Toward Efficient Electrochemical Green Ammonia Cycle

Project deliverable Report D1.5
Second Periodic Review

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EXECUTIVE SUMMARY

The second review period of the project assesses the fulfilment of several aspects, including management, technical issues, critical risks, etc. This deliverable presents, in preparation of the second review, a brief summary of the main activities, milestones 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.

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 values have been chosen as 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.

The objectives are linked to the project milestones as detailed in the next Tables (I and II). Objectives and milestones relative to the second reporting period (M19-M30) are displayed in blue cells; those related to the first period are in grey.

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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}	Partially achieved FE 42%, rate 3.5x10^{-10} mol cm^{-2} s^{-1} Further measurements required for testing at high pressure and temperature
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	Completed D4.2 submitted on 23 Oct 2022
	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 D7.2	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	Completed. D1.2 and D7.3 Submitted as scheduled

3 Activities and Results

From month M19 to M30 of the project, the work has been carried out mainly on the following activities:

1. Planning and monitoring of the activities. Networking and sharing of the results within the consortium. Bi-monthly meeting on critical risks. (WP1)
2. Catalysts development: multi components high entropy alloys and nanostructured catalysts. Implementation of the experimental setup for high temperature and pressure measurements. Improvement of the ammonia detection methods. (WP2)
3. Atomic scale modelling of catalysts. Implementation of multi-physics models and scenario investigation for components and full cells. (WP3)
4. Manufacturing and characterization of the MEA with several catalysts. Implementation of higher pressure. Development of N2- and H2-generating Cell. (WP4)
5. Identification and minimisation of the critical loss factors associated with the design and operation of the direct ammonia fuel cell (DAFC). Strategies to reduce the overall cost without sacrificing the conversion efficiency and durability. (WP5)
6. Investigation of electrochemical cells under fluctuating conditions. Preparation activities for life cycle analysis. (WP6)
7. Dissemination activities. Update of the website and social networks. Preparation of the workshop. (WP7)

The activity on catalysts development and optimization has proceeded as planned. **Objective 1** has been partially achieved with the development of nanostructured catalysts with efficiency up to 42%. The most promising catalysts among High entropy alloys and nanostructured have been identified (see D2.3) considering a compromise between performance and stability.

All the produced catalysts have been characterized with respect to structural and electrochemical properties, changing also the electrolyte and the measurement conditions (pressure and temperature). Optimised catalysts have been delivered for testing in the MEA or in the DAFC.

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Atomistic simulations have been performed and presented in D3.2, submitted 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 second review period, the membrane electrode assembly (MEA) has been prepared with the produced catalysts and tested. However, further measurements at high temperature (<100°C) and pressure (<8bar) are still ongoing.

Materials for the manufacturing of the DAFC have been selected and the first test vehicle, including catalyst containing low amount of metals of the Pt group, in particular (Pt and Pt/Ir) 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 second review period, the effect of fluctuating power on electrochemical cells has been investigated. However, the test of the developed devices (both MEA and DAFC) has been delayed due to the lack of optimized devices.

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. Due to the technical challenges discussed in the next paragraph, some of the next deliverables have been not completed at the expected time and will be submitted with delay.

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	April 2023	
D1.5	Second Periodic Review	Apr 2023	April 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	

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D2.3	Optimised catalysts for MEA and DAFC: Characterization and functional properties	Oct 2022	Oct 2022	
D2.4	Performance and stability of non PGM catalysts for DAFC	Jun 2023		**Sept 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	Oct 2022, revised Apr 2023	
D3.3	Scenario investigations and loss analysis predictions for both ammonia synthesis and direct ammonia fuel cells using simulation models	Jan 2023		**Aug 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	Dec 2021	
D4.2	Establishment of a reproducible method for making MEAs which use the full potential of the catalyst	Apr 2022	Oct 2022	
D4.3	Nitrogen-generating cell and hydrogen generating cell integrated into test set-up and interactive operation of all three cells	Oct 2022		**Aug 2023**
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		**July 2023**
D5.4	Performance of DAFC using low cost materials including non-platinum group catalysts	Apr 2024		
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		**July 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	June 2022	

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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	
D8.3	EPQ – Requirement No. 3	Oct 2021	Jan 2022	

In the following table the reason, the impact and the mitigation measures are reported in detail for each delayed deliverable.

Table IV: Delayed Deliverables

Del	**Title**	**Due date**	**Delayed to**
D4.3	Nitrogen-generating cell and hydrogen generating cell integrated into test set-up and interactive operation of all three cells	Oct 2022	Aug 2023
Reason	The work on the nitrogen generating cell has started later because effort has been focused on the MEA for more time than expected. Now it is ongoing and is advancing well. We are currently able to reduce Oxygen content to 5%. But further work is needed to explore the limits.		
Impact	Low, the ammonia generating cell can be operated without hydrogen and nitrogen generating cells. These would be "nice to have" but not mandatory.		
Mitigation	Device can be operated without these cells.		
		Due date	**Delayed to**
D5.3	Critical loss factors associated with the design and operation of the direct ammonia fuel cell and strategies to minimise them	Jan 2023	July 2023
Reason	Delays in equipment and materials procurement. More catalysts and membranes need to be tested to improve performance. More time is required for a more complete evaluation.		
Impact	High, the deliverable itself is delayed due to issues related to procurement and cell performance. Especially the performance issues may affect later work in WP5 related to the direct ammonia fuel cell (DAFC) of the full ammonia energy cycle setup, thus WP6, and they affect also WP3 (D3.3).		
Mitigation	The work in other WPs can be performed mostly independently of the DAFC development. Testing, e.g. new catalysts in the DAFC to increase power, and a different anion exchange membrane for improved stability and performance are ongoing.		
		Due date	**Delayed to**
D3.3	Scenario investigations and loss analysis predictions for both ammonia synthesis and direct ammonia fuel cells using simulation models.	Jan 2023	Aug 2023

