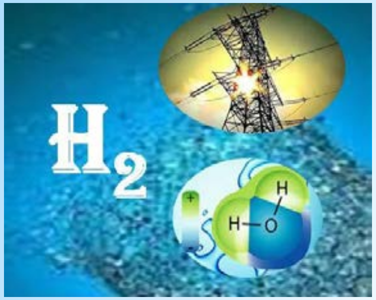


Research Program of the NAS of Ukraine

“Development of Scientific Principles for Hydrogen Production, Storage and Use in Autonomous Energy Supply Systems”

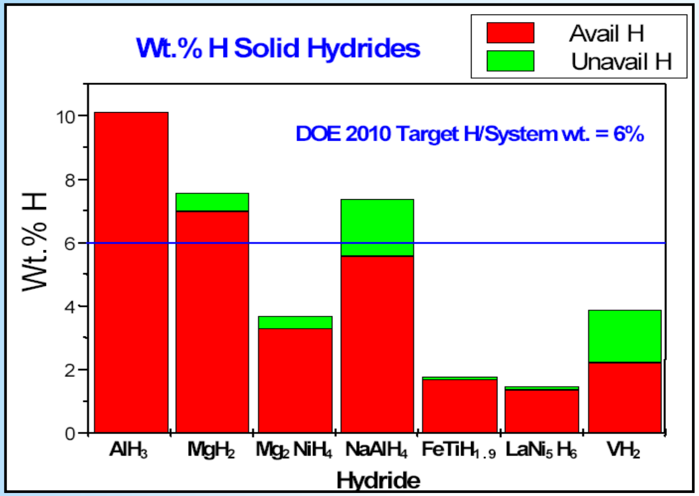
Development of MgH_2-based hydrogen storage & generation materials and optimization of the hydrogen supply system for fuel cells

Project № 12-21

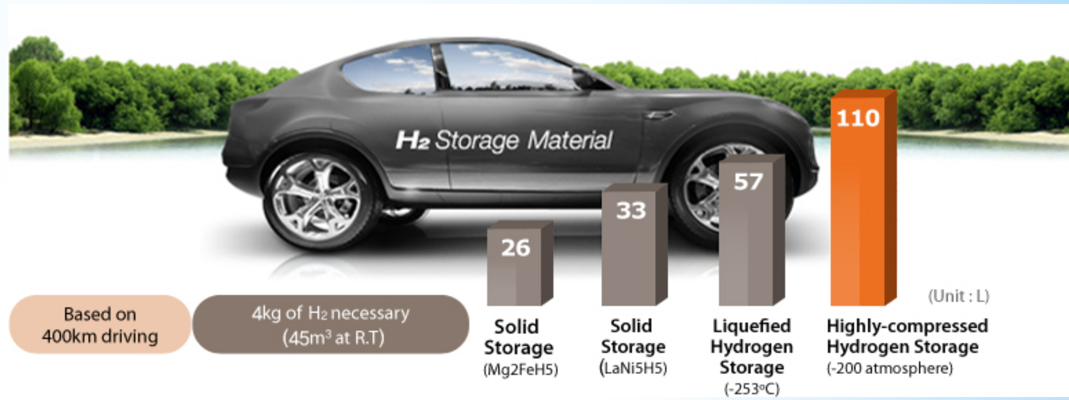
Head of the Project: Prof., Dr.Sci. Ihor Yu. Zavaliy
Participants: Dr. V.V. Berezovets, Dr. A.R. Kytsya, Dr. Yu.V. Verbovytskyy,
Karpenko Physico-Mechnical Institute of the NAS of Ukraine

25 November 2021

PROMISING MATERIALS FOR HYDROGEN STORAGE



L.Schlapbach, A.Zuettel. Hydrogen-storage materials for mobile applications. Nature. 414 (2001) 353-358



ADVANTAGES of MgH_2:

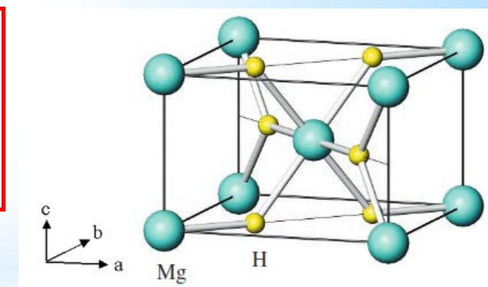
high weight content of hydrogen (7.6%)
reversible adsorption-desorption

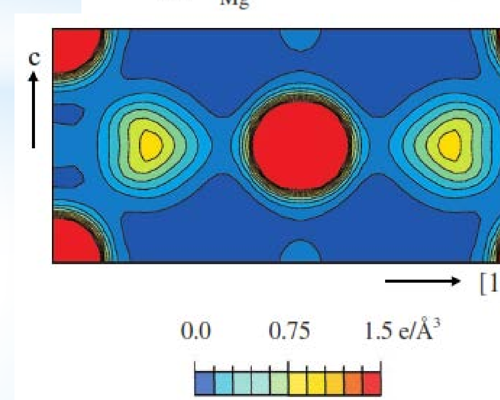
low cost, non-toxicity

DISADVANTAGES of MgH_2:

high temperature and low speed
of the adsorption-desorption,

low cyclic stability





Improving of hydrogen sorption characteristics of MgH_2

- *microstructure change - reducing the size of the grains, creating defects*
- *adding catalysts*
- *structural modification and synthesis of new compounds*

