Toward Efficient Electrochemical Green Ammonia Cycle

Project deliverable Report D1.3
First Periodic Review

Dissemination level:	Public
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EXECUTIVE SUMMARY

The first review period of the project (M18) assesses the fulfilment of several aspects, including technical, management, networking, etc. In preparation of the first review, this deliverable presents a brief summary of the main activities, objectives achieved, challenges, deviations and corrective actions that have been implemented.

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1 Introduction

The main objective of TELEGRAM project is to demonstrate, at the laboratory scale level, a complete green ammonia carbon–neutral energy cycle, based on electrochemical processes, enabling the use of ammonia as a green fuel.
The work is based on the development of two key enabling technologies:

(i) the reactor for electrochemical synthesis of ammonia
(ii) the direct ammonia fuel cell (DAFC).

The realization of a complete ammonia-based energy cycle will be achieved through the development of new materials as efficient catalysts. The developed ammonia reactor, powered by renewable energy sources, and the DAFC will be coupled together to demonstrate the complete ammonia energy cycle at a laboratory scale, with the objective to achieve 95% of the combined efficiencies.

2 Project Objectives and Milestones

The main goal of the project will be achieved through the achievement of the following objectives:

- **Objective 1**: Development of novel catalysts for nitrogen reduction for ammonia synthesis with a faraday efficiency >50% and/or a production rate >10^{-8} mol cm^{-2} s^{-1} (MS2 and MS5)
- **Objective 2**: Understanding of the reaction mechanisms by detailed structural characterization, atomistic simulations and in-operando spectroscopy analyses. (MS7)
- **Objective 3**: Multi stage ammonia reactor with optimised design and catalysts achieving a production rate >10^{-7} mol cm^{-2} s^{-1} (MS3 and MS8).
- **Objective 4**: Direct ammonia fuel cell (DAFC) with optimised design using catalysts with platinum group metal loading lower than 0.05 mg cm^{-2} that achieves a power density of at least 100 mW cm^{-2} with a chemical to electricity efficiency > 25% at operating temperatures below 100 °C (MS4 and MS9).
- **Objective 5**: Full electricity-ammonia-electricity cycle powered by renewable energy sources that achieves 95% of the combined efficiencies of ammonia generation and DAFC (MS10).

The chosen values are targets that may render the electrochemical proposed processes effective for industrial exploitation, while the actual maturity of the technologies studied in the project is still low (TRL3). Therefore the TELEGRAM quantitative objectives are very ambitious and represent a disruptive advancement compared to the state of the art.

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The objectives are linked to the project milestones as detailed in the next Table I and II. Objectives and milestones relative to the first reporting period (M1-M18) are displayed in blue cells.

Table I: List of Objective and technical Milestones

Objective	Milestone	Due date	Verification	Status
1. Novel catalysts for ammonia synthesis	MS2 Criteria for materials selection (WP2)	M15 (Jan 2022)	Catalysts Characterization in D2.2. Materials selection for DAFC in D5.1	Completed D5.1 and D2.2 have been submitted at M15 on time.
	MS5 Choice of best catalysts for ammonia synthesis (WP2, WP4)	M24 (Oct 2022)	FE >50% and/or rate 10^{-8} mol cm^{-2} s^{-1}	In progress
2. Understanding the reaction mechanisms	MS7 Reaction mechanisms clarified (WP2, WP3)	M36 (Oct 2023)	Structural analyses and simulations in D2.5, D2.6 and D3.4	In progress
3. Multi stage ammonia reactor with optimised design and catalysts	MS3 MEA for ammonia synthesis (WP4)	M18 (Apr 2022)	Catalysts FE or rate 50% better than the benchmark	Partially achieved
	MS8 Multi-stage ammonia reactor with optimised design and catalysts (WP2,WP4)	M36 (Oct 2023)	Ammonia reactor with production rate $>10^{-7}$ mol cm^{-2} s^{-1}	In progress
4. Direct ammonia fuel cell (DAFC) with optimised design using low amount of PGM catalysts	MS4 DAFC test vehicle with PGM and low PGM catalysts (WP5)	M18 (Apr 2022)	Pt Group Metals as benchmark. Peak power density >100 mW/cm^2 for PGM loading <0.05 mg/cm^2	Partially achieved
	MS9 DAFC with optimised design and non-PGM catalysts (WP3,WP3,WP5)	M36 (Oct 2023)	Chemical to electricity efficiency > 25% with a peak power density >50 mW/cm^2	In progress
5. Full electricity-ammonia-electricity cycle powered by renewable energy sources	MS10 Full ammonia cycle (WP6)	M42 (Apr 2024)	95% of the combined efficiencies of ammonia generation and DAFC	In progress

Other two milestones are not strictly related to the technical objectives but to the management, dissemination and exploitation activities, as listed in Table II.

