Advanced material and Reactor for ENergy storage tHrough Ammonia

Newsletter – October 2021

Editorial

Welcome to this 3rd ARENHA project newsletter. ARENHA is an European four-year project with global impact seeking to develop, integrate and demonstrate key material solutions enabling the use of ammonia for flexible, safe and profitable storage utilization of energy. Ammonia is an excellent carrier due to its high energy density, carbon-free composition, industrial know-how and relative ease of energy storage. ARENHA demonstrates the feasibility of ammonia as a dispatchable form of large-scale energy storage.

The present newsletter is the third release and it is presenting the progress on the project and highlighting information related to the R&D fields addressed. Hope you will find the info in this newsletter interesting. On our website www.arenha.eu you will find public presentations, all the public information of the project and many other interesting news. Stay tuned!

In this Issue:

What is ARENHA?

The concept

For decades, utility-scale energy storage has been used to balance load and demand within an energy generation system composed mainly of base load power sources enabling thus to large nuclear or thermal generating plant to operate at peak efficiencies. Energy storage has contributed over the time to meet peak demand and regulate frequency beside peak fossil fuel power plants that usually provided the bulk of the required energy. In the aforementioned context where inherent variability of the power generation asset was mainly a minor issue, energy storage capacity remains nevertheless limited for economic reasons storing electricity during low electricity demand and releasing it back into the grid during high demand, typically over a daily cycle.

In the current context of global momentum in favour of renewable electricity catalysed by spectacular levelized production cost decrease, higher storage capacity is required to ensure security and flexibility providing a portfolio of services from grid services to the decarbonization of energy intensive sectors like the transport, industry or heating and cooling sector.

For that purpose, hydrogen produced from electrolysis reveals to be a key pathway to unlock the full potential of renewable and especially for seasonal energy storage of large energy quantity and more specifically for all situations dealing with a large energy-to-power ratio situation. Hydrogen having a low volumetric energy density, it has to be compressed to high pressure, liquefied or combined as hydrogen carrier. Among all possibilities, ammonia is a carbon-free and dispatchable energy carrier allowing storing large quantities of renewable electricity. It is a primary candidate to allow a secure and clean supply of renewable energy for various stationary or mobile applications and with ability to provide a wide range of energy storage services using existing infrastructures and both well-defined regulation and acceptable safety history for over 75 years. If state-of-the-art ammonia production plants produce between 3,000 and 6,000 ton NH_3/day, its well-known process involves H_2 production from natural gas reforming. Technical challenges remain to be overcome in order to ensure a flexible and cost comparable production of ammonia from intermittent renewable electricity sources. In addition to that, efficient energy discharge processes from NH_3 must be developed in order to best leverage the clean energy produced upstream by the renewable asset.

The ARENHA project aims at using ammonia as a green hydrogen carrier and for that purpose it develops its main activities around the green hydrogen production, ammonia synthesis, storage and dehydrogenation (Figure 1). Innovative materials are developed and integrated into ground-breaking systems in order to demonstrate a flexible and profitable power-to-ammonia value chain but also several key energy discharge processes. Specifically, ARENHA is developing advanced SOEC for renewable hydrogen production, catalysts for low temperature/pressure ammonia synthesis, solid absorbents for ammonia synthesis intensification and storage, catalysts and membrane reactors for ammonia decomposition for pure hydrogen (>99.99%) production. Energy discharge processes studied in ARENHA tackle various applications from ammonia decomposition into pure H_2 for FCEV, direct ammonia utilization on SOFCs for power and ICEs for mobility.