SYNTHESIS OF NEW HYDRIDES OF COMPOSITES, INTERMETALLIC COMPOUNS AND ALLOYS

DIFFERENT METHODS OF SYNTHESIS

Cmponents: metal powders RE, Mg, Ti, Ni, Co, etc

Melting in arc furnace in argon atmosphere

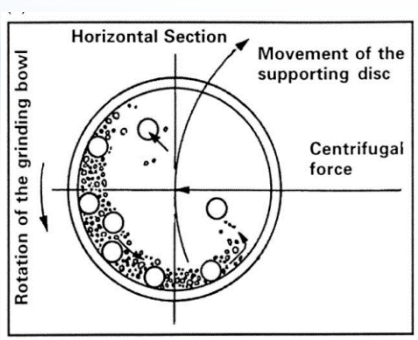
↓

Annealing of the alloys

The product of milliong: nanocrystalline MgH_2

↓

Particle size ≤0.5 мкм



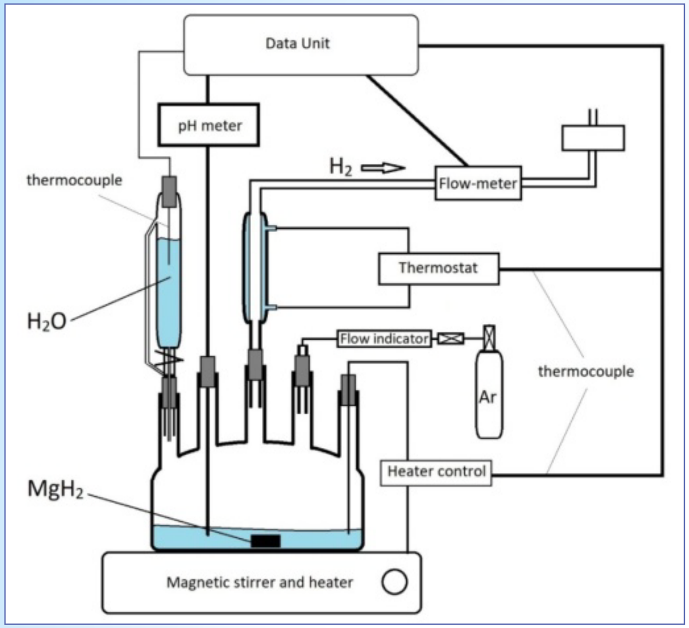
GAS HYDROGENATION AND THERMODESORPTION, 0-2 MPa H_2

