydrogen and Syn-Gas Production



"POVOD" demonstration unit at RRC "Kurchatov Institute" was designed to investigate and demonstrate the whole set of gas-phase plasma chemical processes under effect of stationary microwave discharge with power range from 10kW to 1,000 kW at microwave frequency 915 MHz. Air, nitrogen, water vapor, carbon dioxide, methane, propane-butane, oxygen, argon with a flow rate up to 2,000 m^3/h at pressure between 0.005 atm – 1.0 atm can be used to burn MW discharge.

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Methane Conversion to $CO+H_2$ in Non-equilibrium Microwave Discharge

High power microwave set-up “POVOD” includes double side symmetric microwave energy input from one hand and a high speed (150-200 m/s) gas vortex chamber with vortex number 0.7-1.2 from the other hand.

Stable discharge proved for energy input from 0.1 kWh/m^3 to 1.2 kWh/m^3.

Experimental results have shown high efficiency methane conversion to synthesis gas ($CO + H_2$) in microwave plasma both for steam and carbon dioxide reforming.

Minimum energy cost for conversion degree 50% was about 1 kWh/m^3 and 1.5 kWh/m^3 per 1 m^3 of syn-gas.

Minimum energy cost for conversion degree ~100% was less than 0.8 kWh/m^3 per 1 m^3 of syn-gas, in case of oxygen presence in initial gas mixture.

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Acid Gas (H_2S – CO_2) Conversion in MW Discharge

Direct plasma chemical dissociation of hydrogen sulfide into hydrogen and sulfur

$$H_2S = H_2 + S$$

and syn-gas production from H_2S/CO_2 mixture

$$H_2S + CO_2 > H_2 + CO + S + H_2O.$$

have been experimentally tested under effect of different types of discharges: microwave, radio frequency, arc, gliding arc, etc.

The experimental value of energy consumption can be about 1 kWh per 1m^3 of H_2 or syn-gas, which is very close to an appropriate theoretical limit - 0.6 kWh/nm^3.

The demonstration plant with discharge power up to 1 MW and productivity up to 1000 m^3/h is in operation at the Natural Gas Treatment Plant in Orenburg (Russia).

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Microwave reformers of hydrogen raw material conversion into synthesis gas

Two converter types have been developed: based on the impulse periodical microwave discharge, and on the stationary discharge.

Stationary converter

Synthesis gas production: 20 nm^3/hour;

Converter size: below 350 x 500 x 500 mm,

Mass: 31.5 kg, converter volume: 0.1 m^3.

Typical gas composition at reactor exit:

N_2 < 54.2%; Syngas > 40.0%; CO_2 < 2.5%; $CH_4 + C_2H_4 + C_2H_2$ <3.3%

Electric power expenses for syngas production 0.15 kWh/m^3

Conversion efficiency (with heat recuperation) is 94%.

Reactor: mass – 2 kg; size 80 x 400 mm

Internal heat exchanger: mass – 1.5 kg; size 150 x 350 mm

Microwave generator: exit peak capacity – up to 6 kW, average capacity - 3 kW, mass – 18 kg, size – 203 x 304 x 368 mm.

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HYDROGEN SEPARATION, PURIFICATION AND STORAGE

- Systems with polymer membranes
- High-Performance Membrane Diffusion Hydrogen Purifiers
- MeHy-systems for hydrogen storage and purification
- Nano-structures for hydrogen accumulation
- Cryogenic tanks

Surface modification of polymer membranes for gas separation

MAIN FEATURES:
- Method improves the selectivity of any membrane containing polydimethylsiloxane (PDMS) in the surface layers.
- Productivity of the available apparatus (5 kW) is 0.3 m per minute.
- Higher efficiency

ADVANTAGES:
- prescribed membrane selectivity is available;
- 100 times improvement of selectivity;
- low treatment cost.

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High-Performance Membrane Diffusion Hydrogen Purifiers

The Prototype modules have undergone extensive trials in real industrial environment for uninterrupted period of operation of more than 2 years without any deterioration in performance and other characteristics, without any noticeable changes in appearance, and without any loss of hermeticity.