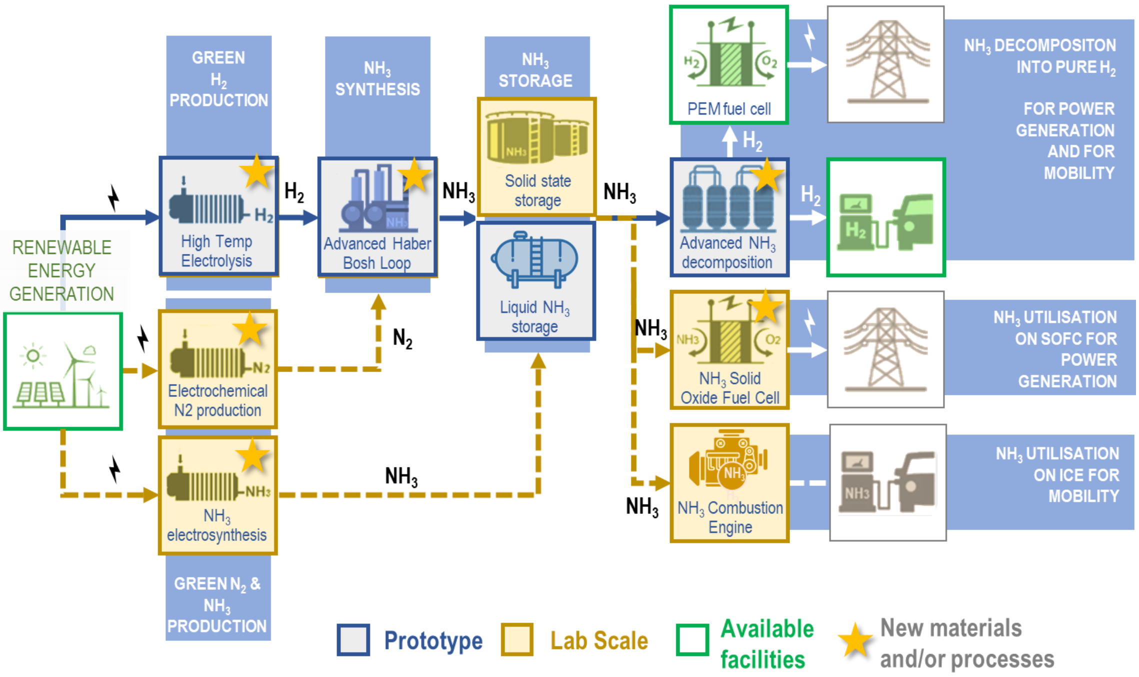

Figure 1. Power-to-ammonia-to-usage value chain in ARENHA

Project objectives.

ARENHA will demonstrate the full power-to-ammonia-to-usage value chain at TRL 5 and the outstanding potential of green ammonia to address the issue of large-scale energy storage through LCA, sociological survey, techno-economic analysis deeply connected with multiscale modelling. For this purpose, breakthrough technologies will be developed and integrated along the overall value chain. The main technical objectives on material and system level are the following:

- To develop and integrate innovative solid oxide cell materials into a flexible high temperature electrolysis demonstration unit producing 1.5 Nm3/hr hydrogen at ambient pressure to be connected on a real PV plant.
- To develop and integrate innovative materials into a synthesis loop enabling to operate a flexible Haber Bosch production unit of 10 kgNH_3/day at lower pressure (<50 bar) and temperature (<450 °C).

- To develop and integrate innovative materials into a decomposition reactor able to generate 10 Nm^3/hr of pure hydrogen (>99.99%) from green ammonia.
- To develop and test innovative materials and solutions for the alternative direct synthesis and utilization of next-generation green ammonia.
- To demonstrate ammonia as a flexible energy carrier through the development of a fully integrated prototype for green ammonia synthesis and decomposition.
- To assess the social acceptance, techno-economic-environmental feasibility, and replication potential of the developed value chains.

Latest news from the project.

Business case definition

In the first period of the project, activities have revolved around finalizing the market analysis to identify promising opportunities for ammonia as a renewable energy storage solution and to pinpoint key stakeholders and competitors. Initial analysis with regards to the Value Proposition of the ARENHA concept through identifying the state-of-the-art technology, underlining the peculiarity about the developed concept, evaluating the impact of the concept on the end-user and assessing the state of development at the end of the project. Specific task included reviewing the current Ammonia market and infrastructure, reviewing the renewable energy market and EU related challenges and analysis the potential role of ammonia in the future European green energy system (Figure 2).