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Reason	Linked to the MEA and to the DAFC. It requires measurements on better performing devices.		
Impact	Medium, for the most part, model development and simulations can be carried out without the ammonia synthesis cell and the direct ammonia fuel cell, but verification requires experimental data		
Mitigation	Models can be developed and simulations performed without the ammonia synthesis cell and the direct ammonia fuel cell. Similarly, these cells can be developed and tested also without models and simulations, if needed.		
		Due date	**Delayed to**
D6.2	First evaluation of ammonia reactor and DAFC stress testing, applied to identify critical operation factors	Jan 2023	Aug 2023
Reason	Linked to the MEA and to the DAFC. Needs optimized devices		
Impact	Medium, limits our ability to iterate on devices and tests based on a first round of stress testing results. I.e. may impact quality of final tests (6.3) but not the schedule.		
Mitigation	Data that are collected as part of the development process of the devices will be used to at least narrow down the critical operation factors as far as possible.		
		Due date	**Delayed to**
D2.4	Performance and stability of non PGM catalysts for DAFC	Jun 2023	Sept 2023
Reason	A better evaluation of the catalysts needs a well performing device		
Impact	Medium/low since the catalysts will be employed in the final optimized device		
Mitigation	Catalysts are studied during the optimization process of the device, therefore will be optimized taking into account the overall ammonia fuel cell		

5 Challenges, Risks and Corrective actions

Some technical challenges have been encountered during the first period of the project (M1-M18), 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

Therefore, in the second period (M19-M30) several efforts have been spent to overcome these challenges. Regarding (i), the indophenol (Berthelot) method has been adopted by the consortium as the main ammonia detection procedure, and common practices have been shared through different laboratories. Results have been checked also by employing an ammonia ion selective electrode (ISE), as an alternative detection method.

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Regarding (ii) and (iii), the lack of reference catalysts to be used as benchmark and/or of well assessed procedures has required numerous trials and additional experimental checks. Considering the presence in literature of data that have been found to be not reproducible due to possible nitrite contaminations, some activity has been also focused to the nitrite determination and to the definition of a protocol to avoid false positives. We have assessed that our results are not affected by nitrite contaminations.

Several risks have been materialized:

Technical Risk 1: The materials selected for catalysis are unsuitable to reach required efficiency

The proposed mitigation measures are: to test other materials and compositions, to test the catalysts in different conditions (e.g. electrolyte, higher pressure and temperature).

The adoption of the modified conditions, with high temperature and pressure, was not originally foreseen into the grant agreement and the set-up has required additional time, determining some delays. Since the adopted method for ammonia measurement is based on the optical absorption of the electrolyte, and since the optical properties of the electrolyte solution are modified after the experiments at high pressure, due to the presence of small gaseous inclusions, the modified testing conditions have required also a modification of the ammonia calibration method. To have a reliable evaluation of ammonia, the calibration has been performed directly on the tested electrolyte, by adding known ammonia quantities.

Technical Risk 3: One or more of the technologies (the NH3 reactor and/or the DAFC) does not reach maturity in the required timeframe

The proposed mitigation measures are the development of various generations of the devices, with a rigorous testing at each stage of the device design.

We systematically applied the mitigation measures, producing different generation of devices and improving the performance. The devices have been also tested under different conditions (temperature, pressure, ammonia concentration) and the performance has been improved over time, although still not reaching the desired values.

Several technical issues have prevented from reaching the expected maturity. In particular, for the MEA, some ammonia contamination has been found at FZJ, but no clear source of the impurities could be identified. This, together with the low amount of produced ammonia, precluded a reliable evaluation of the ammonia yield in the MEA. The work to overcome this issue in ongoing.

For the direct ammonia fuel cell, a newly designed cell has been adopted, to decrease and stabilize the ohmic resistance. However, the performance of the cell still needs improvement. Adoption of higher temperature and ammonia concentration is required to improve the performance. Unfortunately, none of the available ion exchange membranes employed in the

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device seem to be able to sustain these conditions. A compromise should be found between stability and performance.

Two further external risks materialised in the second period, mainly due to the actual unfolding geopolitical situation.

External Risk 3.1: **Delays in procurement of critical equipment caused by long lead times or delays on the supplier side**

Unforeseen risk 3: Increase of the costs of some raw materials and equipment

As mitigation measure, when possible, materials difficult to be procured have been substituted with other materials more easily available.

As an example, we substituted Ni felt with Ni foam, and designed and manufactured locally the electrochemical H-cell operating at high temperature and pressure (<10 bar).

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 second review. A recent update on the planning of the project has been also given in D1.4, the updated project management plan, submitted in April 2023.

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

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