Technical Characteristics:

Hydrogen content in feed gas	30 – 98%	
Output Hydrogen Purity	99.9999%	
Temperature range	300 – 800 ^oC	
Tolerance to fouling feed gas impurities	up to 1.5 % H_2S, 15 % CO, 30 % CO_2	
Input feedstock pressure	0.15 – 10 MPa	
Output pure H_2 pressure	0.1 – 3 MPa	
Pure Hydrogen specific permeability	20 – 300 Nm^3/m^2 hr $MPa^{1/2}$	
Membrane element diameter	50 mm	150 mm
Hydrogen production rate	1.0 – 3.0 Nm^3/hr	70 – 120 Nm^3/hr
Module weight at max production	20 kg	200 kg
Pure Hydrogen output per kg of module weight	0.1 – 1.5 m^3	0.35 – 6.0 m^3

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Metal-hydride Storage and Purification Systems

Institute for High Temperatures (IVTAN) in cooperation with Moscow Power Engineering Institute (MPEI) and Moscow State University (MSU) created experimental MeHy systems for hydrogen storage (1.5 kg H_2) and purification (up to 20 nm^3/h).

To optimization of design and operation of devices the two-dimensional mathematical model of heat and mass transfer in MeHy reactors has been developed.

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Hydrogen-absorbing alloys and Nanomaterials from low-cost raw materials

New intermetallic alloys and composed nanostructures are investigated in Research Institutes of RAS and Moscow State University: $MmNi_5$-based alloys with hydrogen content up to 1.45 mass.% and electrochemical capacity 300-330 mAh/g, and $(Ti,Zr)(V,Mn,Fe,Ni)_2$ alloys with hydrogen content up to 2 mass.% and electrochemical capacity 330-350 mAh/g. Special concern is given to the interconnection of composition and alloy structure with hydride properties, influence of redistribution of metallic components in the alloy within the homogeneity region on AB_2 crystal structure. The mathematical model for prediction of dependence of hydride dissociation pressure on the alloy composition was developed.

Cryogenic hydrogen tanks characteristics JSC "Cryogenmash"

Parameter	РЦВ-63/0.5	РЦГ-250/1	РЦГ-250/0.8	РСВ-1400/1	ЦТВ-25/0.6 t	ЦТВ-45/1.0 t
Capacity, m^3	66.3	246	246	1,437	25	45
Working pressure, MPa	0.5	1.0	0.85	1.05	0.7	1.0
Product mass, t	4.43	15.7	15.7	96.79	1.5	2.74
Evaporation loss daily, %	0.52	0.3	0.35	0.13	1.2	1.0
Dimensions, m						
length		36.35	36.35	-	14.35	15.7
width	3.68	3.7	37.4	-	2.75	2.5
height	12.65	3.92	3.92	20.1	3.92	3.7
Tank mass, t	22	72	72	360	19	21.76

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FUEL CELLS

- Power units on the base of Hydrogen-Air Alcaline FC
- Solid Oxide FC
- Solid Polymer FC
- New Proton Exchange Membranes

Electrochemical Generator "Cascade-IP"

The generator is based on advanced Alkaline Fuel Cell modules. One of the unique features of the generator is a patented zero-waste regenerative scrubber used for the removal of carbon dioxide from the incoming air. The scrubber reduces the operational cost and increases the overall serviceability of the generator.

Performance

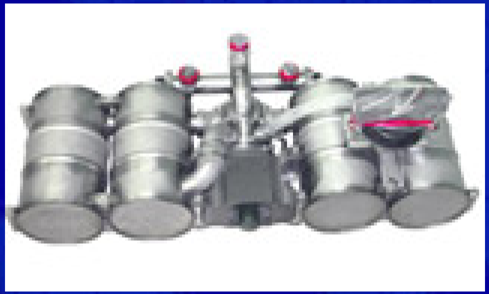
Maximum power: 6.0 kW; Voltage: 30.0 – 42.5 V
Maximum current: 200 A; Fuel: Hydrogen
H_2 consumption < 4.5 m^3/h; Air consumption < 36 m^3/h
Pressure: Atmospheric