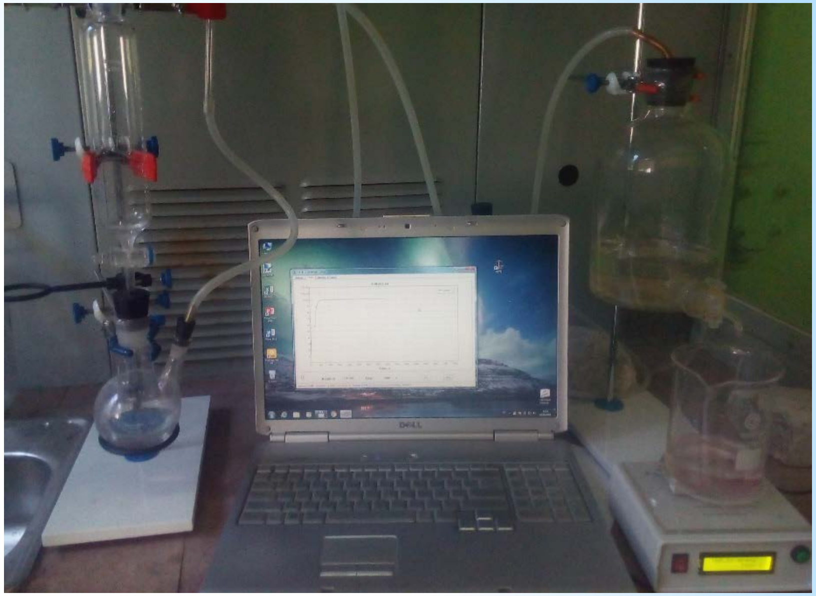
↓

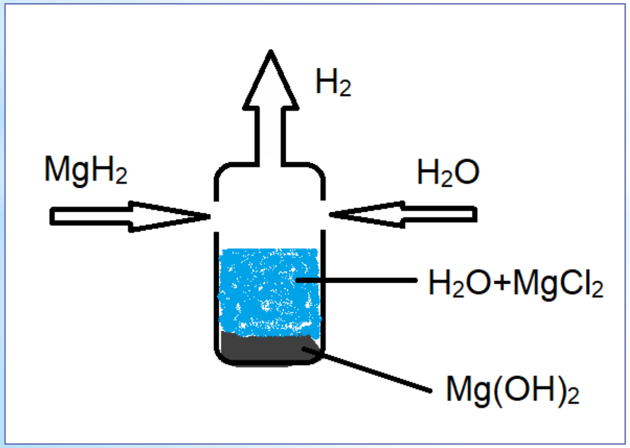
XRD, SEM, EDH studies

METHODS OF HYDROGEN GENERATION STUDIES

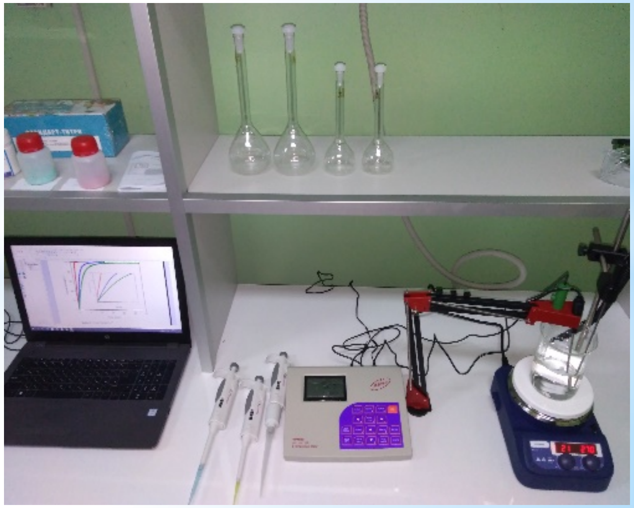
Scheme and device for the hydrolysis reactions studies



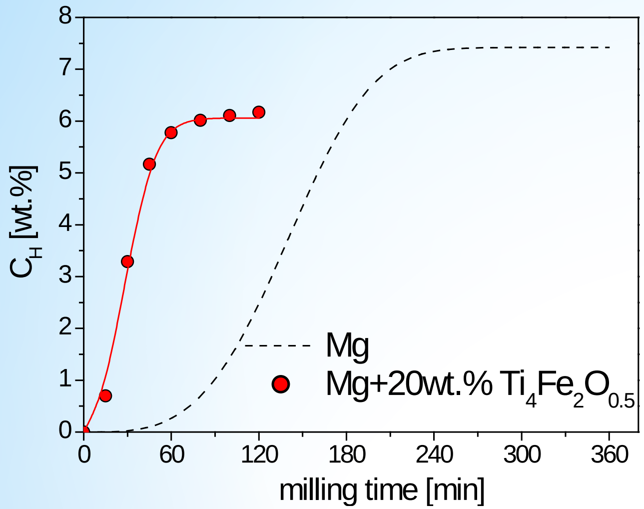




Flowmeter
Sierra Smarttrak-100L



Mechanochemical hydrogenation $Mg + H_2 \rightarrow MgH_2$

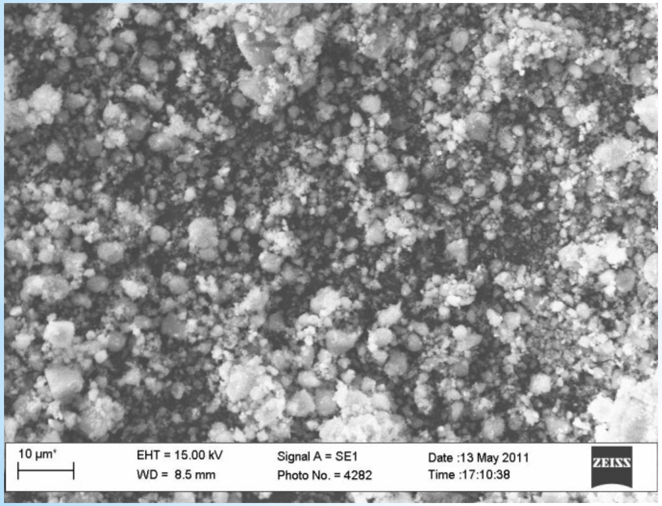


The traditional method of synthesis:

T= 350 °C; P_{H2} = 3-10 MPa; t=6-300 h;
the degree of conversion ≤90%;
required prior activation

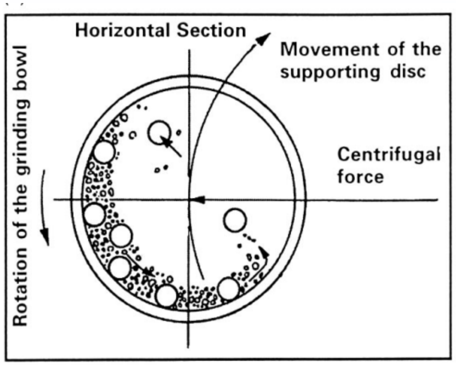
Mechanochemical synthesis:

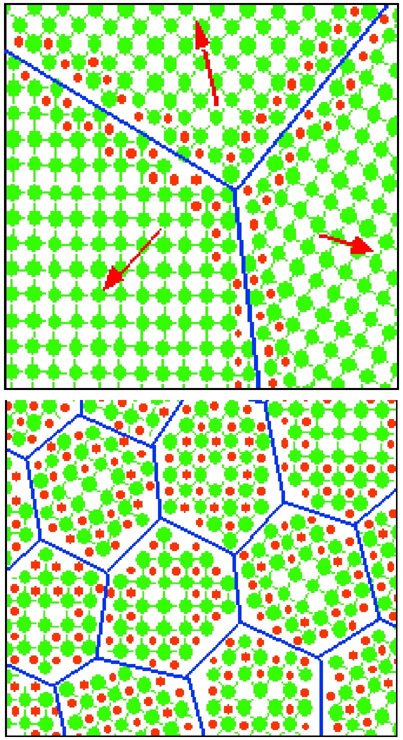
T= 20 °C; P_{H2} = 2-3 MPa; t=4-6 h
not require activation;
100% conversion Mg→MgH_2



Products of milling: nanocrystalline MgH_2

Size crystallites <10 nm
≤0.5 microns particles

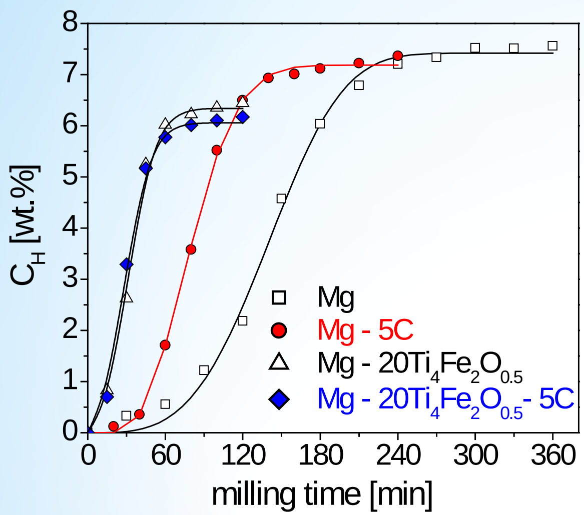


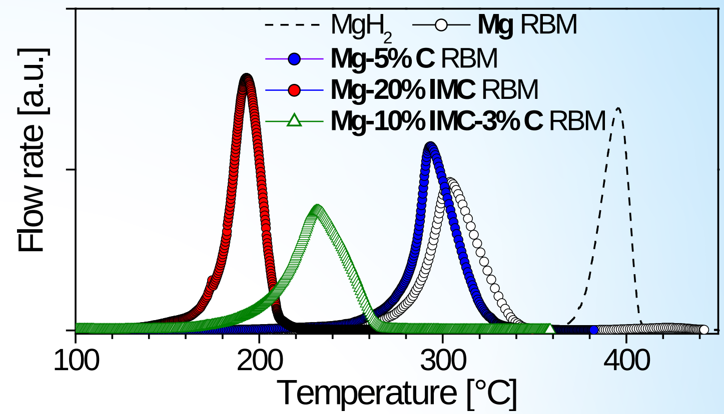


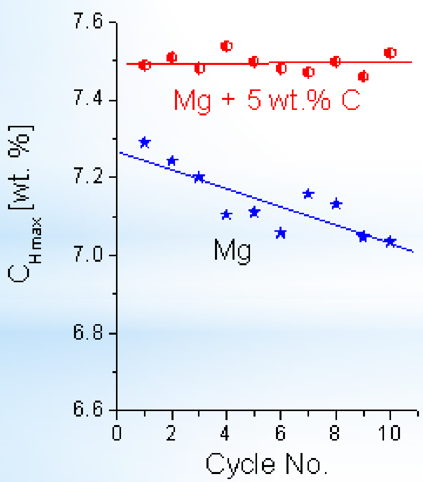
*TERNARY HYDRIDE COMPOSITES : Mg + **IMC + graphite***

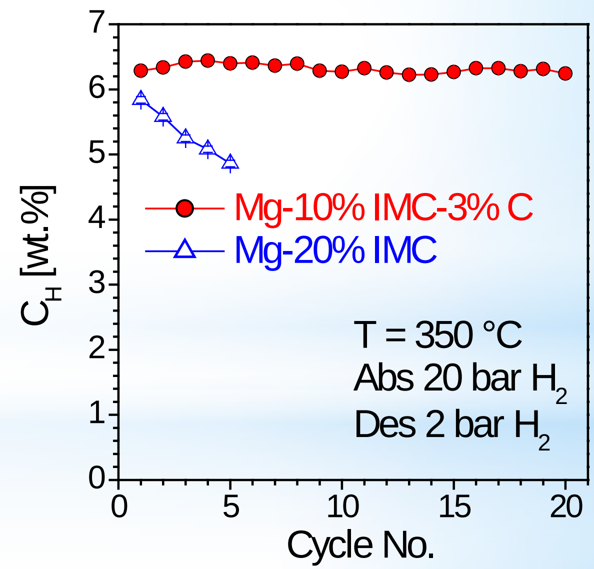
Combining catalytic impact of IMC and stabilizing influence of graphite