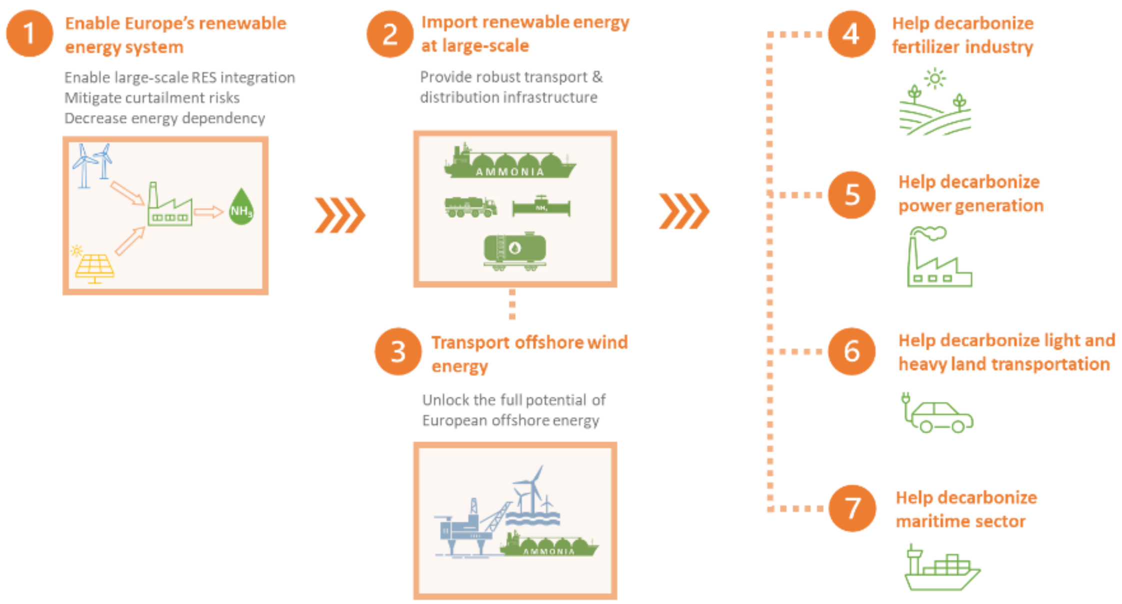

Figure 2. Potential role of ammonia-in the future European green energy system.

System requirements, design and modelling

The main progress on this task are the development of process simulation model for the Advanced Haber-Bosch demonstration plant for ammonia synthesis with integrated sorption and regeneration steps, the development of a dynamic process simulation model for assessment of preferred process control philosophies for plant operation under conditions of varying hydrogen feed flow rate and the development of the ammonia decomposition unit, namely a membrane reactor for ammonia decomposition. The model focuses on the modelling of the membranes that are considered within the ARENHA project as well as on the modelling of the membrane assisted ammonia decomposition reactor. A semi-empirical modelling approach was used throughout this period.

Other tasks included the study and test of new candidate materials for NH_3 absorption and storage and a Model with bi-modal porosity (macroporosity+microporosity) in Comsol Multiphysics®. The model was validated against the experimental data (Kale et al., 2020) and the diffusion coefficient of NH_3 in the sorbent was determined from this data. Based on the model, height of mass transfer zone and purity of the outlet gas were examined for various absorber temperature and absorber radius. Moreover, COMSOL model for NH_3 storage was finalized and validated, and different reactor configurations were developed.

Finally, The BOP of the SOEC system has also been simulated and developed and will be further studied in the upcoming months.