Operating conditions

Ambient temperature: -20 to +40 °C
Relative humidity (max): 98% at 25 °C

General

Dimensions: 1250 x 582 x 863 mm; Gross weight: 240 kg
CO_2 scrubber: built-in, regenerative
Start-up: self-starting with built-in hydrogen burner < 15 min at 20 °C
Electrolyte: 6.6 M KOH (aqueous solution)



The scrubber

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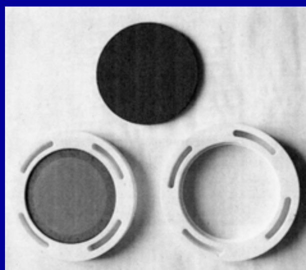
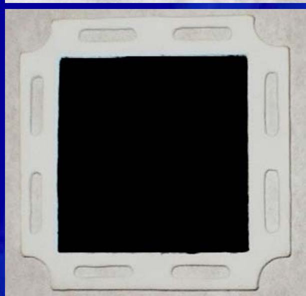
Planar Solid Oxide Fuel Cell





I. Solid oxide electrolyte: YSZ - $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$
Diameter: 60 – 100 mm
Thickness: 250 – 500 μm

II. Electrolyte supported SOFC (operation temperature ~ $950^{O}C$):
Electrolyte: YSZ (thickness 250 – 500 μm)
Anode: NiO + YSZ
Cathode (two layers): (I) LSM ($La_{0.85}Sr_{0.15}MnO_3$) + YSZ; (II) LSM

III. Anode supported SOFC (operation temperature 800 - $850^{O}C$)
Thin-film electrolyte: YSZ (thickness 5 – 20 μm)
Anode: NiO + YSZ (thickness 500 – 1000 μm)
Cathode (two layers): (I) LSM + YSZ ; (II) LSM

Experimental Planar SOFC Stack
Number of cells: 5 – 40; Cell configuration: round or rectangular
Operation temperature: 900 - $950^{O}C$
Stack-average power density: 200 – 250 mW/cm^2
Fuel: H2 or syn-gas Oxidant: air

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Proton exchange membranes and membrane electrode assemblies for PEMFC and DMFC

Russian research center “Kurchatov institute” together with OAO “Plastpolymer” developed perfluorinater membrane with functional sulfo-groups for PEMFC. Small scale production of such membrane was organized by extrusion technology. The parameters of this membrane are close to the Nafion ones. In recent years new methods of membrane material solution production, laboratory methods of membrane production by casting technology, new methods of the membrane electrode assemblies production were developed.

Expected membrane parameters:

Specific resistance – about10 Ohm·cm at 20^0C
Thickness – 30 – 120 μm
Density – 1.95 – 2.10 g/cm^3
Exchange capacity – 0.85 – 1.10 mg * eq./g
Relative elongation at rupture – 40 – 60%
Water concentration 10-50%,
Operating temperature – up to 105^oC

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HYDROGEN COMBUSTION SYSTEMS

Small-scale high-pressure H_2/O_2-steam generators

Small-scale high-pressure H_2/O_2-steam generators are designed for use in stationary and mobile autonomous hydrogen zero emission power units (ZEPU) based on 30-150 kW mini-turbine. The main features of experimental device:

working pressure, MPa: 1-4
steam temperature, K: 600-1000
thermal capacity, kW: 40-156
length, mm: 300
max diameter, mm: 90.

Fields of application: transport, autonomous energy supply systems, including systems based on renewable resources (solar and wind power plants with hydrogen energy storage). In combination with steam or gas-steam mini-turbine and electric generator such systems form compact and ecologically clean power plants for various vehicles: automobiles, locomotives, ships, with efficiency well comparing with fuel cells but much cheaper.