Mechanochemical hydrogenation



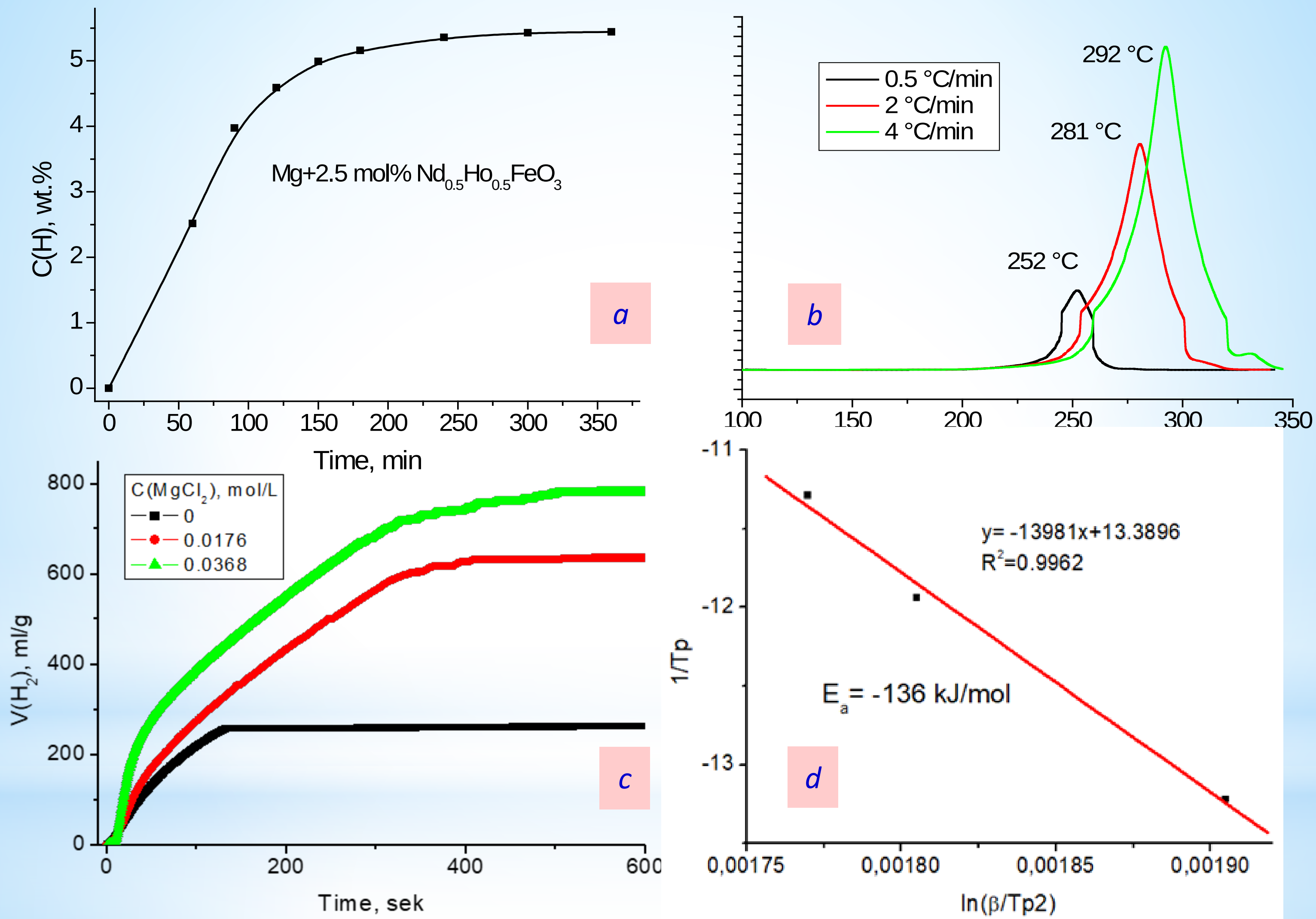






***V.V. Berezovets, R.V. Denys, I.Yu. Zavaliy, Yu.V. Kosarchyn*. Effect of Ti-based nanosized additives on the hydrogen storage properties of MgH_2. *International J. of Hydrogen Energy*. Available online 1 April 2021. https://doi.org/10.1016/j.ijhydene.2021.03.019**

