Photocatalytic Ammonia Production

KEYWORDS: Photocatalysis / Ammonia / Green Fuels / Structured Reactors / Energy vector / Direct Ammonia Fuel Cells

Ammonia has been successfully produced by photocatalysis from water and nitrogen and using metal-free g-C_3N_4 catalysts. Several organic compounds were tested as hole scavengers, and the possibility of using seawater was demonstrated. The unit cell of a mesostructured photoreactor was designed using CFD simulations, and its hydrodynamics and mass transfer behaviour were evaluated. Moreover, a Direct Ammonia Fuel Cell was designed and tested using different catalysts.

Introduction

Ammonia (NH_3) is one of the largest-volume synthetic chemicals produced in the world, being mainly employed in the production of fertilizers. It is also a promising indirect hydrogen carrier, much easier to store and transport. The traditional route for NH_3 synthesis follows the Haber-Bosch process, which depends on methane and is energy-intensive, accounting for 1% of greenhouse gas global emissions. Photo-assisted ammonia production is a rising alternative to this industrially set process based on clean technologies and renewable resources, such as sunlight, water, and air. So far, tremendous advancements have been made on the chemistry side of NH_3 photochemical production. For this technology to meet its full potential in building a carbon-free economy, these results must move to the photoreactor side of the equation.

Graphitic-like carbon nitride (g-C_3N_4) has proven to be a good candidate for photocatalytic N_2 reduction to ammonia. The modification of the materials to increase their efficiency and their immobilization is crucial from an applied point of view.

Besides the use of efficient photocatalysts, the photoreactor configuration and the use of adequate radiation sources also play major roles in the applicability of photocatalytic processes. The possibility of using structured multifunctional photoreactors, with improved mixing and reaction features, where the catalyst is immobilized over a fixed 3D-printed part, may constitute a valuable asset for the sustainable production of NH_3, opening up the possibility of constructing smaller and more sustainable production units with enhanced efficiencies, using inexhaustible resources (air, water and potentially sunlight).

Introducing a zero-carbon process to produce ammonia allows for its use as a sustainable energy carrier since it can be used directly in fuel cells (Direct ammonia fuel cells - DAFCs).

The work presented here is mainly related to the SuN2Fuel project, which involves the contribution of Carbon-Neutral Consulting (USA) company, which will support technology and business development plans. Moreover, the Ammonia Energy Association (USA) is also following the results obtained along the project, as they consider it an opportunity to contribute to a potentially disruptive improvement of the ammonia production processes, enabling extremely low carbon footprints. The application of sunlight for the SuN2Fuel process will be carried out at Plataforma Solar Almeria (Spain) and will consider sunlight as an energy source for the photocatalytic component but also a source of energy for ammonia stripping.

Current Development

Photocatalytic ammonia production

Ammonia has been produced using exfoliated graphitic carbon nitride immobilized over a 3D-printed structure under visible-light irradiation. Different hole scavengers, namely alcohols (ethanol, methanol, and isopropyl alcohol) and biomass-derived compounds such as glucose and glycerol, have been tested. The results show that the presence of such sacrificial reagents plays an important role in the ammonia production process (Fig 1). Isopropyl alcohol was proven to promote the best ammonia rate generation (~355 μmol g_{cat}^{-1} h^{-1}), followed by methanol (~280 μmol g_{cat}^{-1} h^{-1}), and ethanol (~145 μmol g_{cat}^{-1} h^{-1}), when using 100 mM aqueous solutions (ultrapure water) of the respective alcohols.