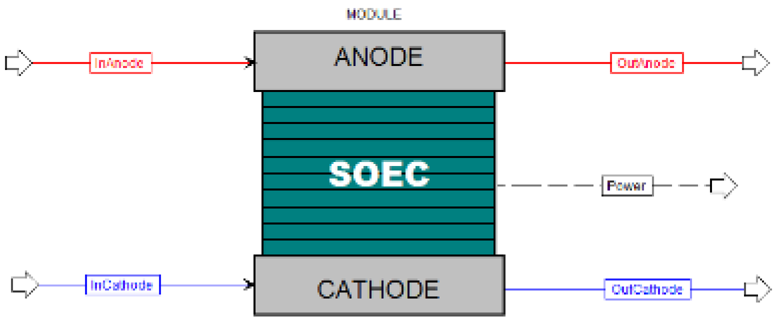

Figure 3. Stack model in Aspen Dynamics developed during this period.

Key component development

Regarding the key component development, the following progress have been achieved as describe hereafter. At IKTS the SOEC development has made progress. In the past months the research was focused on the utilization of thinner electrolytes. Due to the different chemical composition of the delivered substrates an additional adhesion layer for improved contact between electrodes and electrolyte was investigated. To determine whether the adhesion layer as well as the electrolyte thickness had an impact on the cell performance, standard electrodes were printed on said electrolytes, sintered, and characterized by ASR. The ASR describes the combined ionic resistance of the electrodes and the electrolyte in the cell normed by the area. The values were then compared with ASR values of standard cells. The thickness of the investigated electrolytes varied between 165 µm (standard cell) and 45 µm. From the ASR measurements it was derived, that the adhesion layer was sufficient for electrolytes with a thickness equal or above 110 µm. The ASR of a cell with an electrolyte thickness of 165 µm combined with an adhesion layer was approximately 17% lower compared to a standard cell without adhesion layer. Using the adhesion layer, the reduction of the electrolyte thickness from 165 µm to 110 µm led to a further decrease of the ASR by about 15%. With a lower ASR up to 38% higher current densities at constant voltage (0.7 V) were reached using the thinner electrolyte (110 µm) combined with the adhesion layer. However, the electrolytes with a thickness below 110 µm did not show any sufficient results. The utilization of such electrolytes will be the focus of the upcoming investigations.

Elcogen continued research, manufacturing and testing of numerous new materials and microstructural changes to specifically increase the electrolysis performance of the state-of-the-art Elcogen solid oxide cell. These include additives to the nickel network of the functional hydrogen electrode layer for extra activity and stability of the electrode, additions of more active material to the yttria stabilized zirconia structure in the hydrogen electrode and additives to the air electrode material to increase its ionic conductivity. Furthermore, Elcogen has experimented with changing the microstructure of its solid oxide cell to optimise electrolysis performance. Experiments to incorporate totally new materials into the solid oxide cell have also been carried out. These include using nickel-free mixed ionic and electronic conductors in the active hydrogen electrode layer and Sr-free mixed conductors in the air electrode layer.

DTU has developed procedure for absorbent material synthesis and first batch of samples with mono-metal halides were produced. Setups for NH_3 absorption breakthrough curves measurement and kinetics characterization were constructed. Meanwhile, electrochemical cells of 53mm×53mm size for N_2 production were produced.

Tecnalia continue with development of Pd-based membranes and Al-carbon molecular sieve membranes for H_2 separation from ammonia decomposition with higher selectivies in order to achieve higher H_2 purities. Regarding the recycling of Pd-based membranes, a screening of different leaching media has been performed. For the recovery of Pd and Ag from milled solid metallic residue of spent membranes, seven different deep eutectic solvents (DES) and as a benchmark four inorganic leaching medias have been tested. Additives were used to study the effect of increasing acidity together with the effect of oxidizing agents. As observed, DES leaching outperformed inorganic leaching media allowing an extraction rate over 90% of Pd and Ag using additives. Also, the evaluation of direct leaching of spent membranes is under study. Current results show the potential of the ionometalurgical process vs conventional hydrometallurgical process for the recovery of critical raw materials.

At TU/e, the Pd-based membranes prepared at Tecnalia were used to separate the hydrogen produced by decomposition of ammonia in a membrane reactor. The performance of these membranes is very promising for this application since they allow to obtain both a high hydrogen permeation and a high hydrogen purity (Figure 4). Further research is currently addressed on further improving the performance of the membrane reactor technology for ammonia decomposition.