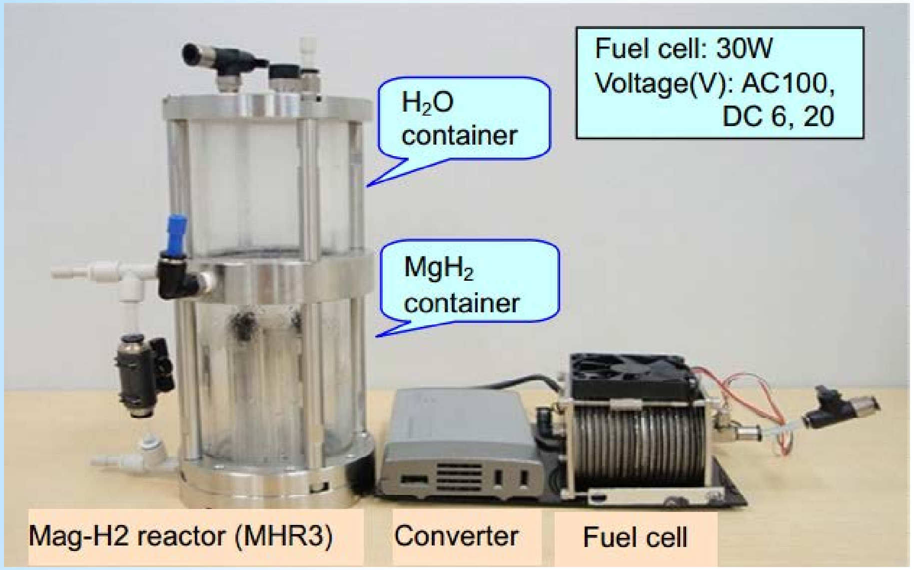
NEW MgH_2-BASED COMPOSITES with ADDITIVES of the $REFeO_3$ NANOPOWDERS



Curves of hydrogen absorption-desorption (*a, b*), hydrogen release by hydrolysis (*c*) and calculation of activation energy (*d*) for Mg–2.5 mol % nano-$Nd_{0.5}Ho_{0.5}FeO_3$

MgH_2-based hydrogen generating systems

BIOCOKE Lab. Ltd., Japan, www.biocokelab.com



Hydrolysis of Magnesium and its Hydride

Mg

- **Low price**
- **Wide industrial base**
- **Non-toxicity**
- **Prevalence**
- **Purity of the received hydrogen**

$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$, w = 3.3 вaг. %

$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2$, w = 6.5 вaг. %

Elimination of Mg disadvantages:

- grinding (powders MPF, AMD);
- temperature rise;
- hydrolysis in salt solutions (KCl);
- use of catalysts;
- alloying.

Elimination of MgH_2 disadvantages:

- grinding/nanostructurin
- temperature rise;
- mechanochemical treatment with additives (<10% NaCl, $MgCl_2$, NH_4Cl);
- hydrolysis in salt solutions (<30% KCl, NaCl, $MgCl_2$, NH_4Cl, $(NH_4)_2SO_4$, etc.)

- **hydrolysis in solutions of inorganic (HCl) and organic (citric) acids**

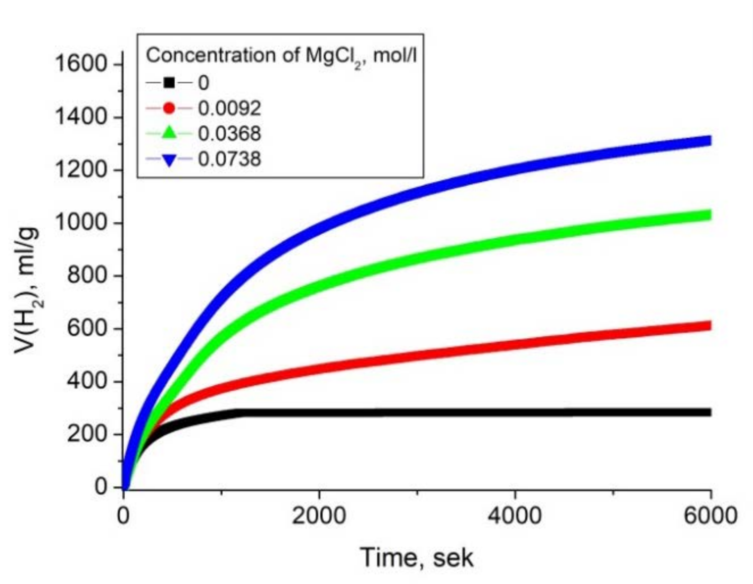
$Mg + 2HCl \rightarrow MgCl_2 + H_2$, $MgH_2 + 2HCl \rightarrow MgCl_2 + 2H_2$

$xMg + 2H_xAcid \rightarrow Mg_x(Acid)_2 + xH_2$, $xMgH_2 + 2H_xAcid \rightarrow Mg_x(Acid)_2 + (x+1)H_2$