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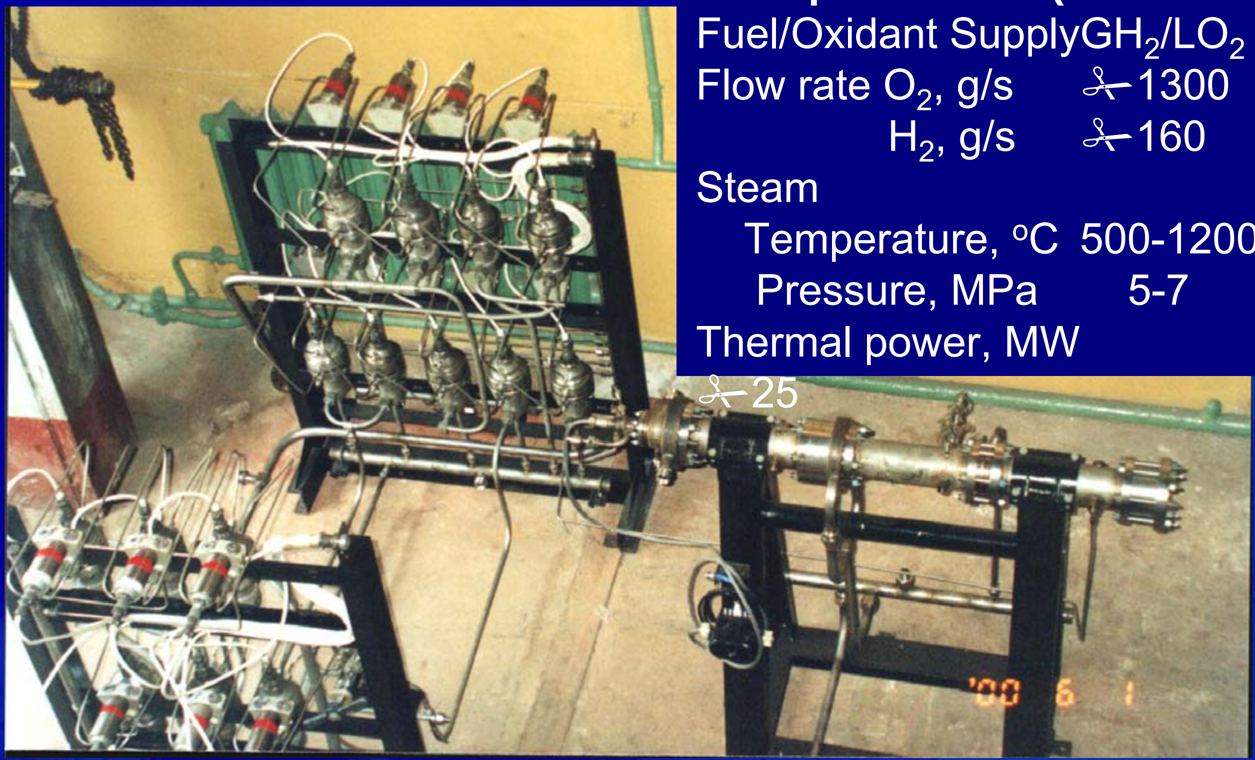
High-pressure H_2/O_2-steam generators



Experimental high-pressure H_2/O_2-steam generator parameters (IVTAN and Keldysh Center):

Fuel/Oxidant Supply	GH_2/LO_2	GH_2/GO_2
Flow rate O_2, g/s	✁1300	✁1400
H_2, g/s	✁160	✁170
Steam		
Temperature, °C	500-1200	500-1200
Pressure, MPa	5-7	7-10
Thermal power, MW	10-18	✁25

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SAFETY AND STANDARDS

- Experimental investigations and mathematical modeling on Fire and Explosion Safety
- Sensors and reburners
- Safety Regulations and Standards

Catalytic Hydrogen Reburner

Features:

Minimal hydrogen concentration in air: 0.7% (T < 70 °C), not limited (T > 70° C)

Water influence: relaxation time increase (T < 70° C), no influence (T > 70° C)

Relaxation time: less than 20 s (T < 70° C)

(4vol.% H_2): less than 1 s (T > 70° C)

Allowed humidity: up to 100%

Model	Dimensions, mm	Capacity, nм^3 /h (4vol.%H_2)
1	100×·100×·300	0.7
2	200×200×1000	7.5
3	500×500×3000	100