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Table II: List of Milestones related to non-technical objectives

Milestone	Due date	Verification	Status
MS1 First version of the exploitation plan (WP7)	M12 (Oct 2021)	Preliminary exploitation plan in D7.1	Completed First version submitted on Oct 2021. Update submitted on Apr. 2022
MS6 Midpoint review (WP1,WP7)	M20 (Jun 2022)	Project management plan update in D1.2. First review meeting. Communication and dissemination activities in D7.3	In progress D1.2 Submitted as scheduled

3 Activities and Results

From month M1 to M18 of the project, the work has been carried out mainly on the following activities:

1. Planning and monitoring of the activities. Recruitment and training of personnel by each beneficiary. Networking and sharing of the results within the consortium. (WP1)
2. Catalysts development: multi components high entropy alloys and nanostructured catalysts. Electrochemical test cell development and characterization. (WP2)
3. Atomic scale modelling of catalysts. Physico-chemical simulation models for the devices (WP3)
4. Development of Cell and Test-Rig for Ammonia Synthesis. Manufacturing and characterization of the MEA (WP4)
5. Materials selection, identification and minimization of critical loss factors in the design of Direct ammonia fuel cell (DAFC). Manufacturing of DAFC test vehicle with platinum group catalysts (WP5).
6. Setup of test bench for operation of ammonia reactor and DAFC under fluctuating conditions (WP6)
7. Dissemination activities and preliminary exploitation plan (WP7)

The activity on catalysts development and optimization is ongoing as planned. The achievement of **Objective 1** is in progress. At this stage it has been partially achieved with the development of nanostructured catalysts with efficiency up to 30%. Full achievement of this objective is expected at M24, with the choice of best catalysts among High entropy alloys and/or nanostructured.

All the produced catalysts have been characterized with respect to structural and electrochemical properties. At present, the characterization has been performed mainly at the level of the materials (as shown in D2.2) and environment (electrolyte and temperature).

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Atomistic simulations have been also performed and will be presented in D3.2 at M24. All progress obtained so far will flow towards the full achievement of **Objective 2**, which is expected at M36.

The fulfillment of **Objective 3** is expected to be completed at M36, with the realization of the multi stage ammonia reactor. Within the first review period, a test-rig for the characterization of the electrochemical ammonia generation was designed and built. Membrane electrode assembly (MEA) has been prepared with the produced catalysts and tested.

Materials for the manufacturing of the DAFC have been selected and the first test vehicle, including catalyst containing metals of the Pt group has been manufactured and tested. The activity is in progress and contributes to the achievement of **Objective 4**, which is expected to be completed at M36.

All the activities are preparatory for the realization of the full ammonia cycle, as **Objective 5**. During the first review period, the renewable energy generation profiles have been identified and a test bench has been built, to test the ammonia reactor using a source measure unit which emulates solar cells.

The work carried out in each WP will be explained in more details in the Technical Report, which will be submitted in two months.

4 Deliverables

The achievement of the Deliverables (D) was constantly monitored and it is summarized in Table III. In green, deliverables submitted and accepted. In yellow, Deliverables submitted waiting approval. In blue deliverables to be submitted.

Table III: List of Deliverables

Del.	Title	Due date	Actual	Expected
WP1				
D1.1	Project Management Plan 1	Dec 2020	Dec 2020	
D1.2	Project Management Plan 2	Mar 2022	Mar 2022	
D1.3	First Periodic Review	Apr 2022	Apr 2022	
D1.4	Project Management Plan 3	Mar 2023		
D1.5	Second Periodic Review	Apr 2023		
D1.6	Final Review	Apr 2024		
WP2				
D2.1	Electrochemical test cell development for novel catalysts evaluation	Apr 2021	Apr 2021	
D2.2	First catalysts for MEA and DAFC: Characterization and functional properties	Jan 2022	Feb 2022	
D2.3	Optimised catalysts for MEA and DAFC: Characterization and functional properties	Oct 2022		