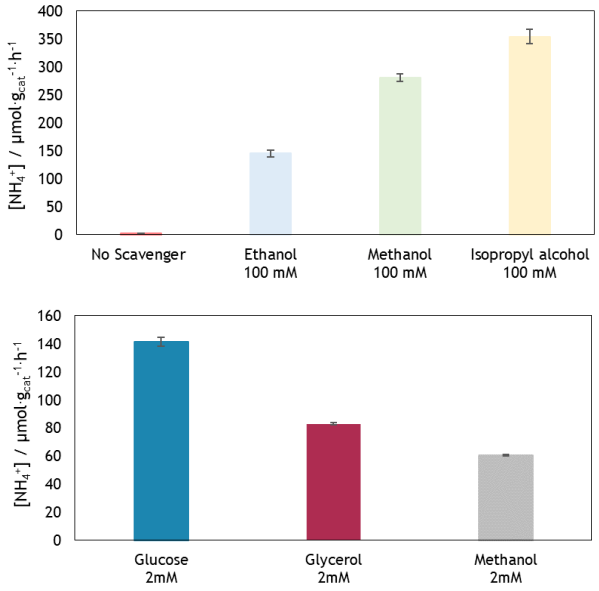

Fig 1. Ammonia production using alcohols and biomass-derived compounds as scavengers.

Both glycerol (~85 μmol g_{cat}^{-1} h^{-1}) and glucose (~141 μmol·g_{cat}^{-1} h^{-1}) show higher ammonia production when compared with methanol (~60 μmol g_{cat}^{-1} h^{-1}) with the same concentration (2 mM). Glycerol and glucose were selected since they may be present in industrial effluents that contain high organic loads and without actual industrial value. In the case of glycerol and glucose, they are by-products of the biodiesel and agro-industries, respectively. Their use in ammonia production could lead to the valorization of these industrial streams. Moreover, the use of tap water and seawater was also evaluated, and the results confirmed that both are suitable options for ammonia production.

Design and simulation of NH_3 mesostructured photoreactors

The present project targets the development of novel multifunctional photoreactor configurations for NH_3 production designed with advanced multiphysics tools that combine Computational Fluid Dynamics (CFD) and simulation of radiation. A unitary element of the reactor will be simulated using CFD tools in order to optimize the photocatalytic performance of the system and geometric parameters [1]. The unitary element will be repeated in a network to generate a structured reactor. Simulations of hydrodynamics, mass transfer, chemical reaction, and radiation [2] will be performed to obtain the best structure configuration.

The 3D prismatic geometry of a unitary element of the structured reactor, i.e., the DeanCell, was designed through Computational Fluid Dynamics (CFD) tools, namely the ANSYS R2 2022 software (Fig 2).

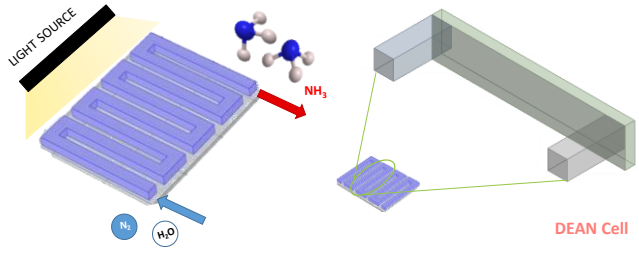

Fig 2. Mestructured photoreactor for ammonia production and geometry of the DEAN Cell.

The study of velocity and vorticity profiles along the length of the cell enabled to optimise its configuration by evaluating the mixing degree and the preferential paths of the flow of the fluid phase. This hydrodynamic study revealed that the chosen configuration of the DeanCell promotes the formation of dynamic structures, i.e. Dean vortices, mainly on the step expansion drawn on the structure (Fig 3).

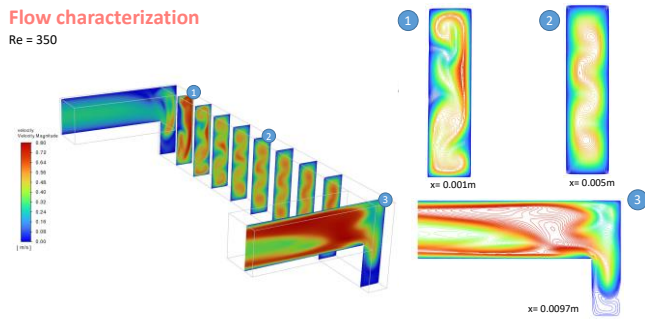

Fig 3. Hydrodinamics simulations: velocity contours for Re = 350.