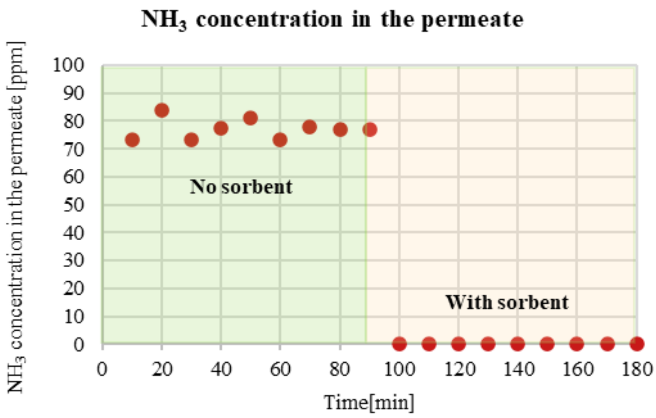

Figure 4. Removing the ammonia content in the permeate of the ammonia decomposition membrane reactor using a sorbent. Experimental conditions: T= 400 °C, $P_{retentate}$= 3 bar, $P_{permeate}$= 1 bar.

UKRI (or STFC) have worked on a new class of ammonia synthesis catalysts which show better performance than current state-of-the-art ruthenium as well as continuing to develop ammonia decomposition catalysts based on non-precious metals.

In a first period, UORL and PSA ID performed tests of ammonia as a fuel in a current Spark Ignition (SI) engine to evaluate the limitation of such combustion as a function of the different operating conditions. In a second period, UORL and PSA ID performed similar tests in a Diesel (DV6) engine, where a sparkplug was added to promote ammonia ignition. This engine configuration tested with ammonia as fuel is a world premiere. The influence of the compression ratio on the combustion process, operating limits, and pollutant emissions has been pointed out, without any optimization of the spark device. UORL and PSA ID confirmed that an increase of the compression ratio leads to an extension of the operating limits especially for low loads and low regime but also at maximum engine speed. Similar trends concerning pollutant emissions were found between the two engine configurations but the diesel architecture seems to induce higher ammonia unburnt due to the combustion chamber design itself.

Environmental LCA, economic and safety assessment

The first 18 months of the project were dedicated to defining the main goal and scope of the sociological survey, LCA, safety analysis and Life Cycle Cost assessment. These goals and scopes are back up with available literature work on both ammonia and hydrogen as energy carriers. Specifically, stakeholders were identified and will be interviewed in the upcoming.

For the LCA, data inventories were developed, and literature review was used to develop the LCA analysis for brown and blue ammonia scenarios.

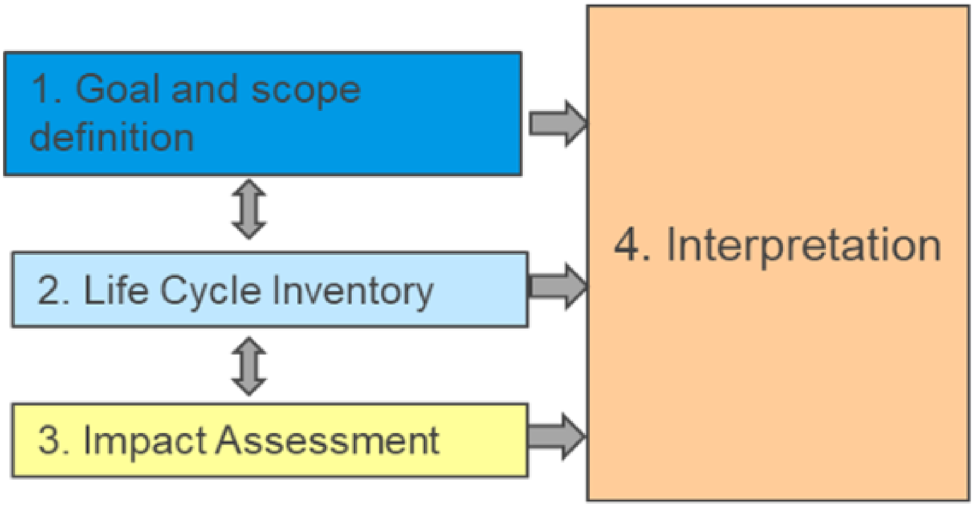

Figure 5. Framework for Life Cycle Assessment (Source: Handbook on life cycle assessment: operational guide to the ISO standards).