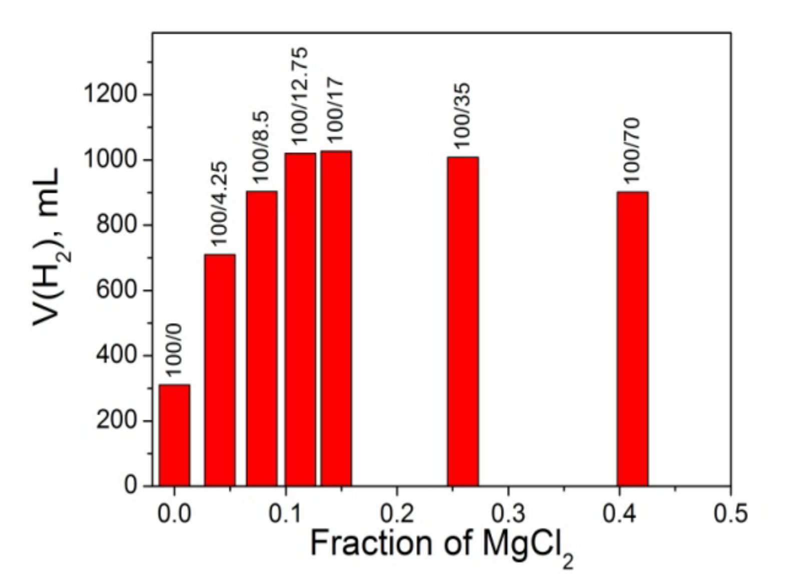
- **use of mixtures (synergistic evolution of hydrogen in combination with RH3 / RMg_3)**

Yu. Verbovytskyy, V. Berezovets, A. Kytsya, I. Zavaliy, V. Yartys. Hydrogen generation by hydrolysis of MgH_2. Materials Science – Vol. 56, No. 1, July, 2020 (Ukrainian Original Vol. 56, No. 1, January–February, 2020).

HYDROGEN GENERATION BY HYDROLYSIS OF MAGNESIUM HYDRIDE



Volume of hydrogen released from synthesized magnesium hydride composites.



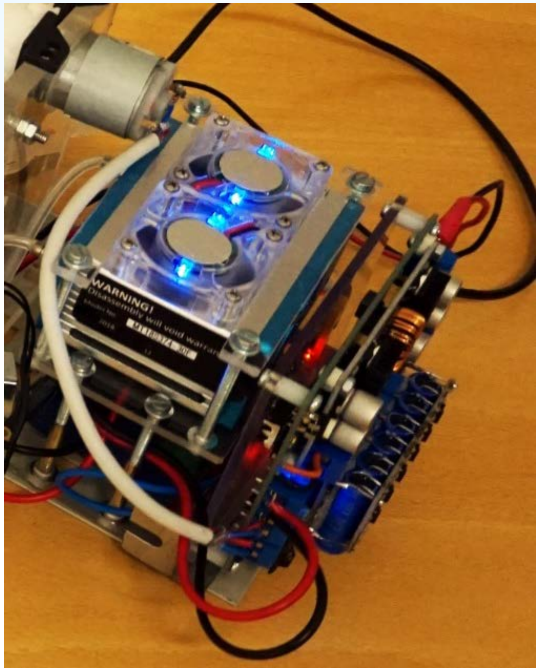
Dependence of the specific volume of generated H_2 from the mixture "MgH_2 + $MgCl_2$" on the share of $MgCl_2$.

An overview of the state of development of one of the most promising classes of materials based on for hydrogen evolution by hydrolysis reactions was published. The advantages of hydrogen generator – FC systems in comparison with other portable energy sources were discussed.

Hydrogen generation by hydrolysis of MgH_2. Yu.V. Verbovytskyy, V. V. Berezovets, A. R. Kytsya, I. Yu. Zavaliy, V. A. Yartys. Materials Science. Vol. 56, No. 1, July, 2020, pp.1-14.