Mass transfer simulations were performed to establish the maximum limits for mass transfer within the unit-cell, to guarantee that the operation of the structured device is under chemical regime. An immobilisation study was carried out to assess the influence of the catalyst position on the ammonia diffusion throughout the reactor. Sherwood numbers evaluated the mass transport and showed that product diffusion is only slightly dependent on the localization of the catalytic material.

The reaction between N_2 and H_2 was also modelled, in gas phase. No validated kinetic parameters were used in these simulations, and so the data retrieved is only an approximate estimative of the results. Nevertheless, the reaction heat and the temperatures reached inside the DeanCell are still too high to enable the use of graphitic carbon nitride as the catalyst, which requires the additional modeling of heat transfer through the walls.

Direct Ammonia Fuel Cell

A 5.0 cm^2 active area DAFC has been designed and mounted and several operation conditions were studied. The influence of operating conditions on the performance of the DAFC was studied namely NH_4OH and KOH concentrations, concentration, the air, and the NH_4OH solution flow rates, and the relative humidity of the air at 40 °C. No significant variation in the performance of the cell was observed by varying these conditions at 40 °C. However, at 60 °C, an increase in performance was observed when air humidity decreased. Additionally, it was demonstrated that increasing the NH_4OH and KOH concentrations at that temperature results in improved cell performance.

Different commercial electrodes and membranes were tested in the DAFC. A maximum peak power density (PPD) of 12.2 mW cm^{-2} was achieved when using the PtIr/C catalyst deposited on carbon cloth (CC) with a load of 3 6 mg cm^{-2} and a commercial FAA-3-PK-130 membrane (Fig 4).

This work results from a collaboration with the Transform Phenomena Research Center (CEFT), a research unit of ALiCE.

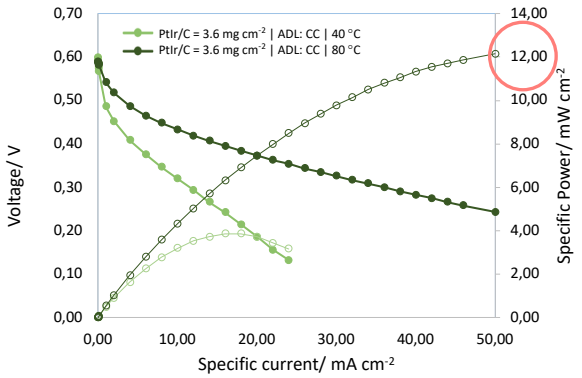

Fig 4. Polarization and power density curves obtained for PtIr/C catalyst deposited over CC.

Future Work

New materials based on g-C_3N_4 are being developed in order to increase the efficiency of photocatalytic ammonia production. These results will be used to validate the CFD model, allowing a deeper understanding of the production limits of the DeanCell. A more in-depth photocatalytic model should also aim to simulate the radiation field inside the DeanCell. Different DAFC configurations are being tested to maximise its performance.

Related Sustainable Development Goals

Outputs

Master Dissertations

Joana Correia Cancela, GREENammonia – Development of photo-assisted systems for green ammonia production, M.EQ, FEUP, 2023.

Maria Teresa Oliveira, CFD process design for photo-assisted production of green ammonia-based fuels, M.EQ, FEUP, 2023.

Margarida Gomes da Silva Jorge, DAFC - Direct ammonia fuel cells as a new energy vector, M.EQ, FEUP, 2023.

Selected Publications

[1] I.S.O Barbosa et al., Chem. Eng. Technol. 46, 1241-1250 (2023).

[2] I.S.O Barbosa et al., Chem. Eng. Technol. 46, 1059-1077 (2023).

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