For the LCS study, the specific task included available project data and definition of the chain links of the project. Moreover, an historical accident regarding hydrogen and ammonia was carried out, aiming to provide a guide to identify and prevent process and equipment failure that may lead to accidents.

Highligths

ARENHA online M18 Consortium Meeting

Due to the current situation the month 12 consortium meeting was celebrated also online with success on October 20. Despite the COVID-19 progress have been made in all the actives WPs as detailed in previous section. Further information on the project can be found at the following link: https://arenha.eu.

Special issue on ammonia synthesis and utilization

Ammonia is a very important molecule. Its role is even becoming more important as it can also be used as energy carrier and fuel. A special issue dealing with ammonia synthesis and utilization is open in Catalyst, being Prof. Fausto Gallucci, Technical Manager of the ARENHA project, one of the editors. Submit your paper here: https://www.mdpi.com/journal/catalysts/special_issues/Ammonia_catal

1st ARENHA workshop (April 2022)

The first ARENHA public workshop will take place in April 2022. The workshop will be focus on introducing the novel technologies related to ammonia-based energy storage. The Agenda and registration will open in the ARENHA project website (www.arenha.eu) soon.

Dissemination activities, publications and presentations

ARENHA public presentations as well as open access articles and public reports are available online in the dissemination section of the project website: www.arenha.eu.

Peer Reviewed Articles

1. Jaysree Pan, Heine Anton Hansen, Tejs Vegge. Vanadium oxynitrides as stable catalysts for electrochemical reduction of nitrogen to ammonia: the role of oxygen. J. Mater. Chem. A, 2020, 8, 24098- 24107. https://doi.org/10.1039/D0TA08313E.
2. Christine Mounaïm-Rousselle, Pierre Brequigny, S Houillé, C Dumand. Potential of Ammonia as future Zero-Carbon fuel for future mobility: Working operating limits for Spark-Ignition engines. SIA POWERTAIN & ENERGY 2020, Nov 2020, Online, France. ⟨hal-03188481⟩.
3. V. Cechetto, L. D Felice, A. Arratibel Plazaola, F. Gallucci. Ammonia inhibition on H_2 produced via ammonia decomposition in a catalytic membrane reactor. Fuel Processing Technology 216 (2021) 106772. https://doi.org/10.1016/j.fuproc.2021.106772

Conference proceedings or presentations.

1. C. Mounaïm-Rousselle, P. Brequigny, S. Houillé, C. Dumand. Potential of Ammonia as future Zero-Carbon fuel for future mobility: Working operating limits for Spark-Ignition engines. International Congress on Energy and Powertrains (Rouen, France, November 2020). Oral presentation. https://www.sia.fr/evenements/193-sia-powertrain-energy-rouen-2020