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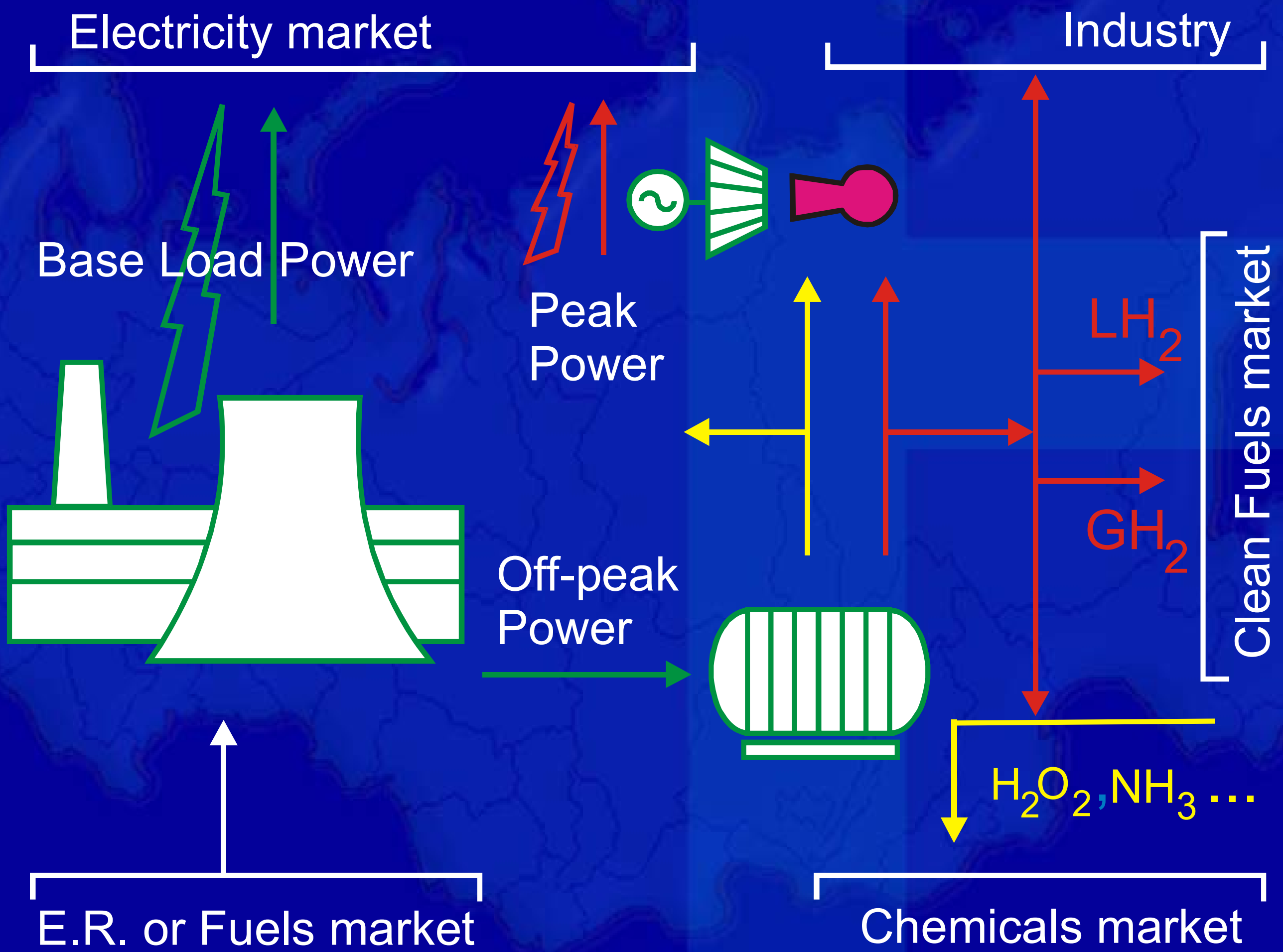
INFRASTRUCTURE
and
SOCIAL ECONOMY
STUDIES

Integrated system of co-production of energy and chemicals from excess resources of Energy System



Liquid hydrogen Production facility. View of construction site.

Firing tests of rocket engines at tilted test stand

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