Components of the system

Board evaluation for LM5118



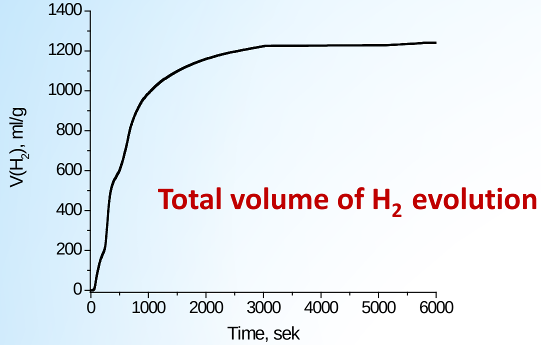
H-30 Fuel Cell Stack

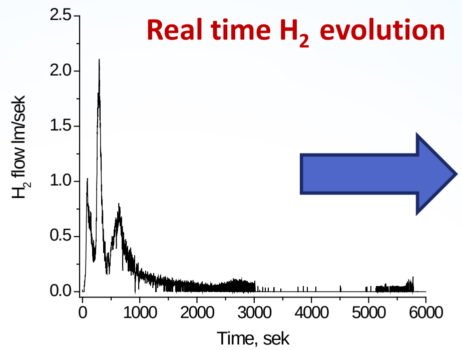
16V1.6F supercapacitor

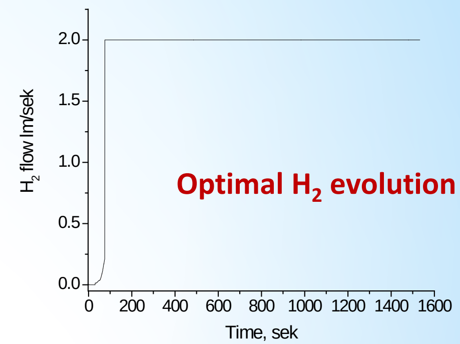
Dosing pump RS385-635, 12B

Optimization of the hydrogen supply system for fuel cells

Hydrogen evolution with controlled addition of water to MgH_2 + 5 wt.% $MgCl_2$

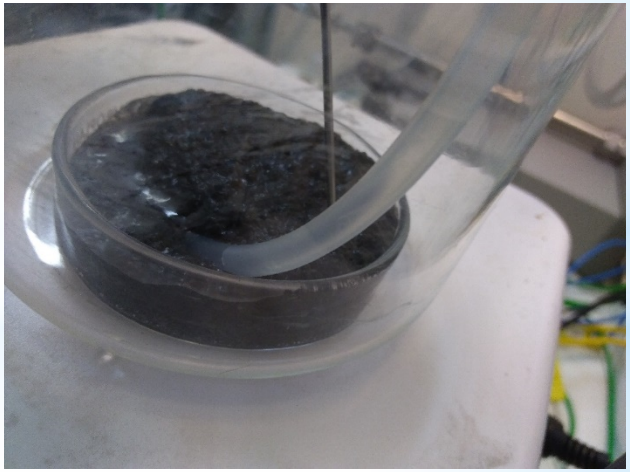






Boiling of the solution was observed at the initial stage of H_2O slow addition

Use of surfactants



CONCLUSIONS

- An experimental basis for studies of hydrolysis of hydrogen generation from magnesium hydride has been created. A new composite MgH_2 - nano-RE_xFeO_3 as a material for hydrogen accumulation and generation was synthesized and studied.

- It is shown that one of the most effective materials for hydrolysis of hydrogen generation are composites based on MgH_2 with catalytic addition of $MgCl_2$. The optimal concentrations is 12-15 wt.% $MgCl_2$, which showed the best characteristics in the hydrolysis reactions of MgH_2. The amount of hydrogen released at room temperature for magnesium hydride exceeds 1000 ml / g.

- An experimental device “hydrolysis block - fuel cell (30 W)” was created with the support of a NATO G5233 grant. Within the framework of both projects, the optimization of hydrolysis of hydrogen supply for efficient operation of the cell was worked out.

List of main publications

1. I. Zavaliy, V. Berezovets, L. Vasylechko, P. Lyutyy, Yu. Kosarchyn. Hydrogen storage and generation properties of new MgH_2-based nanocomposites Hydrogen storage and generation properties of new MgH2-based nanocomposites. In book: “Hydrogen based energy storage: status and recent developments”. Львів-Київ – 2021, в-во: Простір-М, - 246 стор.

2. V.V. Berezovets, R.V. Denys, I.Yu. Zavaliy, Yu.V. Kosarchyn. Effect of Ti-based nanosized additives on the hydrogen storage properties of MgH_2. Int J Hydrogen Energy. Available online 1 April 2021. https://doi.org/10.1016/j.ijhydene.2021.03.019

3. Y.V. Verbovytskyy, V.V. Berezovets, A.R. Kytsya, I.Yu. Zavaliy, V.A. Yartys. Hydrogen Generation by the Hydrolysis of MgH2. Materials Science. 56, (2020) 1–14. https://doi.org/10.1007/s11003-020-00390-5

4. I.Yu. Zavaliy, V.V. Berezovets, R.V. Denys et al. Hydrogen sorption/desorption properties of nanostructured Mg-based composites // Ist Intern. research and practice conf. «Nanoobjects & Nanostructuring» (N&N–2020), September 20–23, – 2020, Lviv, Ukraine. – P. 15.

5. В. Березовець, Ю. Вербовицький, Д. Корабльов, Ю. Солонін, І. Завалій, В. Яртись. Гідриди на основі Mg як джерело водню для автономних енергетичних пристроїв // Матеріали XX міжнародної науково-практичної конференції “Відновлювана енергетика та енергоефек-тивність у XXI столітті”, 15-16 травня 2019 р., Київ, Україна. С.198-201.

6. V.V. Berezovets, Yu.V. Verbovytskyy, I.Yu. Zavaliy, V.A. Yartys. Mg-based materials for application in hydrogen supply systems. 6th International conference «HighMathTech–2019», 28–30 October, 2019, Kyiv, Ukraine - P.143.

7. В.В. Березовець, Ю.В. Вербовицький, І.Ю. Завалій. Синтез нанокомпозитів на основі гідриду магнію та дослідження їх властивостей // Наукова звітна сесія по цільовій програмі НАН України «Розвиток наукових засад отримання, зберігання та використання водню в системах автономного енергозабезпечення», 11 грудня 2019, Київ, Україна. С.22.

8. V.V. Berezovets, I.Yu. Zavaliy, O.B. Pavlovska, L.O. Vasylechko, Yu.V. Kosarchyn. Composites of magnesium hydride with catalytic nanoadditives // Intern. research and practice conference «Nanotechnology and nanomaterials (NANO-2019)» August 27-30, – 2019, Lviv, Ukraine. P.208.

Karpenko Physico-Mechanical Institute of the NAS of Ukraine

Thank you for attention !

25 November 2021