2. Valentina Cechetto, Luca Di Felice, Jose Medrano, Camel Makhloufi, Jon Zuniga, Fausto Gallucci. Ammonia inhibition on H_2 produced via ammonia decomposition in a catalytic membrane reactor. World Online Conference on Sustainable technologies. March 17th-19th, 2021. Oral presentation. https://wocst.org/index.php.
3. Camel Makhloufi. Utilising Liquid Ammonia for Cost-effective storage and distribution of large Quantities of Renewable Energy. 14th Energy World Forum. May 19th, 2021. Oral presentation. https://energystorageforum.com/session/utility-utilising-liquid-ammonia-for-cost-effective-storage-and-distribution-of-large-quantities-of-renewable-energy#.
4. F. Kukka,b, S. Pylypkob, E. Lusta, and G. Nurka. Influence of active layer thickness of Reversible solid oxide cells on the electrochemical performance of water electrolysis. SOFC XVII conference. July 18th-23th, 2021. Oral presentation. https://www.electrochem.org/sofc-xvii/.
5. Christine Mounaim-Rousselle. Ammonia as zero-carbon fuel for Internal Combustion Engine: where are we today? 15th International Conference on Engines and Vehicles. September 12th-16th, 2021. Keynote Lecture. https://www.sae-na.it/.
6. José Luis Viviente. Advanced materials and Reactors for Energy storage tHrough Ammonia (ARENHA). Online workshop: NON-BATTERY BASED ENERGY STORAGE: Four sustainable European solutions. September 15th, 2021. Oral presentation. https://recycalyse.eu/recycalyse-joint-workshop/
7. Zançat Sahin, Valentina Cechetto, Luca Di Felice, Fausto Gallucci, H_2 Production through Ammonia Decomposition in a Catalytic Membrane Reactor: A computational and experimental study, 12th International Conference on Hydrogen Production (ICH2P-2021 – On-line conference). September 19th-23rd, 2021. Oral presentation. https://www.innomem.eu/event/12th-edition-of-the-international-conference-on-hydrogen-production-ich2p-2021/

Press articles

1. Katrin Schwarz, EU-Projekt ARENHA: Grünes Ammoniak für die Energiewende, on Fraunhofer IKTS website. https://www.ikts.fraunhofer.de/de/presse/news/2020_10_13_eu_projekt_arenha.html.
2. Christian Eckart, Ammonia as a tamer for green hydrogen. Public media article on the German newspaper “Background Tagesspiegel”
3. E. Monge, V. Sendarrubias, J. Martín, El proyecto ARENHA demostrará el potencial del amoniaco como forma de almacenamiento energético, Public media article on the Spanish newspaper “Energética”.

https://www.energetica21.com/revistas-digitales/septiembre-2021

Upcoming events

Nov. 29 – Dec. 3, 2021	European Hydrogen Week 2021 https://www.fch.europa.eu/event/european-hydrogen-week-2021
December 7-9, 2021	Argus Green Ammonia – Virtual conference https://www.argusmedia.com/en/conferences-events-listing/green-ammonia
March 21-23, 2022	World Online Conference on Sustainable technologies (WOCST 2022). https://wocst.org/index.php
April 25-29, 2022	HANNOVER MESSE 2022. https://www.hannovermesse.de/en/
April 25-29, 2022	Hydrogen + Fuel Cells EUROPE. Part of HANNOVER MESSE 2022. https://www.h2fc-fair.com/en/
May 18-20, 2022	European Hydrogen Energy Conference 2022 (EHEC2022) Madrid (Spain) http://www.ehec.info/
May 16-17, 2022	11th Edition of International Conference on Catalysis, Chemical Engineering and Technology (CCT 2022), Tokyo (Japan) https://catalysis-conferences.com/
May 22-26, 2022	5th SEE Conference on Sustainable Development of Energy, Water and Environment Systems (SEE SDEWES2022), Vlore, Albania https://www.vlore2022.sdewes.org/
June 2-3, 2022	NH_3 Event Europe 2022: 5th European Power to Ammonia Conference, Rotterdam (The Netherlands). https://nh3event.com/
July 31 – August 4, 2022	15th International Conference on Catalysis in Membrane Reactors Tokyo (Japan) http://iccmr15.org/

ARENHA in figures:

11 partners (6RES, 2 IND, 3 SME)

7 countries

5,684,325 € project

Start: April 2020

Duration: 48 months

Key milestones:

April 2023 - Ammonia synthesis and decomposition prototypes ready

April 2024 - Ammonia- based energy storage system integrated and validated

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More information about ARENHA (including a non-confidential presentation of the project) is available at the project website: https://arenha.eu/

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