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D2.4	Performance and stability of non PGM catalysts for DAFC	Jun 2023		
D2.5	In-operando investigations of the high entropy materials in ammonia synthesis	Oct 2023		
WP3				
D3.1	Simulation frameworks for ammonia synthesis cells and direct ammonia fuel cells based on calibrated and validated multi-physics models	Jan 2022	Jan 2022	
D3.2	Atomic-scale modelling of catalysts	Oct 2022		
D3.3	Scenario investigations and loss analysis predictions for both ammonia synthesis and direct ammonia fuel cells using simulation models	Jan 2023		
D3.4	Modelling of the catalysts, membranes, and evolved species	Oct 2023		
WP4				
D4.1	Reactor-cells and test-rigs available, with verified operando analysis	Jul 2021	Nov 2021	
D4.2	Establishment of a reproducible method for making MEAs which use the full potential of the catalyst	Apr 2022		Jul 2022
D4.3	Nitrogen-generating cell and hydrogen generating cell integrated into test set-up and interactive operation of all three cells	Oct 2022		
D4.4	Full demonstration of lab scale electrochemical ammonia synthesis by a 2-stage membrane reactor under optimized intermittent operating conditions	Oct 2023		
WP5				
D5.1	Materials selection for DAFC components based on the state of the art	Apr 2021	Jun 2021	
D5.2	DAFC test vehicle with PGM catalysts and low PGM	Apr 2022		Jun 2022
D5.3	Critical loss factors associated with the design and operation of the direct ammonia fuel cell and strategies to minimise them	Jan 2023		
D5.4	Performance of DAFC using low cost materials including non-platinum group catalysts	Apr 2021		
WP6				
D6.1	Setup of test bench completed and important generation and consumption scenarios identified	Jul 2021	Nov 2021	
D6.2	First evaluation of ammonia reactor and DAFC stress testing, applied to identify critical operation factors	Jan 2023		
D6.3	Final evaluation of ammonia reactor and DAFC stress testing	Oct 2023		
D6.4	Life cycle assessment of the integrated green NH3 energy cycle	Apr 2024		
D6.5	Setup and characterization of full ammonia cycle	Apr 2024		
WP7				
D7.1	Project website	Apr 2021	Oct 2021	
D7.2	Preliminary version of the exploitation plan	Oct 2021	Apr 2022	
D7.3	First Dissemination and Communication Report	Jun 2022		
D7.4	Report updating the exploitation strategy and plan	Oct 2023		
D7.5	Scientific Workshop	Oct 2023		
D7.6	Special journal issue	Feb 2024		
D7.7	Final dissemination report and exploitation plan	Apr 2024		
WP8				
D8.1	H - Requirement No. 1	Oct 2021	Dec 2021	
D8.2	POPD - Requirement No. 2	Oct 2021	Oct 2021	

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5 Challenges, Risks and Corrective actions

Some technical challenges have been encountered during the project, mainly related to:

i) The lack of an assessed protocol to evaluate the produced ammonia

ii) The lack of reference materials and catalysts for both electrochemical ammonia synthesis and oxidation (for the DAFC)

iii) The lack of fully reliable data available in literature

Ammonia is commonly present in the environment, so it is crucial to distinguish the produced ammonia from the adventitious one. Regarding (i), as corrective action, part of the work has been devoted to the establishment of a viable procedure, adopted by all the involved partners, to evaluate and compare the results. In order to better align the procedures adopted in different laboratories, dedicated meeting have been organized and exchange between PhD students working on the project at CNR and FZJ has been promoted. Although essential for a reliable determination of ammonia, these shared procedures are quite time consuming, requiring daily calibration and long as well as multiple measurements for the performance evaluation of a single catalyst.

Regarding (ii), the first period has been dedicated to the selection of suitable materials to be used within the devices that are going to developed. The lack of references and/or of well assessed procedures requires numerous trials prior to reach the requested performances. Moreover, there are not well known catalysts to be used as benchmark and even literature data may be controversial, presenting data which sometimes are not reproducible [1,2]. These technical challenges might produce some delay or prevent from fully achievement of some of the objectives.

The Consortium also faced a non-technical challenge, as described in D1.2, i.e. the breakage of a critical equipment, with long lead times and delays on the supplier side. To adapt to the situation, the activity has been focused on the most crucial materials; moreover, a collaboration has been established, in order to have access to a system of similar capacity as the broken one. Thanks to these mitigation measures, several five-elements alloys have been prepared and characterized, as shown in D2.2.

Other risks, specifically related to the COVID-19 pandemic, such as limited access to the laboratories, absence of key personnel and low dissemination activity have been also encountered but the impact is expected to be not relevant.

6 Summary and Conclusions

In this deliverable a brief summary of the status of the project has been presented, highlighting the main activities and results, as well as the challenges and corrective actions, in preparation of the first review. A recent update on the planning of the project has been also given in D1.2, the updated project management plan, submitted in March 2022.

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All the activities carried out by each partner in the various workpackages will be described in details in the Technical Report.

References

[1] ACS Energy Lett. 2020, 5, 2095−2097
[2] Journal of Energy Chemistry, Volume 49, October 2020, Pages 51-58

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